Molecular Interactions at Cadmium Selenide Nanocrystal Surfaces

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ABSTRACT
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The synthesis of $n$-alkylamine-bound CdSe-$\text{NH}_2\text{R}'$ nanocrystals from carboxylate-terminated CdSe-$\text{Cd}(\text{O}_2\text{CR})_2/\text{HO}_2\text{CR}$ requires the removal of acidic impurities prior to the addition of primary amine. Otherwise, the formation and subsequent tight binding of $n$-alkylammonium carboxylate ion pairs prevents quantitative removal of carboxylate species. Dimethylcadmium and diethylzinc were used as reagents to deprotonate acidic impurities, which either causes methylation (with a surface density of 0.04−0.22 nm$^{-2}$) and photoinduced reduction of the nanocrystal core or X-type ligand exchange with ethyl species, respectively. The acid-scavenged nanocrystals could be completely isolated from displaced carboxylate ligands ($\leq 0.01$ carboxylates nm$^{-2}$). In addition to traditional selective precipitation procedures, gel permeation and silica chromatography were investigated as alternative purification methods for the isolation of CdSe-$\text{NH}_2\text{R}'$. Both demonstrated no improvement compared to the more convenient precipitation process.

Thin films fabricated from CdSe-$\text{NH}_2\text{C}_4\text{H}_9$ show little to no grain growth upon thermal annealing at 250 °C, maintaining domains (~10 nm) despite complete desorption of $n$-butylamine from the nanocrystal surface above 150 °C. Despite no passivation of the surface and a high density of grain boundaries, thin film transistors of CdSe-$\text{NH}_2\text{C}_4\text{H}_9$ fabricated on thermally grown silicon dioxide gate dielectrics produce field-effect transistors with an average electron mobility of 12 ± 1 cm$^2$ V$^{-1}$ s$^{-1}$, a low threshold voltage hysteresis (4.0 ± 0.6 V$\text{th}$), and an on/off ratio of $8 \times 10^4$.

Colloidal dispersions of amine bound nanocrystals (CdSe−$\text{NH}_2\text{R}'$) are indefinitely stable at amine concentrations of 0.1 M or higher and slowly aggregate at lower concentrations. Dissociation and evaporation of the amine ligands in 4-ethylpyridine, tri-$n$-butylphosphine, or...
molten tri-\textit{n}-octylphosphine oxide solution results in nanocrystal aggregation. Greater stability can be achieved using dimethyl-\textit{n}-octadecylphosphine as the L-type ligand, yielding soluble CdSe-PMe\textsubscript{2}C\textsubscript{18}H\textsubscript{37} nanocrystals with a phosphine coverage of 1.8 nm\textsuperscript{2}. CdSe-PMe\textsubscript{2}C\textsubscript{18}H\textsubscript{37} is the first stable nanocrystal sample bound solely by neutral phosphines.

\textit{Z}\textsuperscript{-}type rebinding was investigated with metal oleate species (M\textsuperscript{\textit{\textit{n}}}\textsuperscript{+}(O\textsubscript{2}CR)\textsubscript{n}, M = Cd\textsuperscript{2+}, Zn\textsuperscript{2+}, Pb\textsuperscript{2+}, In\textsuperscript{3+}), and a relative binding affinity of these complexes can be established. Rebinding of metal oleate species at 25 °C yield lower coverages, yet can reach saturation upon heating to 100 °C. The rebinding of cadmium chloride to aggregated CdSe-PBu\textsubscript{3} stabilizes the particle and aids in their redissolution. L-type ligand exchange and subsequent Z-type rebinding was employed towards the synthesis of a new model compound passivated by dimethyl-\textit{n}-octadecylphosphine and cadmium trifluoroacetate ligands, CdSe-Cd(O\textsubscript{2}CCF\textsubscript{3})\textsubscript{2}/PMe\textsubscript{2}C\textsubscript{18}H\textsubscript{37}, which is characterized by UV-Vis, \textsuperscript{1}H, \textsuperscript{19}F, and \textsuperscript{31}P NMR spectroscopies.

The findings of this dissertation demonstrate the importance of ion-pair species in the colloidal stabilization of colloidal nanocrystal systems. It also indicates the utility of stoichiometric, amine and phosphine-bound CdSe-L to act as both reporter complexes and as a clean reactive reagent for synthesis of novel CdSe-MX\textsubscript{2}/L systems to study the molecular interactions at nanocrystal surfaces.
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“Sub-editors. Bastards. What about all that copy of his they'd cut? Fifteen years of research he'd filed from one planet alone and they'd cut it to two words. ‘Mostly harmless.’ The finger to them as well…” –Douglas Adams

This quote, taken from *Mostly Harmless*, perfectly sums up the PhD experience. Hundreds of experiments are performed and enough results are collected to write a 200+ page document that can, at the end of it all, can usually be summed up in a sentence. I usually enjoy roller coasters, but not so much when they last five years and push my psyche to its limits.

In a way, I’m incredibly jealous of scientists who came before me, not just because of their sheer brilliance, but also because earlier generations had a smaller pool of communal knowledge which made their innovations have a higher percentage of total contribution. The larger our shared knowledge is, the smaller the fractions of one’s research becomes (think of how much more must be added to a large sphere to get the same radius change as a small sphere). One of the most difficult aspects of a PhD program is pulling your head out of the trenches and putting your work within the context of the larger picture of scientific progress. Nobody can do this alone. Every innovation, big or small, is a result of one’s interactions – through conversations, books and publications, etc. – with other people. This dissertation is not an exception. I have so many people to thank for helping me become the scientist I am today, who have either spent countless hours with me in the trenches of the lab or have made sure I didn’t forget to enjoy life outside the doors of Havemeyer Hall. These people have all in their own way repeatedly helped me remember the bigger picture of research and keep the child-like love of science that I’ve almost lost countless of times.

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I want to thank my family and friends for all their love and support. I’m fortunate enough to have a family who does so much for me. It’s a rarity in life to have the opportunity to stress out over a doctorate, but it’s an opportunity my parents worked hard to give me. I’ll never be able to
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Lastly I want to thank you, the reader, for taking the time to read part or all of my dissertation. Whether you’re a future Owen group member, a curious friend or family member, I hope you can learn something and apply it to your own curiosities or research.

Without further ado, let’s begin our adventure into the surfaces of nanocrystals. It’s quite fun, actually. It’s a world of pretty colors, heavy metals, and great problems. Let’s get started, and don’t forget your towel.
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Scientific Abstract

Colloidal semiconductor nanocrystals show remarkable potential for commercialization in the solid state, photovoltaic, and biological markets. Despite remarkable growth in the synthetic tunability of these materials, a lack in understanding of the fundamental molecular interactions that give rise to surface states, colloidal stability, and structural changes limit their application. This chapter provides the reader with background on semiconductor nanocrystals. Using a molecular orbital approach to understanding their band structure, the role of ligands in their surface passivation is discussed. The covalent classification system developed by Green distinguishes between X, L, and Z-type ligands and their molecular interactions at a particle’s surface are introduced. Concepts relating to absorbance, emission, infrared, and nuclear magnetic resonance spectroscopies, as well as imaging techniques, are introduced to calibrate the reader on the characterization methods employed by the Owen research group. The challenges facing nanocrystal surface chemistry that are most relevant to this dissertation are introduced. This chapter concludes with general experimental considerations that are referred to in subsequent chapters.

Plain English Abstract

This chapter gives background on the relevance of semiconductor nanocrystals in various commercial applications. It also introduces some of the more significant challenges that must be overcome to improve the products made from these materials. We give a chemist’s approach to understanding the complicated electronic structure of nanocrystals and show how surface ligands are important in tuning their optical and electronic properties. In addition, methods on how cadmium selenide nanocrystals are synthesized and characterized are described so that the reader can understand the data presented in chapters II-VI.
I.1. Introduction to semiconductor nanocrystals

It is safe to say that our world would not be the same without semiconductors. Their appearance in applied technology as transistors in the 1940s started a revolution that to this day changes the way we interact with the world.¹ The integration of these materials into every aspect of our society, from energy, communication, and business to being one of the primary technologies responsible for the dawn of the information age, is astounding.² Most important to me, without semiconductors, I would be writing this dissertation with a typewriter, gathering my references in a library.¹ Despite the decrease in physical size of our devices, the computing power is still increasing. According to Moore’s law, the number of transistors per processor will double every two years.³ The drive for smaller electronic components has motivated the miniaturization of a multitude of materials, semiconductors included. Not only has the miniaturization of semiconductors been realized with nanocrystals, it also has unlocked new directions of research that has sparked its own revolution which will undoubtedly help our society meet the growing challenges of renewable energy, faster electronics and advanced medical imaging.

The explosiveness that the scientific field has witnessed in semiconductor nanocrystal advancements is indicative to the utility and unique physical properties that describe these materials. Since the first colloidal reported synthesis of semiconductors on the nanoscale level in the early 1980s,⁴ the rapid progress in their synthetic preparation led to methods that allowed us to control their size. It wasn’t long until the photoluminescent and semiconducting properties of these materials were exploited, increasing their utility for a variety of applications ranging from

¹ Primitive libraries used to be a house for these collections of paper resources called books, which were bound according to their subject. I know this is a technical and scientific document, but take a second to think about every book that you have ever seen and how you can access all of it on the 5 inch screen in your pocket. And realize that wasn’t the cultural norm half a generation ago. I’m proud of the work that I’m describing in this dissertation, but this is without a doubt the most mind blowing thing that you will read in this .pdf (unless you actually are reading this on paper).
biological imaging and solid state lighting to solar cells and electronic devices. In a span of approximately 30 years, we have witnessed the progress of a nanomaterial which has already been incorporated into usable technology like record breaking solar cells and efficient LEDs for displays.

The rate at which nanocrystals have been developed and applied is nothing short of amazing and will undoubtedly improve the society we live in. Unfortunately, such rapid progress must come at the expense of fundamental understanding of the molecular interactions which dictate their desired physical properties. This dissertation hopes to shed light on and provide a more chemical understanding of only a small fraction of these intricate and vital exchanges, specifically at the surface-ligand interface. While certainly an extreme viewpoint, many aspects of nanocrystal surface chemistry can be distilled into concepts introduced to scientists as early as their general and inorganic chemistry classes. This chapter, while not meant to be a reference for the theoretical background of every aspect of nanocrystal science (believe me, there are way more people better qualified at doing that than me and I recommend the reader various textbooks and reviews\(^5\)\(^-\)\(^9\)), aims to provide the reader with a chemically intuitive way to approach nanocrystal surface chemistry.

**I.1.1 A molecular orbital approach to semiconductor nanocrystals**

A semiconductor conducts electricity in a manner that is intermediate between metals and insulators. Unlike metals, semiconductors do not conduct electrons at equilibrium. Their transport properties are instead governed by the electronic structure of the material. This has been theorized in several ways;\(^ii\) yet for the purpose of this dissertation the description of the energy levels in

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\(^ii\) By avoiding the quantum mechanical complexities of solid state physics, I am by no means attempting to suppress its importance in understanding the properties of these materials, but am rather emphasizing the power a chemical
semiconductors will be constructed from a concept familiar to chemists: molecular orbital theory. Using molecular orbitals as a starting point, the electronic band structure of a semiconductor can be constructed from numerous atomic interactions via a bottom-up approach. For a homonuclear diatomic molecule, such as H₂, simple molecular orbital theory states that the 1s wavefunctions from both hydrogen atoms will interact and combine to form two new wavefunctions. That which results in a lower energy than a hydrogen’s 1s orbital is described as the bonding orbital, and likewise that which results in a higher energy is referred to as an antibonding orbital. For a more relevant element, such as silicon, the basic concept remains the same. Starting from a single Si-Si bond and growing an infinite silicon solid, an infinite number of both bonding and antibonding orbitals would form, comprising two “bands” of energy levels.

Figure 1.1. A simple molecular orbital diagram of an ideal cadmium selenide semiconductor

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As described in reference 6, the main advantage that chemists have when approaching solid state materials is their unmatched intuition about bonding and orbitals.
For another semiconductor, such as cadmium selenide, the result is similar, but the orbital contribution from cadmium and selenium is not partitioned equally (Figure 1.1). Unlike a semiconductor material like silicon, whose bonds can be considered covalent in nature, cadmium selenide’s bonds are more ionic, resulting in a formal oxidation of cadmium by selenium. Due to selenium’s higher electronegativity than cadmium, its orbitals contribute more to the bonding orbitals, whereas cadmium’s contribute more to the antibonding energy levels. Regardless, filling in the electrons according to Hund’s rule, this approach yields a band completely filled with electrons and one unfilled. Respectively, these bands are called the “valence” and “conduction” bands and are analogous to the HOMO and LUMO energy states of a small molecule. In our chemical description, we attribute the valance band as being “selenium like” and the conduction band as “cadmium like”, according to the element whose atomic orbitals contribute most to the resulting molecular ones. The energy difference between the valance and conduction band is defined as the band gap of the material and dictates many of the fundamental optical and electronic properties of the semiconductor material. Typical II-VI semiconductors have bandgaps between 0 and 3.3 eV (for our purposes the band gap of cadmium selenide is 1.74 eV), making them useful for applications which utilize infrared, visible, and low ultraviolet radiation.

The structural changes introduced upon transitioning from an ideal semiconductor to a nanocrystal results in two new and important changes to its band structure (Figure 1.2). If a semiconductor particle’s size is reduced below that of its Bohr radius (the distance between the excited electron and hole in an exciton), quantum confinement effects change the band gap of the system, with smaller sizes increasing the magnitude of the energy difference between the valence and conduction bands. Cadmium selenide nanocrystals smaller than 11 nm will exhibit quantum confinement. Furthermore, disruption of the infinite lattice causes a decrease in degeneracy at
the band edges, and gives rise to discrete electronic states and distinct peaks in the absorption spectrum of nanocrystals.\textsuperscript{14} This size effect allows for tuning the absorption energy of semiconductor nanocrystals and is one of the key properties utilized in their application.\textsuperscript{7,15}.

Another effect is the introduction of surfaces in the semiconductor system. While the atoms in a perfect CdSe crystal all have a local tetrahedral geometry, the exposure of both surface cadmium and selenides creates 2- or 3-coordinated atoms.\textsuperscript{16} The molecular energy orbitals which mainly derive from these under coordinated species will differ from the energy orbitals derived from the core.\textsuperscript{17} For under coordinated surface selenium atoms, the resulting bonding orbitals will not be as stabilized and will thus be located above the valence band edge. Likewise, the resulting antibonding orbitals from surface cadmium atoms will reside at an energy level below the conduction band edge. These surface states can have negative effects on the properties of nanocrystals, acting as trap states for photogenerated electrons or holes.\textsuperscript{18} Without ways to minimize the effects of these surface states, they can significantly reduce the nanocrystal’s photoluminescence quantum yield (PLQY),\textsuperscript{19-20} increase the number and rate of non-radiative recombination pathways,\textsuperscript{18,21} and hinder carrier transport.\textsuperscript{21-22}

One of the crucial roles that ligands play in semiconductor nanocrystal systems is the passivation of these surface states and shifting their energy level back within their respective bands (Figure 1.2). Assuming that cadmium and selenium form ionic bonds, each cadmium atom has a formal oxidation state of 2\textsuperscript{+} and an empty 5s orbital which can act as a Lewis acid for an incoming pair of electrons. Such an interaction would help passivate the surface cadmium and raise its energy level closer to or within that of the conduction band. On the other hand, surface selenium atoms have a formal oxidation state of 2\textsuperscript{-} and a lone pair which can interact with a Lewis acid. This
passivates the surface state and lowers its energy to that of the conduction band. Such a molecular approach has been demonstrated to describe the changes in optical properties of CdSe nanocrystals.

**Figure 1.2.** Passivation of surface cadmium and selenium derived orbitals with Z-type and L-type ligands, respectively.

I.2 The surface chemistry of II-VI nanocrystals

As synthesized semiconductor nanocrystals are stabilized by aliphatic organic species, such as carboxylates, phosphonates, and long chain primary amines. While these molecules are efficient at maintaining colloidal stability of the particles, they inhibit charge transfer in thin films, are incompatible with aqueous media, and typically have quantum yields below the desired threshold for solid state lighting. To address these limitations, the native ligands must be replaced with molecules designed for the particular application at hand, whether that be in an electronic device, as a biological fluorophore, or as an outer layer stable to prolonged air and high temperature...
exposure. These ligand exchanges, however, can come with their own negative side effects, including lower colloidal stability, changes in trap state densities, and further quenching of the quantum yield.

The rational design of molecules with high binding affinity, the desired solubility, and no damage to the optical and electronic properties of nanocrystals is a challenge that will only be met by learning the fundamental molecular interactions between ligands and the atoms that contribute to the surface binding sites of colloidal materials. This dissertation focuses on some of these fundamental interactions, in particular the binding of X-type ion-pairs, L-type amines and phosphines, and Z-type metal carboxylates and halides. The use of X, L, and Z-type to describe these ligands originates from inorganic chemistry and is described in the next section.

I.2.1 The covalent ligand classification system and its application in nanocrystal chemistry

The fact that surface ligands in colloidal nanocrystal systems dictate so many important aspects of their functionality necessitates a deep understanding of their interaction with the particle surface. Molecules that have been reported for ligands range from simple metal salts and amines to long functionalized polyethylene glycol chains and DNA strands. While some depictions of the nanocrystal-ligand structure are simplified to a ball with squiggly lines attached to the surface, ligand binding is a molecular phenomenon which can be made more precise using concepts developed in small molecule inorganic and organometallic chemistry. One such concept is the covalent ligand classification (or the XLZ) system developed by Malcolm Green in 1995.27 Along with the Hens research group, the Owen lab has helped apply the XLZ formalism to nanocrystals to better describe and understand the molecular interactions at the surface.19, 23, 28-30
In the covalent ligand classification system, a molecule is described by the number of electrons it contributes to bond formation with a metal center in its charge neutral electron configuration (Figure 1.3). For example, a halogen such as chlorine has 7 valence electrons and uses only its one unpaired electron in bonding to a metal center. A ligand which donates one electron is classified as an X-type ligand. Other examples of X-type ligands are monodentate carboxylate species and hydrides, and carry a charge of -1 if counting electrons via formal oxidation states. Of particular importance to this dissertation is the classification of ion pairs of the general form [LH][X]: As we propose in chapter II, the ion pair binds to the nanocrystal surface through the anionic species as an X-type ligand. L-type ligands can be thought of as Lewis bases, as they contribute two electrons when binding to a metal center. Examples of L-type ligands are
amines and phosphines. Ligands which contribute 0 electrons are classified as Z-type. Z-type ligands act as Lewis acids and examples include boranes and metal centers with empty orbitals such as CdCl$_2$. Both L and Z-type ligands have a formal charge of 0 and can be considered neutral. For a more extensive overview of the XLZ classification system the reader is referred elsewhere.\textsuperscript{27, 30-31}

Applying the XLZ formalism to nanocrystal surface chemistry allows for a better understanding of the atoms involved in bonding and therefore the surface states which are being most directly affected. The majority of reported syntheses of II-VI, III-V, and IV-VI semiconductor nanocrystals produce particles which contain an excess of metal cation ($M^{n+}$) with respect to the core anionic species.\textsuperscript{32-38} Thus, charge balance necessitates the presence of X-type ligands, resulting in surface bound $M^{n+}X_n$ species. This view of nanocrystals being non-stoichiometric and balanced by anionic X-type ligands includes excess metal cations as part of the nanocrystal. Another, more relevant approach to this document is viewing the $M^{n+}X_n$ species as being a moiety separate from a stoichiometric nanocrystal, acting instead as a Z-type ligand through the metal center towards a surface anion.

\textbf{I.2.2} Early descriptions of CdSe nanocrystal surfaces

The earliest reports of CdSe nanocrystals bound by organic ligands described the particle surface as being protected by phenyl ligands produced from the Ph-SeTMS precursor.\textsuperscript{39} A few years later, the seminal paper on CdSe nanocrystal synthesis proposed a CdSe nanocrystal bound by tri-$n$-octylphosphine, or TOPO, molecules.\textsuperscript{40} Subsequent ligand exchange on these “CdSe-TOPO” systems included L-type ligand exchange with pyridine to create “CdSe-py” nanocrystals, and even further proposals of nanocrystal linking via ligands such as ethylenediamine showed
dramatic increases in the charge transport properties of these materials.\textsuperscript{41-42} These first ligand exchanges assumed an initial stoichiometric nanocrystal core bound exclusively by neutral L-type ligands. Only later was it discovered that the particles were predominantly terminated with phosphonate or carboxylate species. Currently, the field is in agreement that CdSe nanocrystals contain an excess of cadmium cations at the surface, necessitating charge balance by anionic X-type ligands.\textsuperscript{25, 43-44} Previous surface chemistry in the lab has utilized the presence of these X-type ligands to optimize ligand exchanges for smaller ligands such as chloride, demonstrating high quality charge transport properties for applications in thin film devices.\textsuperscript{45-46}

I.2.3 The neutral fragment model

As stated above, anionic X-type ligands in CdSe nanocrystal samples can be viewed as being part of a larger molecular species, namely a Z-type ligand with the formula CdX$_2$. With this view, the two major nanocrystal ligands that exist are Z-type metal salts and neutral L-type ligands.

![Neutral fragment model of a metal chalcogenide nanocrystal.](image)

**Figure 1.4.** Neutral fragment model of a metal chalcogenide nanocrystal.
like amines and phosphines (Figure 1.4). This neutral fragment model views the nanocrystal ligand as being inherently stoichiometric, with excess cadmium cations acting as Lewis acids towards surface selenides. Likewise, L-type ligands form dative bonds with unpassivated surface cadmium atoms. However, these are not the only two acid-base adducts that can be formed in these dynamic systems, as L and Z-type ligands can also interact with each other. This third interaction displaces both ligands from the surface, creating unpassivated surface states that have dramatic effects on the optical properties of the nanocrystal. Referred to as L-type promoted Z-type displacement, this reaction has been extensively studied by our group and is a fundamental step in the synthesis of many of the compounds reported here.19, 47

1.3 Characterization techniques of colloidal nanocrystals

The characterization of nanocrystal systems incorporates traditional chemical methods with modern imaging techniques to probe the structure of both the inorganic core and organic ligand shell. The following sections describe the techniques that are frequently used in this dissertation and how they can be used for characterizing CdSe nanocrystals. However, it is important to state that these methods do not encompass all of the common techniques used by the field. Of particular importance is X-Ray diffraction (XRD), which can be used to determine the crystal phase and size distribution of the CdSe core. While CdSe have tetragonal lattices, they can crystallize in either the wurtzite (hexagonal) or zincblende structure. XRD analysis has been crucial to the understanding of which phases are formed under various synthetic conditions.20, 48 All the nanocrystal samples discussed in this dissertation were synthesized from literature protocols that used XRD to characterize the inorganic core. For all but one nanocrystal sample this report focuses exclusively on zincblende CdSe.
Figure 1.5. UV-Vis absorption spectrum of a 3.54 nm cadmium selenide nanocrystal.

1.3.1 UV-vis absorbance and fluorescence spectroscopies

UV-vis absorbance spectroscopy is the most common tool used to characterize colloidal CdSe nanocrystals (Figure 1.5). Quantum confinement allows for the tuning of the band gap of these particles between ~1.9 and 2.5 eV, which coincides with the visible light region of the electromagnetic spectrum. The location of the 1S_e-2S_{1/2} transition maximum\(^{49}\) is dependent on the size of the nanocrystal. Pioneering work in the nanocrystal field by the Peng\(^{50}\) and Mulvaney\(^{51}\) groups empirically derived size dependent transition maxima, and Beecher and Owen recently expanded this to include small cluster sizes.\(^{52}\) In addition to determining the size of the nanocrystals, UV-Vis also provides a way of measuring the size dispersity of the sample by examining the width of the 1S_e-2S_{1/2} transition. Although this line width is affected by additional aspects, such as intrinsic single particle broadening,\(^{53}\) state of the art CdSe nanocrystal syntheses have size dispersities with standard deviations \(\leq 5\%\), corresponding to a \(~100\) meV line width.

Previous reports have also demonstrated that the density of states of CdSe nanocrystals at \(\lambda = 350\) nm is constant across all sizes. Thus, a size-independent extinction coefficient \(\varepsilon_{350}\) is
indicative of the total number of CdSe unit cells present rather than the oscillator strength of a particular electronic transition. In this dissertation, concentrations for both total CdSe and nanocrystals are reported. The total [CdSe] is determined using $\epsilon_{350}$. Determining the concentration of nanocrystals requires dividing [CdSe] by the number of CdSe units per unit volume of a particle, which is estimated assuming a spherical shape and using the single crystal density of CdSe to calculate the molar volume. The numbers we calculate using this method match the nanocrystal concentrations derived from reported size-dependent extinction coefficients.$^{50-51}$

Fluorescence spectroscopy is the other method that is frequently used for most reported nanocrystals. The fluorescence spectrum of a particle contains information about the polydispersity of the sample, but it also is used to measure the photoluminescence quantum yield (PLQY) of nanocrystals, which is one of the key physical properties of these materials. For the samples reported in this dissertation, the PLQYs are unanimously low, with the highest values ranging from 15-30 %.\textsuperscript{19, 24} Thus, while an invaluable tool to characterize semiconductor nanocrystals, this thesis does not heavily rely on fluorescence spectroscopy.

I.3.2 Nuclear magnetic resonance spectroscopy

The application of nuclear magnetic resonance (NMR) spectroscopy to studying CdSe nanocrystal systems allows for detailed analysis of their ligand composition, making it as indispensable as UV-Vis spectroscopy. In fact, this dissertation utilizes NMR more than any other technique, and therefore it is imperative that the reader understands how our research group interprets each spectrum. In addition to the $^1$H nucleus, $^2$H, $^{13}$C, $^{15}$N, $^{19}$F, and $^{31}$P nuclei also provide useful information about the chemical environments of ligands.
Figure 1.6. $^1$H NMR spectra of oleate terminated CdSe nanocrystals before (blue) and after (red) purification and removal of unbound oleate species.

The three most important spectral features in NMR are the chemical shift, intensity, and line width of the signal. Example spectra in Figure 1.6 demonstrates these features. The chemical shift of a resonance is highly sensitive to the chemical environment of the nucleus being analyzed, and allows us to determine which ligands or organic impurities are present in the sample. The $^1$H NMR chemical shifts of cadmium oleate terminated CdSe nanocrystals are assigned according to Figure 1.6. The alkenyl protons of the oleate species are particularly useful, as their chemical shifts are resolved from the other signals and therefore act as a useful spectroscopic handle for calculating the oleate concentration. The intensities of hydrogen nuclei in NMR spectroscopy are proportional to the number of nuclei in the sample. With the addition of an internal standard, the integrated intensities can be used to determine the concentration of each organic species in

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\[iii\] This is not always the case. In chapter II we will describe how some trace impurities, whose presence drastically alters the properties of the nanocrystal, cannot be observed using NMR techniques.
solution. The internal standard chosen for these studies is bis(η⁵-cyclopentadienyl) iron, or ferrocene, as it does not interact with the nanocrystals or organic ligands and is easily soluble in the organic solutions used.

The line width of chemical shifts in NMR spectra is affected by two major phenomena. Fast, dynamic exchange of a ligand causes changes in the chemical environment of the studied nuclei, which gives rise to homogeneous line broadening. The line broadening due to this exchange is dependent on ligand concentration and the chemical exchange rate. The second phenomenon that is of particular interest to colloidal solutions is the organic molecule’s interaction with the nanocrystal surface. Molecules that are surface bound undergo heterogeneous line broadening due to the slower tumbling rate of the larger size particle. Thus, broad resonances in the NMR spectra of nanocrystals is indicative of bound species. Free ligands, non-binding organics, and solvent have narrow line widths that are common to small molecule NMR analysis. Because of this difference, it is possible to distinguish surface bound and free organic moieties. For example, the appearance of a sharp alkenyl resonance in oleate-terminated nanocrystals implies free cadmium oleate species (Figure 1.6). The presence of this excess ligand is not desired for future surface chemistry studies, and these samples are usually further purified until only surface bound resonances can be observed.

Taking the ratio between the concentration of ligand (derived from NMR spectroscopy) and nanocrystals (derived from UV-Vis spectroscopy), we can calculate the number of ligands per particle. This number is usually normalized with respect to nanocrystal size and is reported in a ligand surface density with units nm⁻². While this density is likely not homogeneous across the entire particle surface, it acts as a useful value to compare ligand coverages across different
samples. For CdSe-Cd(O_2CR)_2 samples free of excess ligands, carboxylate surface densities are on average 3.5 nm^2.

### 1.3.3 Fourier transfer infrared spectroscopy

Fourier transfer infrared spectroscopy (FTIR) is another technique used to characterize the organic species in nanocrystal samples. Characteristic frequencies of carboxylic acid can be distinguished from carboxylate species, which can be difficult using NMR. Likewise, both amine and ammonium species can be seen. FTIR has also been used to characterize the various binding geometries of carboxylates to nanoparticles, providing more detail than NMR in some cases. As we will see in chapter II, FTIR has proven to be invaluable in studying ion pairs in nanocrystal samples.

In addition, diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) can be performed on solid nanocrystal samples slurried in potassium bromide. An inert air sample chamber equipped with a heating stage and vacuum line can be used to study the desorption of ligands from nanocrystal surfaces, making it useful to investigate changes in the surface composition under annealing/device fabrication conditions (see chapter IV).

### 1.3.4 Imaging techniques – Transmission electron microscopy, atomic force microscopy, and scanning electron microscopy

In addition to the traditional UV-vis, fluorescence, NMR, and FTIR spectroscopies, imaging techniques have proven to be useful tools to study nanoparticle morphology. Transmission electron microscopy (TEM) is commonly used as a visual complement to UV-vis spectroscopy measurements, and high resolution methods can give information about lattice spacing and
exposed facets. Atomic force microscopy (AFM) was used to obtain information on the height of quantum dot thin films. In addition to being an additional imaging technique, scanning electron microscopy (SEM) can perform energy-dispersive X-ray spectroscopy for elemental analysis of films.

I.4 Applications of semiconductor nanocrystals

The stability, large absorption cross-section, and high quantum efficiency of nanocrystals have caused them to be a leading candidate for the next breakthrough material for applications in biological imaging, photovoltaic cells, and solid state lighting. While applications of nanocrystals have been the subject of a number of reviews, a brief summary of the current state of the art technologies will help contextualize this report.

I.4.1 Biological imaging

By exchanging the native aliphatic surfactants on nanocrystals for species such as mercaptoacetic acid, phospholipid micelles, dihydroxylipoic acid, or by coating the particles in silica, siloxane, or polymer shells such as polyacrylic acid, the original hydrophobic nanocrystals can be made water soluble. This allows for their photoluminescent properties to be utilized as a powerful fluorophore for biological imaging. Additional modification of the surface can be performed to attach functionalized species that allow for specific binding to biological targets. Compared to organic fluorophores, quantum dots are photostable and resistant to metabolic degradation. Furthermore, nanocrystals exhibit quantum confined stark effects in their fluorescence properties, which change upon exposure to an electric field. Thus, these materials are also interesting for neuroimaging applications.
I.4.2 Photovoltaic cells

The low-cost of solution based processing of semiconductor materials has the potential to make renewable energy technologies even more widespread. Some of the earliest devices utilizing semiconductor nanocrystals had Grätzel cell architectures using TiO$_2$ nanocrystals as the light absorbing layer.\textsuperscript{68} As time progressed, type II bulk heterojunctions were fabricated using semiconductor nanocrystals.\textsuperscript{69} Emerging materials such as lead sulfide have shown an improvement in efficiencies from < 1% to 8% within a decade.\textsuperscript{70} As of 2016, the efficiencies of semiconductor nanocrystal based solar cells have matched and exceeded that of silicon (26.3%), with CdTe (21%, First Solar), CIGS (21%), InP (22.1%, Spire), and GaAs (28.8%, Alta) based solar cells emerging as leaders of renewable solar technologies.\textsuperscript{71}

I.4.3 Solid state lighting

The narrow emission bandwidth and the tunable size of nanocrystals make them ideal for solid state lighting purposes. Conventional rare earth phosphors exhibit intrinsic energy losses in wavelengths past the visible range of the eye of up to 40%, which can be significantly lowered by their substitution with quantum dots. With the advent of high quality core-shell nanocrystal samples, quantum yields have approached unity, and their utilization as downconverting LEDs has the potential to save 4,896 trillion British thermal units of energy annually, which translates into an annual cost saving of $49 billion for the US alone.\textsuperscript{72} iv Semiconducting nanocrystals have already begun to have commercial success, with products such as the Amazon Kindle Fire HDX and Sony’s QLED TV incorporating them as their LED material. However, the replacement of all

\textsuperscript{iv} For a fun comparison, this is approximately the entire amount of energy used annually by Mexico…like, the entire country.
incandescent lightbulbs with LEDs is still far from realized, leaving much of the current lighting market open for replacement with nanocrystal-based LED technologies.

1.5 Selected challenges in nanocrystal surface chemistry

Despite the promising utility of semiconductor nanocrystals, there remains significant hurdles that must still be overcome if these materials are to be developed into realized technologies. As mentioned before, aqueous compatibility of as synthesized nanocrystals generally requires exchange of organic ligands for those which will aid in the solvent change. Incorporation into a biological system for imaging applications poses further problems, as the particle must be able to diffuse into a cell membrane. In addition, the nanocrystal must be stable to its biological environment, whose changes in pH can cause irreversible aggregation. Furthermore, the choice of ligands must display a high binding affinity, outcompeting biological molecules such as glutathione which can also tightly bind and cause quenching of the photoluminescence through oxidation processes.\textsuperscript{57}

While it is intuitive that shorter, inorganic ligands limit inter-dot electronic coupling far less than long, aliphatic organic ones,\textsuperscript{46, 73} there remains a lack of knowledge concerning the effect ligands have on the energy levels of surface states. The modification of the energy landscape of these surface states is crucial for charge transport applications, and a deeper understanding requires a well defined model system which can easily tune the molecular identity of the surface. In addition, some ligands are known to promote grain growth in semiconductor systems,\textsuperscript{45-46, 74-75} and more knowledge about this growth mechanism is necessary to control domain size.

The characterization of all ligands in nanocrystal systems, including small amounts of impurities, is required if studies on the kinetics and thermodynamics of subsequent ligand
exchanges are to be accurately performed. For example, the observation of L-type promoted Z-type displacement can complicate the chemical equilibria self-exchange. This uncertainty does not originate from incorrectly performed surface exchange or measurements, but from an incompletely understood starting surface composition. Thus, a starting nanocrystal sample with no impurities and minimal inter-ligand interactions is essential to ascertain precise information about binding affinities, exchange rates, and equilibrium constants.

Core-shell nanocrystals have emerged as the leading candidate for solid state applications, but still display significant “blinking” in which the particle’s photoluminescence switches between an emitting state and an off dark state under continuous illumination. While the cause of blinking is not well understood, it has been proposed that strain caused by the lattice mismatch of the core and shell materials is one of its primary causes. Given the right choice of ligands, the surface chemistry of core semiconductor nanocrystals could possibly act as a model to understand the molecular interactions that take place at this interface.

This dissertation aims to provide insight into the chemistry behind these three nanocrystal surface challenges. In particular, chapter II discusses the high binding affinity of anionic species from ion pairs, which might offer a new structural motif for the design of tightly bound ligands that are resistant to displacement in biological systems. Chapter IV compares the ligand composition of two cadmium selenide nanocrystal samples and their different structural changes in thin films. The fifth chapter introduces new and well-defined nanocrystal samples bound solely by neutral L-type ligands, whose exchange kinetics and thermodynamics can be quantitatively studied in subsequent projects. Lastly, chapter VI proposes a synthetic method for novel CdSe-MX₂ nanocrystals whose Z-type ligand could be chosen to study core-shell interfaces. Because of its long history in the field, reproducible synthetic methods, and our group’s expertise in its surface
chemistry, cadmium selenide was chosen as the semiconductor material for this work. Ideally, conclusions derived here can be applied to various other materials.

1.6 General Experimental

Below are general experimental procedures for the rest of the dissertation, as well as the synthesis and purification of the cadmium carboxylate bound CdSe-Cd(O₂CR)₂ starting nanocrystal material.

**General Methods.** Cadmium nitrate tetraaquo (99%), sodium hydroxide, myristic acid (99%), selenium dioxide (99.8%), anhydrous oleic acid (99%), 1-tetradecanol (95%), tri-n-butylphosphine (99%), methanol (99.8%), ¹³CO₂ (99% atom enriched, 1L lecture bottle), deuterium chloride (35 wt % in D₂O), and 1-octadecene (90%) were purchased from Sigma-Aldrich and used without further purification. Ferrocene (98%) was purchased from Sigma-Aldrich and purified by sublimation before use. Tri-n-octylphosphine oxide (99%) was purchased from Sigma-Aldrich and recrystallized from acetonitrile before use. Benzene-₆ (99.6%), toluene-₈ (99.5%), tetrahydrofuran-₈ (99.5%), methylene chloride-₂ (99.5%), acetonitrile-₃ (99.5%), anhydrous acetonitrile (99.5%), anhydrous tetrachloroethylene (99%), and anhydrous methyl acetate (99.5%) were purchased from Sigma-Aldrich, shaken with activated alumina, filtered, and stored over 4 Å molecular sieves in an inert atmosphere glovebox at least 24 h prior to use. Pentane, tetrahydrofuran, methylene chloride, diethyl ether, and toluene were dried over alumina columns, shaken with activated alumina, filtered, and stored over 4 Å molecular sieves in an inert atmosphere glovebox at least 24 h prior to use. Dimethylcadmium and diethylzinc were purchased from Strem and vacuum distilled prior to use. **CAUTION:** Me₂Cd is extremely toxic and because
of its volatility and air sensitivity should only be handled by a highly trained and skilled researcher.

N,N,N′,N′-Tetramethylethlenediamine (TMEDA, 99.5%), 1,2-diaminocyclohexane (mixture of cis and trans isomers), n-octylamine (99%), n-hexylamine, n-butylamine, tri-n-butylphosphine (99%), and tri-n-octylphosphine (99%) were purchased from Sigma-Aldrich and dried over CaH₂, distilled, and stored in a nitrogen glovebox. Highly p-doped, 1 20 Ωcm, [100] silicon wafers with 200 nm of dry thermal oxide were purchased from Silicon Quest International. n-Octadecylphosphonic acid was synthesized as described previously. Cadmium myristate and cadmium oleate were synthesized from Cd(NO₃)₂·4H₂O and the corresponding carboxylic acid on a 25 mmol scale following a modified procedure reported previously.

All manipulations were performed under air-free conditions unless otherwise indicated using standard Schlenk techniques or within a nitrogen atmosphere glovebox. NMR spectra were recorded on Bruker Avance III 300, 400, and 500 MHz instruments. ¹H NMR spectra were acquired with sufficient relaxation delay to allow complete relaxation between pulses (30 s). ¹³C NMR spectra were collected using an inverse gated decoupling pulse program. ³¹P NMR spectra were recorded with 2 s delays between pulses. ¹⁹F NMR spectra were recorded with 2 s delays between pulses. The first 32 points of the FID were discarded due to fast relaxing fluorine nuclei in the NMR probes, and a linear prediction in Bruker’s TopSpin program (“LPbr”) was performed to obtain the processed spectra. DOSY measurements were performed using a double-stimulated echo sequence. The gradient strength was varied linearly from 2% to 95% of the probe’s maximum value. The diffusion parameters consisting of the pulse length (δ/2) and delay (Δ) were chosen to ensure that > 90% of the signal decayed at the highest magnetic field gradient. UV–vis data were obtained using a PerkinElmer Lambda 950 spectrophotometer equipped with deuterium and
tungsten halogen lamps. Photoluminescence spectra and quantum yields were measured using a FluoroMax-4 equipped with an Integrating Sphere from Horiba Scientific according to a previous report.\textsuperscript{19} FT-IR spectra were obtained using either a sodium chloride or lithium fluoride liquid cell in tetrachloroethylene with a Thermo Scientific Nicolet 6700 spectrometer equipped with a liquid N\textsubscript{2} cooled MCT-A detector. DRIFTS spectra were obtained using a Harrick Praying Mantis high pressure high temperature sample chamber using anhydrous KBr as the matrix. Scanning electron microscopy was performed using a Hitachi 4700 tungsten cold field emission scanning electron microscope. Electrode deposition was performed using an Angstrom Amod deposition system installed in a nitrogen glovebox. Electrical measurements were performed in a nitrogen glovebox using an Agilent 4155C semiconductor parameter analyzer.

**Synthesis of CdSe–Cd(O\textsubscript{2}CR\textsubscript{2}/HO\textsubscript{2}CR.** CdSe nanocrystals were synthesized using a previously reported procedure.\textsuperscript{24, 28, 46} Purified nanocrystals without \textsuperscript{1}H NMR signals from free oleyl chains were used to make stock solutions in benzene-\textit{d}\textsubscript{6} ([–O\textsubscript{2}CR] = ~ 200 mM; [nanocrystal] = ~ 2 mM). These stock solutions were diluted 10-fold prior to NMR and 1000-fold prior to UV–vis absorption spectroscopy and PLQY measurements. The concentrations of nanocrystals and ligands in benzene-\textit{d}\textsubscript{6} stock solutions were determined using a combination of NMR and UV–vis absorption spectroscopies according to a previous report.\textsuperscript{19} A stock solution of ferrocene (10– 25 μL, 0.05 M) was added to a known volume of nanocrystal stock solution and the ferrocene signal used as an internal concentration standard.
I.7 References


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CHAPTER II: TUNING ION-PAIR COMPOSITION IN COLLOIDAL SEMICONDUCTOR CdSe NANOCRYSTALS

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Scientific Abstract

To completely displace the carboxylate surface ligands from cadmium selenide nanocrystals, oleic acid impurities are first removed using dimethylcadmium or diethylzinc. In addition to metal carboxylate and methane coproducts, reactions with CdMe₂ produce surface bound methyl groups ($\delta = 0.4$ ppm, 0.04–0.22 nm$^{-2}$) that photolytically dissociate to methyl radicals and n-doped nanocrystals. Without oleic acid impurities, cadmium carboxylate can be completely displaced from the surface using $n$-alkylamines ($\text{NH}_2R'$, $R' = n$-butyl, $n$-hexyl, $n$-octyl) ($\leq 0.01$ carboxylates nm$^{-2}$). Colloidal dispersions of amine bound nanocrystals (CdSe–$\text{NH}_2R'$) are indefinitely stable at amine concentrations of 0.1 M or higher and slowly aggregate at lower concentrations. CdSe–$\text{NH}_2R'$ reacts with oleic acid, $n$-octadecylphosphonic acid, or carbon dioxide to form surface bound $n$-alkylammonium oleate, phosphonate, and carbamate ion pairs that bind with greater affinity than primary $n$-alkylamines. The results indicate that nanocrystal dispersions solely stabilized by neutral donor ligands are relatively unstable compared to those stabilized by adsorbed metal carboxylate or phosphonate complexes or by ion pairs. The challenge of differentiating between the neutral ligand bound form and adsorbed ion pairs is discussed.

Plain English Abstract

Complete ligand exchange on nanocrystal systems has historically been difficult to achieve, with reactions going to $\sim 90\%$ completion. We report that the cause of this is due to the presence of impurities which bind tightly to the particle surface. Procedures to remove these impurities are described, allowing for the first time the synthesis of cadmium selenide particles bound exclusively by neutral ligands. These new nanocrystal compounds that act as ideal model systems to study fundamental ligand exchange reactions.
II.1 Overview of ion pair chemistry in colloidal nanocrystal systems

The interaction between charged species and colloidal surfaces is of fundamental importance across a variety of chemical systems. For example, ion pairs dictate the uptake of metals in soils and the solubility of minerals, thus acting as a key species in life as we know it. In addition, charges in aqueous and polar media dictate the structure and dynamics of colloidal suspensions. Systems such as polystyrene have been extensively studied to better understand general phenomena such as ion exchange and surface complexation.¹

In II-VI semiconductor nanocrystal research, ion pairs have gained traction as an important class of ligands to both dictate the solubility of particles as well as enhance the electronic coupling between them. One of the most central ideas that has motivated the development of colloidal semiconductor nanocrystal ligand exchange methods is the concept of enhancing the electronic coupling between neighboring particles.²⁻⁵ While the ligands used during the synthesis of nanocrystals excel at stabilizing the particles in organic solvents, their long-chained aliphatic nature does not allow for efficient transport of charge carriers in their solid-state films.⁶ Thus, considerable effort has been put forth to develop techniques that replace the native insulating shell with shorter molecular complexes. Ion pairs have been a particularly relevant class of ligands that have been used to synthesize ligand shells that allow for this enhanced electronic coupling in thin films. A variety of reports have utilized these species to achieve nanocrystal samples that can be fabricated into high quality electronic devices.³⁻¹⁷ Metal chalcogenide molecules, in particular, have emerged as the leader in surface ligands that provide the highest reported carrier mobilities in CdSe nanocrystal thin films.¹⁸⁻¹⁹

The exchange between insulating carboxylates and phosphonates for charged ion pair ligands not only causes drastic improvements in their electronic transport properties, but also
brings with this significant changes in the solubility of the resultant nanoparticles. The recent examples of metal chalcogenide, metal oxide, metal, and metal halide nanocrystals discussed above have been synthesized with carboxylate,\textsuperscript{20-23} chalcogenide,\textsuperscript{12, 24-25} thiocyanate,\textsuperscript{3} halide,\textsuperscript{2, 11, 25-27} citrate,\textsuperscript{28} or other polyanionic surface ligands that balance their charge with an outer sphere counterion and dissolve in polar media. Zeta-potential measurements of several of these materials support a negatively charged surface, implying strong interaction between the anions and nanocrystal.\textsuperscript{3, 15} Even more recent work has utilized the tight-binding of ions to nanocrystal surfaces to synthesize colloidal dispersions in molten inorganic salts, potentially offering greater stability in solid-state applications.\textsuperscript{29} In the Owen lab, the presence of tri-\textit{n}-butylphosphonium chloride ion pairs in CdSe-CdCl\textsubscript{2}/PBu\textsubscript{3} samples was shown to greatly influence the solubility of the resulting particles.\textsuperscript{27, 30} Nanocrystals free of ion pairs exhibited solubilities similar to carboxylate-capped nanocrystals. However, increasing amounts of phosphonium chloride led to a reversal of solubility, causing the particles to become insoluble in non-polar solvents such as pentane and toluene yet easily dispersed in acetonitrile, a commonly used anti-solvent for purification of CdSe-Cd(O\textsubscript{2}CR)\textsubscript{2} systems.

The electric double layer formed by adsorbed by ion pairs is perhaps one of the most common modes of stabilizing a colloidal dispersion. The sorption of ions on metal oxide surfaces in particular has been a subject of interest for decades.\textsuperscript{31-33} Colloidal dispersions of organic micelles and polymer beads in aqueous media share a similar motif.\textsuperscript{34} Using this knowledge of ion pair formation in colloidal systems, a growing interest in our research group has been to manipulate zwitterionic ligands to aid in nanocrystal compatibility into biological systems. The charged zwitterion has the potential to solubilize the particles in aqueous media, yet maintain the correct hydrophobic structure to easily incorporate into cell membranes as an opto-electrical probe.
While it is obvious that ion pairs allow for increased tunability of nanocrystal properties, fundamental knowledge about their formation is lacking, particularly in non-polar solvents. In addition, their high binding affinity to the surface may also hinder complete chemical exchanges where the ion pair is sought to be removed from the nanocrystal system. This chapter describes my work done to understand the formation and binding of ion pairs to CdSe nanocrystals in non-polar media, and proposes methods to remove them in order to achieve samples that are bound solely by neutral Z or L-type ligands. It is my hope that the insight I have gained about these modes of ligand binding will aid in the development of ligand systems that incorporate ion pairs, such as the zwitterionic ligand proposal described above, to achieve high stability in biological or optoelectronic applications.

II.2 Formation of ion pairs in colloidal CdSe systems

Ion pairs can be formed in colloidal nanocrystal systems by the deprotonation of an acidic species by common L-type ligands, such as amines or phosphines (Scheme 2.1). While purification of nanocrystal systems by centrifugation methods has been commonly accepted to remove excess

![Scheme 2.1](image)

**Scheme 2.1.** Deprotonation of an acidic species X-H by a Lewis basic L-type ligand can result in the formation and subsequent binding of an [L-H]⁺[X⁻] ion pair.
small molecules, including carboxylic acids, the conclusions reported herein indicate that acidic impurities may interact with nanocrystal surfaces more tenaciously than previously thought. Their presence in our nanocrystal systems could possibly result in the formation of ion pairs, perhaps even in non-polar media. Two previous observations in the Owen lab led to the questioning of the presence of acidic impurities in CdSe nanocrystal samples: the formation of tri-n-butylphosphonium chloride species during the synthesis of CdSe-CdCl₂/PBu₃,²⁷,³⁰ and the inability to completely remove oleate species from CdSe-Cd(O₂CR)₂ nanocrystals using L-type promoted Z-type displacement.³⁵

Our hypothesis of tenacious acidic impurities arose from a recent study of ligand cleavage using trimethylsilyl chloride, where protic impurities in the starting CdSe-Cd(O₂CR)₂ nanocrystals led to the formation and adsorption of hydrochloride salts. Characterization of the various phosphorous containing species by ³¹P NMR showed a resonance pertaining to [HPBu₃]⁺ cationic species. Multiple purification cycles failed to remove the phosphonium species, implying a high binding affinity to the nanocrystal surface. More recent work on the displacement of cadmium carboxylate ligands from zincblende cadmium selenide nanocrystals found that both diamines and n-alkylamines are effective displacement reagents, removing cadmium carboxylate from the particle surface in the form of a Lewis acid-base adduct (Lₙ-Cd(O₂CR)₂). Such strong bases were able to remove as much as 90-95% of the ligand shell as measured in situ using °H NMR spectroscopy.³⁵ However, even after repeated cycles of displacement and purification under optimized conditions, 3-10% of the starting carboxylate ligands remain bound to the nanocrystal surface.
II.3 Acidic impurities in colloidal CdSe nanocrystal systems

The difficulty in completely removing carboxylate ligands from the surface of CdSe nanocrystals raised questions pertaining to the identity of the remaining species. Our previous results with chlorinated CdSe systems, as well as the common use of ion pairs in general colloid science, led us to suggest that the formation of ion pairs in both CdSe-Cd(O$_2$CR)$_2$ and CdSe-CdCl$_2$/PBu$_3$ systems is a result of carboxylic acid impurities remaining after purification of the carboxylate bound CdSe nanocrystal starting material.

CdSe-CdCl$_2$/PBu$_3$ nanocrystals are synthesized by the cleavage of cadmium carboxylate bonds using trimethylsilyl chloride (Scheme 2.2). While the side-product of this reaction is trimethylsilyl esters, the presence of oleic acid causes an additional reaction to occur that generates hydrogen chloride.$^1$ This X-type ligand exchange is done in the presence of tri-$n$-butylphosphine,

Scheme 2.2. Chlorination of CdSe-Cd(O$_2$CR)$_2$/HO$_2$CR result in the formation of tri-$n$-alkylphosphonium chloride ion pairs.

$^1$ These chlorination reactions are typically done in large excess of the trimethylsilyl chloride reagent (12 equiv. per carboxylate), so there is not an issue of incomplete cleavage of the carboxylate ligands from the surface cadmium species.
which acts as an L-type ligand to keep the nanocrystals stable in toluene. However, it is basic enough to undergo protonation by hydrogen chloride and form the ion pair observed by $^{31}$P NMR.

**II.3.1 Oleic acid impurities from CdSe-Cd(O$_2$CR)$_2$ synthesis**

Commonly used CdSe nanocrystal syntheses report the use of oleic acid,$^{36}$ either during the in situ generation of cadmium carboxylate, as an agent to quench nanocrystal growth,$^{ii}$ or as a byproduct of nanocrystal monomer generation.$^{iii}$ Purification of the crude nanocrystal solution is achieved by multiple rounds of particle precipitation with an anti-solvent and centrifugation, which removes solvent and unbound organic molecules from the system. The amount of oleic acid that remains in the nanocrystal sample post-purification is difficult to assess, as its spectroscopic signal is indistinguishable from that of an X-type oleate ligand. Previous studies indicate that carboxylic acids can undergo rapid proton-mediated X-type exchange with metal carboxylates, including a preliminary step where the acid first intercalates within the aliphatic ligand shell of the nanocrystal.$^{37}$ This combination of fast exchange and surface interactions causes the oleic acid resonances in $^1$H NMR to appear broad and in the same chemical shift range as bound carboxylate. Methods to quantify the amount of acidic impurities in the nanocrystal sample have been developed here and are presented in section **II.4**.

While it is generally accepted that acidic species can undergo exchange with bound X-type ligands, there still remained a question surrounding the effectiveness of the typical precipitation-centrifugation cleaning method in removing excess oleic acid. To assess this, oleic acid was added

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$^{ii}$ The mechanism by which oleic acid quenches the growth rate of nanocrystals is not well understood, but it might act as a competing ligand with CdSe monomers for the growing particle’s surface.

$^{iii}$ This has been proposed as a product of the reaction between chalcogenidoureas and metal oleates during the synthesis of cadmium and lead chalcogenide nanocrystals and is currently under investigation by graduate students in the Owen lab.
to a sample of acid-scavenged\textsuperscript{iv} CdSe-Cd(O\textsubscript{2}CR)\textsubscript{2} with a carboxylate coverage of 0.59 nm\textsuperscript{2}. Such a sample has a carboxylate coverage that is low enough to expose approximately 80\% of the particle’s surface area, offering many binding sites for oleic acid to interact with. The product was analyzed by \textsuperscript{1}H NMR spectroscopy (Figure 2.1). Five cycles of precipitation, centrifugation, and redissolution leave a coverage of 1.14 oleate ligands nm\textsuperscript{2}, or roughly twice the initial coverage. The protons on these oleic acids have a line width and diffusion constant that is consistent with bound ligands (Figure 2.2). Thus, \(~50\%\) of the carboxyl ligands in the sample are oleic acid and the other half derive from cadmium oleate.

Figure 2.1. Alkene region of the \textsuperscript{1}H NMR spectra of CdSe-Cd(O\textsubscript{2}CR)\textsubscript{2} treated with oleic acid \textit{in situ} (i) and CdSe-Cd(O\textsubscript{2}CR)\textsubscript{2}/HO\textsubscript{2}CR obtained after isolation and purification (ii). Integration against an internal ferrocene standard (δ = 4.0 ppm, not shown) yields an oleate surface coverage of 1.14 nm\textsuperscript{2}, roughly twice the coverage of the starting Cd-Cd(O\textsubscript{2}CR)\textsubscript{2} nanocrystals (0.59 nm\textsuperscript{2}).

\textsuperscript{iv} In order to maintain structure to this chapter, I have decided to introduce acid-scavenged nanocrystals before discussing the method behind which these are synthesized. For an in-depth discussion on how acidic impurities are removed, please refer to section II.4.
Figure 2.2. Mono-exponential fits of the decay curves of the alkene resonances generated from DOSY spectra of oleic acid bound CdSe-Cd(O$_2$CR)$_2$ (top) and oleic acid (bottom) in methylene chloride-$d_2$.

The FT-IR spectrum of this independently prepared CdSe-Cd(O$_2$CR)$_2$/HO$_2$CR is indistinguishable from the starting CdSe−Cd(O$_2$CR)$_2$, with no carboxylic acid band ($\nu$(C=O) = 1710 cm$^{-1}$) (Figure 2.3) and no signals from selenol ($\nu$(Se−H) ~ 2300 cm$^{-1}$) or hydroxyl ($\nu$(O−H) ~ 3000−4000 cm$^{-1}$) groups. This does not rule out the possibility that surface bound oleic acid might exhibit a vibrational frequency that is significantly different than free oleic acid, even if it remains protonated. A $^1$H NMR signal from the acidic hydrogen could not be identified. Adsorption of oleic acid-$d_1$ (O−D) does not produce distinct FT-IR signals associated with the
Figure 2.3. FT-IR spectra of CdSe-Cd(O₂CR)₂ (dashed, red), CdSe-Cd(O₂CR)₂/HO₂CR (solid, black), and oleic acid (faded, blue) in tetrachloroethylene. The absence of a selenol stretch around 2300 cm⁻¹ and a CO₂H stretch around 1710 cm⁻¹ make it difficult to identify the manner in which oleic acid binds to the nanocrystal surface.

deuterium label nor a visible ³H NMR signal (Figure 2.4). It is possible that proton exchange occurs on a timescale that makes the proton and deuterium signals unobservable. Hens et al have studied the self-exchange of carboxylates and carboxylic acid on the surfaces of CdSe nanocrystals, concluding that the exchange occurs faster than the observable time scale, namely > 600 s⁻¹.³⁷ However, addition of ZnEt₂ to the labeled nanocrystals CdSe-Cd(O₂CR)₂/DO₂CR results in the formation of CH₂D–CH₃ (Figure 2.4). While the site of protonation is uncertain, it is clear that added oleic acid binds the nanocrystal and is not easily separated by precipitation.

II.4 Controlling acidic impurity content

The inability to remove tri-n-butylphosphonium chloride or n-alkylammonium oleate species from the nanocrystal surface by repeated purification, even with the use of polar organic antisolvents such as methyl acetate and acetonitrile, led us to hypothesize that that these ion pairs
Figure 2.4. \(^1\text{H}\)\(^2\text{H}\) NMR spectra of oleic acid-\(d_1\) (bottom), CdSe-Cd(O\(_2\)CR)\(_2\)/RCO\(_2\)D (middle), and CdSe-Cd(O\(_2\)CR)\(_2\)/RCO\(_2\)D treated with 10 uL of diethylzinc (top). The resonance at 0.8 ppm corresponds to ethane-\(d_1\) produced from the deprotonation of oleic acid-\(d_1\) by diethylzinc.

have a high binding affinity towards the nanocrystal surface. The tight binding nature of these ion pairs and the low volatility of the oleate anion makes their removal from the nanocrystal sample difficult. We therefore attempted to prevent ion pair formation in these systems by the removal of the acidic impurity (in both cases oleic acid) prior to addition of any basic L-type ligands. The presence of a carboxylic acid is unavoidable in current state-of-the-art nanocrystal syntheses, and the tenacity of carboxylic acids towards cadmium selenide surfaces was described in section II.3. Thus, one logical approach to removing acidic impurities in these systems was to remove the obstinate proton in question using a strong and easy to eliminate base.
Scheme 2.3. Proposed reactions between ion pairs (top) or acidic impurities (bottom) with dimethylcadmium.

II.4.1 Deprotonation of acid with organometallic reagents

Previous work in the Owen group has demonstrated the effectiveness of dialkylmetal species at deprotonating oleic acid impurities. Specifically, dimethylcadmium can be added to a CdSe-Cd(O\textsubscript{2}CR\textsubscript{2})\textsubscript{2}/HO\textsubscript{2}CR sample to deprotonate any present oleic acid to form methane and cadmium oleate (Scheme 2.3). Subsequent chlorination of these acid scavenged nanocrystals resulted in CdSe-CdCl\textsubscript{2}/PBu\textsubscript{3} samples free of phosphonium chloride ion pairs. This method of deprotonation has the major advantage of producing a volatile alkane, which can easily be removed under reduced pressure, and cadmium oleate which already exists in the sample as a Z-type ligand for the CdSe nanocrystal surface. In addition to dimethylcadmium, alternative dialkylmetal species such as diethylzinc offer similar advantages. Described below are the effects of treating CdSe-Cd(O\textsubscript{2}CR\textsubscript{2})\textsubscript{2}/HO\textsubscript{2}CR with these two organometallic reagents.
II.4.1.1 Deprotonation with dimethylcadmium

The addition of CdMe₂ to CdSe-Cd(O₂CR)₂ causes the immediate formation of methane (δ = 0.16 ppm), which is visible by eye and can also be monitored in situ using ¹H NMR spectroscopy. This rapid formation supports the presence of an impurity sufficiently acidic to rapidly protonolyze the Cd-Me bond. Integration of the total methane signal against an internal ferrocene standard indicates that there are approximately 15 methane molecules produced per nanocrystal. This number corresponds to ~10% of the initial surface carboxylate coverage, and also matches the amount of intractable oleate species that persist in nanocrystal samples after multiple treatments with n-alkylamines. These observations suggest that dimethylcadmium deprotonates acidic impurities, most likely oleic acid, that would otherwise convert to tightly bound anions upon addition of a Lewis base.

II.4.1.1.1 Methylation of CdSe-Cd(O₂CR)₂

After letting the reaction run for 24 hours, unreacted CdMe₂ (b.p. = 105.5 °C) can be removed under vacuum leaving nanocrystals with surface bound methyl groups, CdSe-Cd(O₂CR)₂/CdMe₂, that can be detected by a broad ¹H NMR resonance of low intensity in benzene-δ₆ solution (δ = 0.4 ppm, Figure 2.5). Quantification of this bound methyl species indicates a surface density of 0.15 nm², or roughly 7 methyls per nanocrystal. To the best of our knowledge, this was the first report of metal chalcogenide nanocrystals with metal-alkyl ligands.
Figure 2.5. (A) Reaction of CdSe-Cd(O$_2$CR)$_2$/HO$_2$CR with CdMe$_2$ methylates the nanocrystal surface. Key: white, stoichiometric metal chalcogenide nanocrystal; red, surface selenium; green, surface cadmium. (B) $^1$H NMR spectrum of the product nanocrystals showing resonances from carboxylate ligands, a ferrocene internal standard ($\delta = 4$ ppm), as well as a broad signal from surface bound methyl groups ($\delta = 0.4$ ppm).

II.4.1.1.2 Reversible photodoping of CdSe-Cd(O$_2$CR)$_2$/CdMe$_2$

These bound methyl species are stable in the dark, yet rapidly react in the presence of light. Photolysis of CdSe-Cd(O$_2$CR)$_2$/CdMe$_2$ eliminated the broad $^1$H NMR signal from surface bound methyl groups and produces CH$_4$ in benzene-$d_6$ and a mixture of CH$_4$ and CH$_3$D in tetrahydrofuran-$d_8$ solution (Figures 2.6). In addition to changes in the $^1$H NMR spectrum, photolysis also reduces the extinction of the lowest energy excitonic transition in the UV-vis absorbance spectrum and quenches the photoluminescence (Figure 2.7B). This bleaching of the first electronic transition in the UV-vis spectrum is well documented and is assumed to be due to a reduction of the nanocrystal core. Simultaneously, an absorption feature appears in the infrared spectral range ($\nu = 2000-4000$...
Figure 2.6. (left) Methane region of the $^1$H NMR spectra of (CdSe)-Cd(O$_2$CR)$_2$ treated with CdMe$_2$ that shows the decrease in bound methyl and formation of methane before (green) and after exposure (red) to UV-light. The intensities of the resonances are normalized to an internal ferrocene standard (δ = 4.0 ppm, not shown). (right) Methane region of the $^1$H NMR spectra of CdSe-Cd(O$_2$CR)$_2$ treated with CdMe$_2$ in a solution of THF-d$_8$ (0.14 methyls per nm$^2$, (i) that shows the formation of CH$_3$D upon exposure to UV-light (ii). Both a decrease in the amount of methyl species (broad resonance from -0.1 to -0.5 ppm) and an increase in the amount of CH$_3$D (1:1:1 triplet centered at 0.17 ppm) are seen upon light exposure. The intensities of the resonances are normalized to an internal ferrocene standard (δ = 4.0 ppm, not shown).

cm$^{-1}$, Figure 2.7C). This new feature corresponds to transitions between electronic states within the conduction band and has been studied for both lead and cadmium chalcogenide nanocrystals.\textsuperscript{39-42} Exposure of the sample to UV-light gradually recovers the original absorbance and photoluminescence properties of the starting CdSe-Cd(O$_2$CR)$_2$ nanocrystals. During this time, a visible amount of grey precipitate, presumably cadmium metal, forms, indicating that the doped nanocrystal can reduce surface Cd$^{2+}$ cations. The same recovery is observed if CdSe-Cd(O$_2$CR)$_2$/CdMe$_2$ is exposed to air, presumably because dioxygen oxidizes the reduced nanocrystal. Related spectroscopic changes have been reported upon exposure of nanocrystals to
Figure 2.7. (A) UV-Vis spectra and (B) FT-IR spectra of CdSe-Cd(O_2CR)_2 before (green) and after (blue) the addition of CdMe_2, and after exposure of CdMe_2 treated CdSe-Cd(O_2CR)_2 with UV-light for 12 hours (red). Upon treatment with CdMe_2, bleaching of the first electronic transition and broadening of higher order transitions can be seen in the UV-Vis absorption spectrum. In the IR region, the appearance of a broad transition centered around 2800 cm\(^{-1}\) follows brief exposure to UV-light, and then gradually dissipates over 12 hours with continued irradiation.

triethyl borohydride, sodium biphenyl, and other reductants.\textsuperscript{41, 43-44} We conclude that the photoexcited nanocrystal oxidizes the surface bound methyl groups, eliminating methyl radicals that abstract a hydrogen or deuterium atom from the carboxylate ligands or tetrahydrofuran-\textit{d}_8 solvent.

II.4.1.2 Deprotonation with diethylzinc

While CdMe_2 offers a clean and efficient route at removing acidic impurities, its unexpected photochemistry could possibly complicate further ligand exchanges through unwanted
redox chemistry. In addition to the high toxicity of organocadmium reagents, this led us to investigate the effectiveness of diethylzinc as an alternative path for producing acid free CdSe-Cd(O_2CR)_2 nanocrystals. Addition of ZnEt_2 to CdSe-Cd(O_2CR)_2/HO_2CR causes the immediate formation of ethane (δ = 0.8 ppm) and photochemical reduction of the nanocrystals, as well as quenching of the photoluminescence quantum yield. However, after removal of the volatiles, no NMR signals from surface bound ethyl groups could be observed.

At the time of this dissertation, there was only one other report of photochemical reduction of CdSe nanocrystals in situ using ZnEt_2.\textsuperscript{44} It was proposed that ethylation of the nanocrystal occurs at oxidized selenide surface sites. While this is indeed possible, we independently hypothesized that photodoping of the nanocrystal particle most likely occurred in the same manner as with CdMe_2 treatment, namely through alkylation of surface cadmium cations. We therefore sought to understand the chemical exchange processes at the nanocrystal surface that led to both photochemical reduction in situ, yet no ethylation of the particle after the removal of volatiles.

**II.4.1.2.1 X-Type exchange between M(O_2CR)_2 and MEt_2 species**

Interestingly, addition of ZnEt_2 (2 equivalents per carboxylate) to CdSe-Cd(O_2CR)_2/HO_2CR induces desorption of ~50% of the carboxyl ligands and produces diethylcadmium (Figure 2.8). In addition, a new quartet is visible that is upfield of typical aliphatic resonances (δ = 0.7-0.9 ppm). We tentatively assign this resonance to the methylene fragment of a pentanuclear zinc cluster, Zn_5Et_4(O_2CR)_6, on the basis of its chemical shift, the lack of Cd satellites, and an analogous structurally characterized cluster (Zn_5Et_4(OAc)_6) that forms upon conproportionation of zinc acetate and ZnEt_2.\textsuperscript{45} An independent study of the reaction between ZnEt_2 and cadmium oleate also produces CdEt_2, which matches the chemical shift and J_{Cd-H}
couplings reported earlier ($\delta = 1.25$ ppm, $^3J_{Cd-H} = 30$ Hz; $\delta = 0.3$ ppm, $^2J_{Cd-H} = 50$ Hz). After removal of the volatiles under vacuum and precipitation of the nanocrystals from toluene, zinc and oleate ligands can be recovered from the supernatant as verified using FT-IR, $^1$H NMR, and energy dispersive X-ray spectroscopies (Figure 2.9).

**Figure 2.8.** (A) Reaction of CdSe–Cd(O$_2$CR)$_2$/HO$_2$CR with ZnEt$_2$ leads to CdEt$_2$ and Zn(O$_2$CR)$_2$. Key: white, stoichiometric metal chalcogenide nanocrystal; red, surface selenium; green, surface cadmium. (B) $^1$H NMR spectrum of reaction between CdSe–Cd(O$_2$CR)$_2$/HO$_2$CR and ZnEt$_2$. (*) is assigned to ethane. Unlabeled signals are from carboxyl chains bound to the nanocrystal or free in solution. (C) $^1$H NMR spectrum of the reaction between Cd(O$_2$CR)$_2$ and ZnEt$_2$ in benzene-$d_6$. $^{111/113}$Cd satellites can be seen surrounding both signals from the methylene and the methyl groups of CdEt$_2$ ($\delta = 0.30$ and $1.25$ ppm).
Figure 2.9. (A) FT-IR, of Zn(O_2CR)_2 isolated from a CdSe-Cd(O_2CR)_2 solution treated with diethyl zinc (blue), independently prepared zinc oleate (red), and oleic acid (green). (B) ^1^H NMR, and (C) EDX spectra of Zn(O_2CR)_2 isolated from a CdSe-Cd(O_2CR)_2 solution treated with diethylzinc.

These observations indicate that ZnEt_2 and Cd(O_2CR)_2 undergo metathesis to CdEt_2, Zn(O_2CR)_2, and Zn_5Et_4(O_2CR)_6. We conclude that the conversion of ZnEt_2 to Zn(O_2CR)_2 causes desorption of the carboxylate ligands, presumably because Zn(O_2CR)_2 and Zn_5Et_4(O_2CR)_6 have a weaker affinity for the cadmium selenide surface compared to Cd(O_2CR)_2. The decreased carboxylate coverage helps explain the observed reduction in the PLQY from 10% to 2%.^35 In
addition, we also speculate that diethylcadmium is the active species responsible for the photochemical reduction of the nanocrystals. However, its decreased Lewis acidity due to the more electron donating ethyl groups results in a weaker binding affinity to the surface compared to CdMe$_2$, explaining the lack of $^1$H NMR signals from bound ethyl groups.

The rapid formation of ethane and methane upon addition of ZnEt$_2$ or CdMe$_2$ to CdSe–Cd(O$_2$CR)$_2$/HO$_2$CR supports the presence of an impurity sufficiently acidic to rapidly protonolyze the Zn–Et or Cd–Me bond. Integrating the $^1$H NMR signals from the ethane and methane byproducts indicates the acidic impurity makes up 10 mol % of the ligand shell. This quantity is consistent with our previous study of ligand exchange using trimethylsilyl chloride. We hypothesize that the oleic acid present in the ligand shell is the source of these acidic hydrogens (the presence of water was ruled out in our previous study by the lack of a bis-trimethylsilylether coproduct); however, another protic impurity produced by the synthesis could also be involved.

II.5 The elusiveness of a CdSe-L system

Nanocrystal systems bound exclusively by neutral donor ligands has been pervasive samples throughout the community. However, it has become apparent that these nanocrystal surfaces were often oversimplified, and well-characterized nanocrystals solely stabilized by neutral ligands are rare. In many cases, samples that were thought to be stabilized by neutral donors, including TOPO and primary $n$-alkylamines, are actually stabilized by impurities such as phosphonate and phosphinate anions or $n$-alkylammonium-$N$-$n$-alkylcarbamate salts formed from primary amines and carbon dioxide (Scheme 2.4). In principle, a nanocrystal bound solely by labile neutral donors could be obtained by completely displacing adsorbed anions or surface bound metal complexes using Lewis bases. However, previous attempts to do so using $n$-
Scheme 2.4. Common modes of stabilizing a colloidal dispersion. (White) stoichiometric metal chalcogenide nanocrystal, (red) surface selenium, (green) surface cadmium.

alkylamines,\textsuperscript{51-53} phosphines,\textsuperscript{51} and pyridine\textsuperscript{6,54-57} consistently report partial ligand exchange with a small fraction (10−15\%\textsuperscript{56-57}) of the ligands proving difficult to remove.

Until now, steps to rigorously remove acidic impurities in nanocrystal systems has not been pursued, with the assumption that traditional precipitation and centrifugation methods were adequate to purify samples. This work has demonstrated the difficulty in removing protic species in this manner and provides a more potent protocol for synthesizing acid free CdSe nanocrystals. With this sample in hand, L-type promoted Z-type displacement can be performed without the added complication of ion pair formation and binding to CdSe nanocrystal surfaces.
Figure 2.10. (A) Synthesis of CdSe–NH$_2$R’ by displacement of Cd(O$_2$CR)$_2$ with primary amines. Key: white, stoichiometric metal chalcogenide nanocrystal; red, surface selenium; green, surface cadmium. (B) $^1$H NMR spectrum of CdSe–NH$_2$R’ in benzene-$d_6$. The inset shows the lack of an alkenyl resonance from oleate ligands. The signal at $\delta = 4$ ppm is from ferrocene, which is used as an internal standard.

II.5.1 Synthesis and characterization of CdSe-NH$_2$R

Prior attempts to completely displace Cd(O$_2$CR)$_2$ from CdSe-Cd(O$_2$CR)$_2$/HO$_2$CR using primary $n$-alkylamines or diamines only partially eliminated the carboxylate ligands (to 0.3 nm$^{-2}$). However, if acidic hydrogens are first removed using ZnEt$_2$ or CdMe$_2$, the carboxylate ligands can be completely displaced from the surface and amine bound nanocrystals isolated (oleate coverages $\leq 0.01$ nm$^{-2}$) (Figure 2.10). V Acid digestion of CdSe-NH$_2$R samples and subsequent characterization by $^1$H NMR of the organic by product also supports the absence of carboxylate signals (This is further discussed in section IV.2.1). Thus, the formation of tightly bound $n$-

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V Synthesizing CdSe-NH$_2$R species required an incredible amount of optimization and still suffers from phenomenon our lab is in the process of investigating. Details of what has been learned is discussed in chapter III.
octylammonium oleate can explain the difficulty of removing the final 0.3 nm$^{-2}$ carboxylates from CdSe–Cd(O$_2$CR)$_2$/HO$_2$CR.

The $^1$H NMR spectrum of CdSe-NH$_2$R is free of any resonances corresponding to alkenyl protons and consists solely of resonances from the bound $n$-alkylamine. The line widths of these resonances are highly dependent on the concentration of amine in the sample with an increasingly upfield chemical shift and sharper signal accompanying the addition of the L-type ligand. $^{15}$NMR spectroscopy with a CdSe-$^{15}$NH$_2$C$_4$H$_9$ sample shows a single resonance at 25 ppm whose chemical shift is minimally dependent on the amine concentration (Figure 2.11). A greater discussion into amine exchange in CdSe systems will be presented in chapter V of this thesis. However, the amine ligands bound to CdSe-NH$_2$R prove to be labile at room temperature, which is most likely correlated to their colloidal instability, to be discussed in section II.5.2.

![Figure 2.11. $^{15}$N NMR spectrum of CdSe-$^{15}$NH$_2$C$_4$H$_9$](image-url)
Figure 2.12. FT-IR spectrum of CdSe-NH$_2$C$_8$H$_{17}$ in tetrachloroethylene.

The FT-IR spectrum of CdSe-NH$_2$R is presented in Figure 2.12. The absence of both $\nu$(C=O) modes at 1408 and 1564 cm$^{-1}$, and a sharp $\nu$(C-H) mode at 3005 cm$^{-1}$, characteristic of the oleyl alkenyl group,$^{35, 58}$ are additional spectroscopic evidence of the complete removal of carboxylate species from these nanocrystals. Instead, FT-IR spectra of CdSe-NH$_2$R show three distinct bands: (1) $\nu$(C-H) = 2700 – 3000 cm$^{-1}$ from alkyl chains, (2) a strong band for the coordinated amine ($\nu$(N-H) = 3000 – 3400 cm$^{-1}$) that is absent in the spectrum of the pure amine ligand, and (3) bending modes of the NH$_2$R species ($\nu$ = 1417, 1558 cm$^{-1}$).

The UV-vis absorbance spectrum of CdSe-NH$_2$R species (Figure 2.13) retains most major features compared to CdSe-Cd(O$_2$CR)$_2$. Namely, the first excitonic transition is unchanged. However, broadening of the higher order transitions can be seen, most notably with the second transition whose peak intensity drastically decreases. Such a broadening of the higher order electronic transitions in CdSe nanocrystal systems was also observed during Z-type displacement, as well as in the absorption spectrum of CdSe-CdCl$_2$/PBu$_3$. The broadening was correlated with both a decrease in the photoluminescence quantum yield and an increase in the hole trapping rate of CdSe-Cd(O$_2$CR)$_2$ nanocrystals. The relation between this second absorption feature and surface
complexation has been studied yet is still not clearly understood. Cao and coworkers have suggested that a decrease in carboxylate coverage can influence the energy difference between the $1S_{3/2h}$ and $2S_{3/2h}$ states causing a change in the splitting of absorption features. In addition, we have hypothesized that the exposure of undercoordinated surface atoms can cause surface reconstruction and new electronic states that can become resonant with the $2S_{3/2h}$ state, the consequences being a lifetime broadening of the $1S_e-2S_{3/2h}$ transition. While not reported in this

Figure 2.13. UV-Vis spectra of CdSe-NH$_2$C$_8$H$_{17}$ of various sizes (d = 3.1, 3.4, 3.9, 4.8, and 5.2 nm).
dissertation, we have studied this surface reconstruction with pair distribution function (PDF) analysis. This method has recently been used to study surface reconstruction of small InP clusters.\textsuperscript{60} A detailed description of the experiment, as well as preliminary results of this project, can be found elsewhere.\textsuperscript{61}

**II.5.2 Colloidal stability of CdSe-NH$_2$R**

Without the passivation of either ion pairs or Lewis acidic cadmium carboxylates, it is not surprising that CdSe-NH$_2$R nanocrystals are less stable than CdSe-Cd(O$_2$CR)$_2$ samples. In fact, amine bound particles are very sensitive to aggregation at both low nanocrystal concentrations\textsuperscript{vi} or

![Figure 2.14](image-url)

**Figure 2.14.** (left) Dynamic light scattering (DLS) measurements of a CdSe-NH$_2$C$_8$H$_{17}$ sample in a 2.5 mM octylamine solution in toluene. (right) Diameters of the species calculated from DLS measurements as a function of amine concentration. For all measurements the concentration of nanocrystals was 50 µM (50 amines per NC). Note: over a period of months these particles aggregated and precipitated at this concentration.

\textsuperscript{vi}This is an issue when attempting to gather a UV-Vis spectrum of CdSe-NH$_2$R samples, as often times the particles will aggregate just by dilution of the stock solution. It is possible to circumvent this issue by using a blank solution of 33% amine in toluene (by volume).
low concentrations of amine. Typical stock solutions used in this study have nanocrystal concentrations of 1-3 mM and are stable indefinitely in amine solutions above 0.1 M, corresponding to 30-100 amines per nanocrystal. However, the UV-vis spectra of stabilized particles are consistent with unaggregated nanocrystals. Dynamic light scattering (DLS) also supports this (Figure 2.14). Depending on the degree of aggregation, these precipitates can be partially redispersed upon stirring in \( n \)-alkylamine solution at 60 °C.\(^\text{vii}\)

Transmission electron microscope (TEM) images of CdSe-NH\(_2\)C\(_4\)H\(_9\) prepared from a 0.1 M amine solution show disordered aggregates regardless of the conditions used for the grid preparation (Figure 2.15). This aggregation persists even with an increase in the chain length of the bound \( n \)-alkylamine (NH\(_2\)R, R = \( n \)-butyl, \( n \)-hexyl, \( n \)-octyl).\(^\text{viii}\) The aggregation of CdSe-NH\(_2\)R seems to be specific to nanocrystal samples with labile ligands. When the sample is converted to CdSe-Cd(O\(_2\)CR)\(_2\) by readorption of cadmium oleate, monolayers of well separated nanocrystals are visible using TEM (Figure 2.16). Thus, we conclude that CdSe-NH\(_2\)R is unstable to aggregation, particularly when the sample is dried on a TEM grid. This most likely causes issues

\[^{vii}\text{Various L-type exchanges were performed on CdSeNH\(_2\)R, many of which led to unstable nanocrystal products which aggregated. While this is an important observation, I have decided to discuss these experiments in chapter V.}\]

\[^{viii}\text{CdSe nanocrystals bound by \( n \)-dodecylamine was also prepared, but the nanocrystals could not be seen in the TEM images due to the presence of a large amount of carbon from the non-volatile amine species.}\]
**Figure 2.16.** Transmission electron micrographs of CdSe-Cd(O<sub>2</sub>CR)<sub>2</sub> (left), CdSe-NH<sub>2</sub>C<sub>8</sub>H<sub>17</sub> (right), and CdSe-Cd(O<sub>2</sub>CR)<sub>2</sub> synthesized from rebinding cadmium oleate to the surface of CdSe-Cd(O<sub>2</sub>CR)<sub>2</sub>. Scale bar is 20 nm (d = 4.2 nm).

when attempting to form well-defined monolayers on other substrates, which will be discussed at greater length in chapter IV.

Several observations made here indicate that *n*-alkylamine ligands also provide relatively weak stabilization: (1) the tendency of CdSe-NH<sub>2</sub>R′ to aggregate at low amine concentrations, (2) the well known lability of amine ligands on the <sup>1</sup>H NMR time scale (~ms), and (3) the complete desorption of amines from nanocrystal thin films. We also conclude that ammonium carboxylate, phosphonate, or carbamate ion pairs bind the nanocrystals strongly and at low coverage more strongly than *n*-alkylamines, perhaps because of their ability to chelate the [100] surface. This may explain the difficulty of displacing the last few carboxylate or phosphonate ligands using amines and pyridine. Given the challenge of spectroscopically differentiating between an ammonium carboxylate ion pair and separate amine and carboxylate ligands, these findings suggest that surface bound ion pairs formed from amines are likely more pervasive than realized. More broadly,
the formation of an adsorbed ion pair by deprotonation of an adventitious acid or displacement of a cationic metal complex provides a reasonable alternative to the simpler dative ligand–surface interaction. Such models are likely to be important for bulky N-heterocyclic carbenes\textsuperscript{63-65} or multidentate ligands such as brush polymers with amine or imidazole terminated side chains\textsuperscript{66} or polyvinylpyrrolidinone (PVP) where steric properties may prevent high density surface ligation.\textsuperscript{28, 67-68} Distinguishing between these modes of stabilization is essential to controlling ligand exchange reactivity by design.

**II.6 Generality of ion pair chemistry in CdSe systems**

The instability of CdSe nanocrystals bound by neutral ligands raises questions about the ligand composition of previously reported CdSe-L samples. While there are several explanations as to why our samples behave differently than previously reported amine bound CdSe nanocrystals – for example size effects, crystal phase of the CdSe core, and different nanocrystal syntheses might also induce different solubility properties of the resulting particles – we hypothesized that

![Scheme 2.5](image)

**Scheme 2.5.** Addition of Acidic Molecules to CdSe–NH\textsubscript{2}R’ Leads to Acid Dissociation and the Adsorption of an Ion Pair
nanocrystals can be stabilized more efficiently with tightly bound ion pair species. CdSe-NH$_2$R samples are an ideal starting point for the generation of $n$-alkylammonium ion pairs, as the amines bound to the sample should readily be able to deprotonate a range of acidic species (Scheme 2.5). Various acids were chosen to react with CdSe-NH$_2$R, namely due to their relevance to the colloidal nanocrystal field.

II.6.1 Regeneration of $n$-alkylammonium oleate ion pairs from CdSe-NH$_2$R

To further explore the binding of ammonium oleate to the nanocrystals, oleic acid (1 equivalent per amine) was added to CdSe-NH$_2$C$_8$H$_{17}$ (Scheme 2.5A) and the product (CdSe-NH$_2$R/[O$_2$CR][H$_3$NR]$^+$) analyzed by $^1$H NMR and FT-IR spectroscopies where signals characteristic of surface bound amine, ammonium, and oleate chains are visible (Figures 2.17). Repeated precipitation of CdSe-NH$_2$R/[O$_2$CR][H$_3$NR]$^+$ from toluene only partially eliminates the ammonium oleate ion pair. In addition, a broad resonance centered at 7.5 ppm can be observed in the $^1$H NMR spectrum (Figure 2.18), which is in the range previously reported for the [H$_3$N-]$^+$ fragment of $n$-alkylammonium species in the presence of metal oxide nanocrystals.$^{23}$

FT-IR spectra of purified samples of CdSe–NH$_2$R$'$/[O$_2$CR][H$_3$NR$'$$]$$^+$ (Figure 2.17) showed small differences in the region known to support ammonium stretching vibrations ($\nu$(N–H) = 2700–3100 cm$^{-1}$), which overlaps with the $\nu$(C–H).$^{69}$ However, the broad $\nu$(N–H) band from the [H$_3$N-]$^+$ fragment is more clearly visible upon subtraction of a spectrum of CdSe–NH$_2$R$'$. In addition, carboxylate stretching bands are visible ($\nu$(CO$_2$) = 1408, 1564 cm$^{-1}$) that are distinct from oleic acid ($\nu$(CO$_2$H) = 1710 cm$^{-1}$),$^{70}$ or a mixture of oleic acid and CdSe–Cd(O$_2$CR)$_2$ ($\nu$ = 1435, 1536, 1749 cm$^{-1}$) or the bending modes of CdSe–NH$_2$R$'$ (\nu = 1417, 1558 cm$^{-1}$). The retention of broad $^1$H NMR signals and FT–IR bands from $n$-alkylammonium and oleate ligands following
Figure 2.17. (A) FT-IR spectrum of CdSe-NH$_2$R'/[O$_2$R][NH$_3$R]$^+$ in tetrachloroethylene. (A) FT-IR spectrum of (i) CdSe–NH$_2$R' [O$_2$CR] [H$_3$NR'] (R = oleyl, R' = n-octyl) prepared from oleic acid that had not been dried. A prominent water stretching band is visible ($\nu$(O–H)) = 3300–3700 cm$^{-1}$), (ii) CdSe–NH$_3$R’ (R’ = n-octyl), and (iii) their difference spectrum. [H$_3$N]$^+$ ($\nu$(N–H)) highlighted in light blue. (B) FT-IR spectrum of (i) CdSe–NH$_2$R'/ [O$_2$CR][H$_3$NR']+ (R = oleyl, R' = n-octyl) prepared from anhydrous oleic acid, (ii) CdSe–NH$_3$R’ (R’ = n-octyl), and (iii) their difference spectrum. [H$_3$N]$^+$ ($\nu$(N–H)) highlighted in light blue. The spectra were normalized to amine $\nu$(N–H) stretching band at 3200 cm$^{-1}$ prior to subtraction. Spectra in (A) and spectra in (B) were obtained from samples with the same nanocrystal concentration.

precipitation supports the formation and tight binding of ammonium oleate to the nanocrystal surface, despite the relatively high concentration of primary amines which might be expected to displace the carboxylate ligands. Even in 4.5 M $n$-alkylamine solution, surface bound $n$-alkylammonium oleate is visible in the $^1$H NMR spectrum. Moreover, their oleate coverage only drops from 0.59 to 0.16 nm$^2$ following three cycles of precipitation from 4.5 M $n$-octylamine
Figure 2.18. $^1$H NMR spectrum of CdSe-NH₂R’/[O₂CR][H₃NR’]+ nanocrystals in CD₂Cl₂. The sharp resonances around 7.1 ppm are due to residual benzene and toluene. The asterisk (*) denotes the center of a broad resonance tentatively assigned to [NH₃R’]+.

solution. Additional precipitations fail to reduce the coverage further. These observations support an affinity of the ion pair that is much higher than primary $n$-alkylamines, a feature that may stem from their ability to chelate the surface (see discussion in section II.6.3).

II.6.1.1 Deprotonation of $n$-alkylammonium oleate in CdSe-NH₂R systems

The tightly bound ammonium oleate species in CdSe–NH₂R’/[O₂CR][H₃NR’]+ can be removed by the addition of ZnEt₂ (Figure 2.19). In this case, a slight blue shift in the UV-Vis absorption and the formation of CdEt₂ (Figures 2.20 and 2.21) were observed, indicating cation exchange between Cd²⁺ and Zn²⁺ in the nanocrystal. This blue shift is not seen in the UV-Vis spectrum of CdSe-Cd(O₂CR)₂/HO₂CR treated with diethylzinc. The different reactivity, compared to what is observed with CdSe-Cd(O₂CR)₂/HO₂CR, may result from polymeric amides that form in a side reaction between $n$-octylamine and ZnEt₂. Indeed, the addition of too much diethylzinc
results in a gel. Thus, both cation exchange and the formation of polymeric material limit the usefulness of removing ion pairs by the addition of diethylzinc. Based on these observations, it is synthetically less challenging to synthesize CdSe-NH$_2$R samples by the initial removal of acidic impurities, instead of deprotonating the ion pair once formed.

**Figure 2.19.** Vinyl region of the $^1$H NMR spectra for CdSe-NH$_2$C$_8$H$_{17}$ (a, red), CdSe-NH$_2$R’/[O$_2$CR][NH$_3$R’]$^+$ (b, green), and, CdSe-NH$_2$R’/[O$_2$CR][NH$_3$C$_8$H$_{17}$]$^+$ treated with one equivalent of ZnEt$_2$ (c, blue).

**Figure 2.20.** UV-Vis spectra of CdSe-Cd(O$_2$CR)$_2$ (i), CdSe-NH$_2$C$_8$H$_{17}$ (ii), and CdSe-NH$_2$C$_8$H$_{17}$/[O$_2$CR][NH$_3$C$_8$H$_{17}$]$^+$ after addition 0.5 equivalents of diethylzinc (iii). The vertical dashed line defines the location of the peak maximum of the first electronic transition in (i).
Figure 2.21. $^1$H NMR spectrum of CdSe-NH$_2$R'$/[\text{O}_2\text{CR}$]/[\text{NH}_3\text{R}']^+$ treated with one equivalent of ZnEt$_2$. Two peaks are seen in the region between 0.0 and 0.5 ppm. The larger quartet at 0.15 ppm is resonances from the methylene protons in diethylzinc. The smaller resonance at 0.33 ppm indicates the formation of diethylcadmium.

II.6.2 Generation and binding of $n$-alkylammonium phosphonate to CdSe-NH$_2$R

Figure 2.22. $^{31}$P NMR spectrum of CdSe− NH$_2$R' (R' = $n$-octyl). ([n-octylamine] = 0.021 M) and $n$-octadecylphosphonic acid (1 equiv./NH$_2$R'). Sharp and broad signals are assigned to free and bound $n$-octadecylphosphonate anions, respectively.

The heavy use of $n$-alkylphosphonic acids in the nanocrystal field motivated us to also investigate the generation and binding of $n$-alkylammonium phosphonates to CdSe-NH$_2$R samples. Upon addition of $n$-octadecylphosphonic acid to CdSe-NH$_2$R, two broad $^{31}$P NMR resonances are
Figure 2.23. $^{31}$P NMR spectra of neat octadecylphosphonic acid (ODPA) in benzene-$d_6$ (red) and 1, 2, 3, and 10 equivalents of $n$-octylamine. The addition of $n$-octylamine deprotonates ODPA ($\delta = 32$ ppm), forming the monohydrogen RPO$_3$H$^-$ ($\delta = 27$ ppm) and RPO$_3^{2-}$ ($\delta = 17$ ppm) species.

observed that we assign to surface bound monohydrogen $n$-octadecylphosphonate ($\delta = 27.2$ ppm) and $n$-octadecylphosphonate ($\delta = 18.8$ ppm) (Scheme 2.5B and Figure 2.22). $n$-Alkylphosphonic acids are sufficiently acidic to protonate $n$-alkylamines in the absence of nanocrystals, which we verified by an independent titration experiment (Figure 2.23).$^{71}$ Although a minor sharp signal overlays the broad resonances, we conclude the majority of the phosphonate anions bind the
nanocrystal even in 0.02 M amine solution. This relatively strong binding helps explain the difficulty of displacing native phosphonic acid ligands from nanocrystals using amine donors.\textsuperscript{72-74}

\textbf{II.6.3 Generation and binding of }n\text{-alkylammonium carbamate to CdSe-NH}_2R\text{ }

Liquid primary amines are known to dissolve significant quantities of carbon dioxide if stored under ambient conditions, leading to \textit{n}-alkalammonium and \textit{N}-\textit{n}-alkylcarbamate ions via the generation of a carbamic acid intermediate. This ion pair does not only dictate the outcome of nanocrystal syntheses that use amine surfactants,\textsuperscript{49} they can also be a potential source of organic contamination during device fabrication. To study their generation and surface interactions, CdSe-NH\textsubscript{2}R nanocrystals with \textit{n}-octylammonium-\textit{N}-\textit{n}-octylcarbamate ion pairs (CdSe–NH\textsubscript{2}R′/[O\textsubscript{2}C-NHR][H\textsubscript{3}NR′]+) were generated through the addition of carbon dioxide (Scheme 2.5C). After isolation of the product nanocrystal, the FT-IR spectrum of CdSe–NH\textsubscript{2}R′/[O\textsubscript{2}C-NHR][H\textsubscript{3}NR′]+ shows signals from \textit{n}-octylammonium and \textit{N}-\textit{n}-octylcarbamate ions, including three bands (\(\nu = 3028, 3064, \text{ and } 3087 \text{ cm}^{-1}\)) that appear in an authentic sample of \textit{n}-octylammonium \textit{N}-\textit{n}-octylcarbamate (Figure 2.24).\textsuperscript{ix,x,75}

Upon adding labeled carbon dioxide–\textsuperscript{13}C to a solution of CdSe-NH\textsubscript{2}R, a broad \textsuperscript{13}C NMR signal from the carbonyl carbon of a surface bound carbamate anion appears ((\(\delta = 165 \text{ ppm, } \Delta \delta = 1.95 \text{ ppm}\)). Integration of the \textsuperscript{13}C NMR signal (acquired using an inverse gated decoupling scheme) and comparing it to a natural abundance ferrocene standard shows that \(\sim 0.1 \text{ carbamates nm}^{-2}\) remain bound to the nanocrystal following one round of precipitation using methyl acetate. This coverage remains unchanged following three cycles of precipitation from concentrated \textit{n-}

\textsuperscript{ix} The \(\nu(\text{NCO}_2)\) of the carbamate anion cannot be seen due to N–H and C–H bending modes of the amine ligands.

\textsuperscript{x} A vibrational band from water is also observed unless the added oleic acid or carbon dioxide are anhydrous.
Figure 2.24. (A) $^{13}$C NMR spectrum of reaction between CdSe-$\text{NH}_2\text{R}'$ (R' = n-octyl) and $^{13}$CO$_2$ ([n-octylamine] = 0.04 M, toluene-$d_8$). The inset shows the region from $\delta$ = 160–170 ppm where a broad resonance centered at 165 ppm corresponding to the carbamate carbon (blue) is visible and the same regions of a spectrum of n-octylammonium N-n-octylcarbamate in the absence of nanocrystals (green). (B) FT-IR spectrum of CdSe-$\text{NH}_2\text{R}'$/[O$_2$C-NHR][NH$_3$R]$^+$ in tetrachloroethylene. (C) $\nu$(C-H) and $\nu$(N-H) region of the FT-IR spectrum of (i) n-octylammonium N-n-octylcarbamate, (ii) CdSe-$\text{NH}_2\text{R}'$/[O$_2$C-NHR][NH$_3$R]$^+$, and (iii) CdSe-$\text{NH}_2\text{R}'$ in tetrachloroethylene.
octylamine solution (4.5 M). CdSe–NH₂R’ or other nanocrystals stabilized by amine surfactants must, therefore, be stored free from air to avoid reaction with atmospheric carbon dioxide and contamination of the ligand shell.

II.7 pKa argument for ion pair generation

The presence of acid impurities helps explain the origin of \( n \)-alkylammonium oleate ion pairs in CdSe-Cd(O₂CR)₂ nanocrystal samples treated with \( n \)-alkylamines. However, additional questions arise in relation to the stability of the formed ion pair. In nonpolar solution, \( n \)-octylamine is not sufficiently basic to fully deprotonate a carboxylic acid, as can be demonstrated using FT-IR spectroscopy. Solvents with a higher dielectric can solvate the charged species and help facilitate ion pair formation. This explains the commonly reported observation of a change in solubility of nanocrystals upon the generation and binding of charged ion pair ligands from nonpolar media to polar organic solvents.\(^{11-12, 15, 76-77}\)

In the systems discussed here, we document examples where the ion pairs are organic and the nanocrystals remain soluble in nonpolar media such as toluene. This mode of stabilization is well documented in the literature on metal nanocrystals where surfactants such as hexadecyltrimethylammonium bromide (CTAB) can stabilize dispersions of metal nanocrystals in toluene.\(^{78}\) Our experiments show that carboxylate, phosphonate, and carbamate ions bind the nanocrystal tightly and are challenging to unambiguously distinguish from metal oleate and/or amine ligands. Moreover, the ease of forming these impurities from atmospheric carbon dioxide or acidic impurities in CdSe–Cd(O₂CR)₂/HO₂CR or so called TOPO capped nanocrystals suggests these adsorbed ions play a significant role in the chemistry of nanocrystals thought to be bound solely by amine ligands.
II.8 Conclusions

Acidic species interact with the surface of CdSe nanocrystals and cannot be quantitatively removed with traditional precipitation and redissolution methods. The deprotonation of acidic molecules such as carboxylic acids, phosphonic acids, and carbamic acids is facilitated by the Lewis acidic surface of CdSe nanocrystals. The surface tightly binds the resultant carboxylate, phosphonate, and carbamate anions and prevents the complete displacement of the native ligands with primary amines. To address this limitation, we used ZnEt₂ and CdMe₂ to scavenge acidic hydrogens prior to displacing the surface metal oleate complexes. This strategy provides CdSe nanocrystals without anionic impurities, but the nanocrystals proved relatively unstable to aggregation unless the amine concentration was maintained near 0.1 M or higher.

We argue that the oleate anions bind with a high affinity towards CdSe nanocrystal surfaces, and remain bound even upon addition of a polar organic solvent during precipitation of the particles. While the chelating nature of carboxylate species helps explain the stabilization of the formed anions, the driving forces behind tight binding of ion pairs still remain uninvestigated. It is possible that higher dielectric screening at the cadmium selenide surface might also play a role.

In the case of zincblende CdSe, the binding of the carboxylate is strongest on the [100] facets, which supports a multitdentate bridging coordination mode involving adjacent cadmium centers. The competitive binding of amines to these same sites is perhaps less favorable because the amine ligands are unlikely to bridge adjacent cadmium centers. Given that the density of atoms on this facet (5.9 nm⁻²) is higher than the aerial packing density of crystalline n-alkane chains (4.9 nm⁻²), complete coverage of this facet with one amine per cadmium atom will passivate only one of two dangling bonds at each cadmium center. On the other hand, each carboxylate ligand can
passivate two to three binding sites per aliphatic chain, provided it binds in a $\eta^2$- or $\eta^3$-bridging bidentate mode (Scheme 2.6). Because of their chelating ability, we expect that carboxylate, carbonate, and phosphonate ligands will have a greater affinity for the [100] facet than will primary $n$-alkylamines. This difference helps explain the persistent binding of these ligands in concentrated amine solution and points to a difference between zincblende and wurtzite structures, which lack a polar facet with analogous atomic structure.

The CdSe-$\text{NH}_2\text{R}$ nanocrystals reported here also serve as a valuable starting material both for synthesizing nanocrystals with novel ligand compositions and understanding fundamental chemical properties of nanocrystal surfaces, such as trap state passivation and ligand binding affinity. These stoichiometric nanocrystals provide a convenient starting point for monitoring both L-type and Z-type ligand exchange, which will be investigated in chapters V and VI of this dissertation. This material demonstrates that metal chalcogenide nanocrystals can be fully stoichiometric, implying non-stoichiometry is due to Z-type ligands, specifically metal carboxylates, bound to the nanocrystal surface. Non-stoichiometry is not inherent to CdSe nanocrystals samples but a result of unreacted metal precursor in the initial synthesis. This meshes well with a neutral fragment model of metal chalcogenide nanocrystals, where electron-accepting Z-type ligands bind selenide sites and electron donating L-type ligands bind metal sites of a
nanocrystal containing equal amounts of metal and chalcogenide. These results also shed light on
the relative high binding affinities of Z-type and anionic X-type ligands compared to labile L-type
ones, which fail to stabilize the nanocrystals in solution at low concentrations.

II.9 Experimental

Reduction of Cadmium Carboxylate Coverage with TMEDA. Reduction of the cadmium
carboxylate coverage in CdSe–Cd(O₂CR)$_₂$ nanocrystal samples was performed following a
previously reported method. In a typical reaction, CdSe–Cd(O₂CR)$_₂$ that was previously reacted
with ZnEt$_₂$ according to Reaction of CdSe–Cd(O₂CR)$_₂$ with CdMe$_₂$ or ZnEt$_₂$ was dissolved in
5 mL of neat TMEDA and allowed to stir for 10 min. The solution was then precipitated with 25
mL of methyl acetate, and the nanocrystals were isolated by centrifugation. The clear supernatant
was discarded and the pellet subjected to two additional cycles of TMEDA/methyl acetate/
centrifugation. The nanocrystals were then separated from adventitious TMEDA by two cycles of
dissolution in toluene (5 mL), precipitation with methyl acetate (25 mL), and centrifugation. The
resulting nanocrystals were insoluble in pentane but could be redispersed in toluene or benzene.

Binding of Oleic Acid to CdSe–Cd(O₂CR)$_₂$ with Reduced Oleate Coverage. In a typical
reaction, to a stock solution of CdSe–Cd(O₂CR)$_₂$ (500 μL, [nanocrystals] = 0.48 mM, [Cd(O₂CR)$_₂$
= 0.013 M, 0.53 carboxylates nm$^{-2}$) that had previously been treated with TMEDA according to
Reduction of Cadmium Carboxylate Coverage with TMEDA in either benzene-$d_₆$ or
tetrachloroethylene was added oleic acid (12 μL, 394 equivalents per nanocrystal), and the solution
was allowed to stir for 3 hours. The nanocrystals were then precipitated by addition of methyl
acetate (10 mL) and isolated by centrifugation. The red pellet was then purified by five cycles of
dissolution in pentane (1 mL), precipitation with methyl acetate (10 mL), and centrifugation. The
nanocrystals were then dispersed in benzene-\textit{d}_6 for NMR spectroscopy.

\textbf{Reaction of CdSe–Cd(O_2CR)_2/HO_2CR with CdMe}_2 or ZnEt}_2. CdMe}_2 or ZnEt}_2 was added (1.7
mg CdMe}_2, or 1.9 mg ZnEt}_2) using a microliter syringe to a CdSe stock solution (5 mL) and the
solution protected from light. The solution was stirred for 12 h and distilled to dryness under
vacuum to remove unreacted CdMe}_2 or ZnEt}_2. The residue was dissolved in toluene (5 mL), and
methyl acetate (40 mL) was added to precipitate the nanocrystals, which were isolated by
centrifugation and decanting the supernatant. The precipitation and centrifugation process was
repeated twice and the final nanocrystal powder dried under vacuum before being dissolved in
benzene-d6 for 1H NMR and UV–visible absorption analysis.

\textbf{Synthesis of CdSe–NH}_2\textit{R'} (R' = C_{12}H_{25}, C_8H_{17}, C_4H_9). A solution of \textit{n}-octylamine in toluene (5
mL, 4.5 M) was added to a stock solution of CdSe nanocrystals (2 mL, [Cd(O_2CR)_2] = 0.1 M) and
the red solution stirred for 10 min. Methyl acetate (25 mL) was added and the precipitate isolated
by centrifugation. This process was repeated 10- fold or until no alkenyl resonance was visible in
the \textit{^1}H NMR spectrum. After the final centrifugation, the nanocrystals were dissolved in toluene,
dried under vacuum, and characterized by NMR and UV–visible absorption. If partial precipitation
of nanocrystals occurs, 20 \textmu L of primary amine was added to the nanocrystals to aid in
redissolution. The photoluminescence quantum yield of isolated CdSe–NH}_2\textit{R'} is 1–2\%. \textit{n}–
Octylamine ligands were exchanged for \textit{n}-butyl- or \textit{n}-dodecylamine by three rounds of
dissolution/precipitation/centrifugation procedure from a 1 M solution of the desired alkylamine
in toluene.
Replacement of *n*-Octylamine Ligands with Cadmium Oleate. A solution of CdSe–NH$_2$C$_8$H$_{17}$ ([nanocrystals] = 2.26 mM) was dried under vacuum for 3 h to remove the volatiles. To this residue was added cadmium oleate dissolved in toluene (2 mL, 0.165 M). The resulting solution was allowed to stir overnight at room temperature and then was purified by precipitation with 10 mL of methyl acetate and centrifugation, affording a red powder that was redissolved in toluene prior to analysis with TEM.

Reaction of Oleic Acid and CdSe–NH$_2$C$_8$H$_{17}$. A stock solution of CdSe–NH$_2$C$_8$H$_{17}$ was diluted with a solution of oleic acid in benzene-$d_6$ ([nanocrystal] = 0.135 mM, [NH$_2$C$_8$H$_{17}$] = 24 mM, [RCO$_2$H] = 240 mM), and the sample was allowed to sit overnight. The nanocrystals were then purified by three cycles of precipitation with methyl acetate (5 mL), centrifugation, and redissolution. The nanocrystal pellet then dissolved in pentane (5 mL), transferred to a 20 mL vial fitted with a stir bar and placed under vacuum to remove the volatiles. The final nanocrystal powder was dissolved in 1 mL of benzene-$d_6$ or $^1$H NMR and UV–vis absorption analysis. Attempts to displace surface bound *n*-octylammonium oleate using *n*-octylamine followed three cycles of precipitation from 4.5 M amine solution according to the procedure described in Synthesis of CdSe–NH$_2$R$'$.

Reaction of *n*-Octadecylphosphonic Acid and CdSe–NH$_2$C$_8$H$_{17}$. To a solution of CdSe–NH$_2$C$_8$H$_{17}$ (600 μL, [nanocrystals] = 0.12 mM, [amine] = 21 mM) in a J-Young tube was added 4.28 mg (12.3 μmoles) of *n*-octadecylphosphonic acid. The mixture was sonicated to aid the
dissolution of the phosphonic acid and then allowed to react overnight prior to analysis with \(^{31}\text{P}\) NMR spectroscopy.

**Reaction of Carbon Dioxide and CdSe–NH\(_2\)C\(_8\)H\(_{17}\).** A solution of CdSe-NH\(_2\)C\(_8\)H\(_{17}\) in toluene-\(d_8\) (600 \(\mu\)L, [nanocrystals] = 0.24 mM, [amine] = 42.7 mM) was placed in a J-Young tube and degassed. Meanwhile, the gas manifold of a Schlenk line was filled with carbon dioxide obtained from the sublimation of dry ice. Carbon dioxide was then admitted to a volumetric gas addition bulb (209 mL) until the internal pressure was 10 Torr as measured with a mercury manometer. This volume of gas was then condensed into the J-Young tube at liquid nitrogen temperature for 5 min. The J-Young tube was then sealed and allowed to warm to room temperature. Addition of isotopically enriched \(^{13}\text{C}\)O\(_2\) (10 \(\mu\)mol) to CdSe-NH\(_2\)C\(_8\)H\(_{17}\) was performed identically to the procedure described above using a lecture bottle of \(^{13}\text{C}\)-labeled carbon dioxide. After the bottle was allowed to stand for 4 h at room temperature, methyl acetate (10 mL) was added and the nanocrystal precipitate isolated by centrifugation. The isolated nanocrystals were further purified by three cycles of dissolution in toluene, precipitation with methyl acetate, and centrifugation.

**II.10 References**


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CHAPTER III: Z-TYPE REMOVAL EFFICIENCY IN CdSe-Cd(O_2CR)_2 SYSTEMS

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**Scientific Abstract**

Precipitation/redissolution, gel permeation and silica interaction chromatographic methods were explored as purification methods in the synthesis of amine bound CdSe-NH$_2$R nanocrystals. The carboxylate surface coverage was monitored as a function of the number wash cycles performed. The efficiency of precipitation/dissolution methods increased with primary amine concentration, yet had no observable dependence on chain length, time, or diamine concentration. In addition, a temperature dependence on the displacement of cadmium carboxylate was observed at high reaction temperatures (140 °C). Chromatographic methods removed cadmium carboxylate from the nanocrystal sample at a comparable rate to precipitation cycles, yet proved to be unfeasible for large scale preparations of CdSe-NH$_2$R. Solubility studies of cadmium carboxylate indicate that additional factors affect the difficulty in achieving complete removal of Z-type ligands.

**Plain English Abstract**

The preparation of amine bound CdSe nanocrystals is time intensive, usually taking multiple weeks. This chapter attempts to improve on the efficiency of the nanocrystal synthesis by exploring different purification methods. Out of the procedures investigated, none proved to be better than our current procedure. We investigated the causes of why the removal of the initial ligands is difficult. Our results show that the solubilities of the initial ligands and nanocrystals are similar, making it hard to selectively precipitate one while keeping the other soluble. However, this is not the only cause, and we propose novel ligand binding motifs as another reason why this purification is so difficult.
**III.1 Purification techniques for colloidal nanocrystals**

As-synthesized colloidal nanocrystals typically contain excess ligands and synthesis byproducts generated from precursor conversion. In addition, the reaction solvent, which must typically be both non-polar and high boiling, is rarely the same as the medium in which the nanocrystals are transferred to for measurements and applications. Thus, the isolation and purification of the nanocrystals is a crucial process for post synthetic studies. Not only does it remove unwanted impurities from the sample, but it helps normalize the surface composition of particle samples across research groups which in turn makes comparisons across the field more accurate. Various techniques have been employed to isolate purified nanocrystals. The most widely used purification technique is selective precipitation of the nanocrystals followed by subsequent redissolution. For the case of nanocrystals prepared in non-polar organic solvents, the addition of a polar solvent, such as methyl acetate, acetonitrile, or methanol raises the overall polarity of the mixture and causes flocculation of the particles. The supernatant, containing reaction byproducts, excess ligands, and other impurities, can be removed by centrifugation. It is assumed that multiple wash cycles, typically ranging from 3-5 in reported procedures, is enough to isolate purified nanocrystal products. Since it is commonly observed that larger nanocrystals precipitate easier than smaller ones, this method also was used early on as a means of increasing the monodispersity of the particles. Similar to precipitation, two-solvent extraction techniques have been used for the purification of semiconducting and gold nanoparticles.

In addition to precipitation, multiple purification techniques have been developed that exploit other physical properties of the nanocrystals (Table 3.1). For example, the differences in mobilities between a nanocrystal and impurities in an electric field have been exploited in electrophoretic separation techniques. Using this concept, gold nanoparticles with differing surface densities of thiolated DNA strands have been separated from each other. The same
 electrophoretic method has been applied to separating PEG-functionalized Au and CdSe/ZnS systems and particles embedded with charged polymers. \textsuperscript{23-24} While electrophoresis methods generally require aqueous systems, electrophoretic methods have been used to isolate CdSe and CdTe quantum dots and nanoplatelets in non-polar media.\textsuperscript{25} Size-based techniques, such as ultracentrifugation and membrane-based separations, have also been used for the purification of metal, semiconducting, and metal oxide nanoparticles. \textsuperscript{26-32} The Dubertret group has used ultracentrifugation to separate excess phospholipid after nanocrystal encapsulation,\textsuperscript{33} and dialysis has been utilized by Ren and coworkers to purify CdTe nanoparticles in water.\textsuperscript{34} Chromatographic methods, which will be discussed in more detail during section III.3 of this chapter, have been

\textbf{Table 3.1} Current purification methods applied to nanocrystal samples

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<td>first used for size selective precipitation of nanocrystals</td>
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<td>less application for nanomaterials in organic solvents</td>
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<td>electrophoresis</td>
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<td>20-25</td>
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<td></td>
<td>CdTe, CdSe</td>
<td>generally requires aqueous systems</td>
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<td>porous membranes</td>
<td>CdTe, CdSe/ZnS, Au, Si</td>
<td>process can be time consuming</td>
<td>32, 34</td>
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<td></td>
<td></td>
<td>currently exclusive to aqueous media</td>
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</tr>
<tr>
<td>size exclusion chromatography</td>
<td>Au, silica, InP, Fe₃O₄</td>
<td>most extensively applied to Au nanoparticles</td>
<td>35-40</td>
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<tr>
<td></td>
<td></td>
<td>has been successfully been used for nanocrystals in organic solvents</td>
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extensively reported for purifying Au nanoparticles, and are currently being studied by the Greytak group for purification of II-VI nanocrystal materials.

Despite the advantages that some of the above techniques offer (mainly reproducibility between different samples), the traditional precipitation and redissolution technique still reigns supreme as the most commonly reported way to purify nanocrystals. This simple method, while originally developed to remove reaction byproducts from as-synthesized carboxylate or phosphonate terminated nanocrystals, has been adapted to act as the medium in which multiple ligand exchange reactions occur. For example, solutions of carboxylic acids have been used as the solvent from which nanocrystals are precipitated, causing X-type exchange to occur in solution prior to purification of the excess acidic species. Similarly, L-type ligand exchange can occur by dissolving CdSe-CdX₂/L nanocrystals in a solution containing another L’ ligand (Scheme 3.1).

Multiple rounds of precipitation from a solution containing the desired surface ligand can result in quantitative exchange, as in the case for CdSe-CdCl₂/NH₂R samples synthesized from a CdSe-CdCl₂/PBu₃ starting particle.

Scheme 3.1. Quantitative ligand exchange can be achieved in some systems in tandem with precipitation/centrifugation cleaning methods using a solvent containing the desired surface ligand.
While understanding the thermodynamics of reported surface reactions has not been a center focus of the field, it is generally assumed that these ligand exchanges can be made quantitative by forcing the equilibrium to the side of products. This is usually achieved by exploiting Le Chatlier’s principle and consistently forcing the reaction conditions to have a high concentration of incoming ligand while decreasing the concentration of the initial ligand through removal of the supernatant after precipitation of the nanocrystals. For many ligand exchanges, such as between carboxylates, there is negligible differences in the binding affinity of the two species, and the resulting surface concentration of each matches the molar fraction of each in the solution. This simple concept is quite useful for our lab, as we can easily control the ratio of cadmium myristate and cadmium oleate in purified CdSe-Cd(O\textsubscript{2}CR\textsubscript{2})\textsubscript{2} samples by the volume of oleic acid added during the synthesis.\textsuperscript{3, 6-8} Even though this approach is not the most elegant of systems, the ease by which many ligand exchanges can be made quantitative makes this a standard approach in the field. Other examples of ligand exchanges in the literature focus on driving this equilibrium across solution interfaces. The synthesis of nanocrystals with bound metal chalcogenide, ammonium lead bromide, borate, and ammonium thiocyanate ligands are driven by a phase exchange between non-polar organic and polar solutions such as DMSO or DMF.\textsuperscript{15-18}

For other ligand exchanges, however, a simple manipulation of the ligand concentrations is not enough to guarantee quantitative exchange. Previous results in our lab have shown that performing L-type exchange with CdSe-CdCl\textsubscript{2}/NH\textsubscript{2}R and Bu\textsubscript{3}P to synthesize CdSe-CdCl\textsubscript{2}/PBu\textsubscript{3} does not happen under ambient conditions even in high concentrations of phosphine.\textsuperscript{42} As discussed in chapters II and V, removal of tightly bound ion-pairs from nanocrystal surfaces is

\textsuperscript{1} This exchange is related to the L-type studies discussed in chapter V of this dissertation.
also not easily achieved through multiple washing cycles. In part, the difficulty in fully exchanging these ligands is due to larger differences in binding affinity towards the particle surface.

The L-type promoted Z-type displacement used to synthesize amine bound CdSe-NH₂R samples is another ligand exchange process whose intricacies include more than the careful prevention of ion-pair formation discussed in chapter II. Additional considerations, such as differences in binding affinities of cadmium carboxylates, solubility of the free Lₙ-CdX₂ adduct, and rebinding of the Z-type ligand can all influence the efficiency of the Z-type removal process. This chapter discusses various conditions and parameters that were tuned in an attempt to make the synthesis of CdSe-NH₂R synthetically easier. While the conventional precipitation/centrifugation purification procedure remains the method used to drive the complete displacement of cadmium carboxylates, the results reported here were indispensable in optimizing this synthetic protocol and also reveal new insights into the binding of Z-type ligands to nanocrystal surfaces. Most of the data presented in this chapter monitors carboxylate surface density as a function of the number of purification cycles under investigation. These surface coverages were calculated from ¹H NMR and UV-vis spectroscopies following the general procedures described in chapter I.

Ideally, this chapter will serve as a reference aimed at the future graduate students whose projects require large stock solutions of amine bound CdSe nanocrystal. While the synthesis of large colloidal particles with hundreds of binding sites requires familiarity of the sample (which is difficult to put a cookie cutter recipe to), a recipe can be developed for this challenging synthesis. I hope that this chapter allows for those scientists to continue the Owen group’s study of fundamental ligand interactions on nanocrystal surfaces without having to reinvent the wheel.
III.1.1 Remarks on the synthesis of CdSe-NH$_2$R nanocrystal samples

Before segmenting the conditions into rational sections, some remarks about the synthesis of amine-bound nanocrystals will be presented. These observations, which cannot be quantified like the remainder of the chapter, are qualitatively important for understanding CdSe-NH$_2$R.

While the reported syntheses of amine-bound nanocrystals use either a 5 M $n$-alkylamine or a 5 M/0.5 M $n$-alkylamine/1,2-diaminocyclohexane cleaning solution, the synthesis requires less wash cycles and is more reproducible if a neat solution of TMEDA is used for the initial cleaning cycles. The largest scale synthesis of CdSe-NH$_2$R particles (~5 grams, [NC] = 2.34 mM) was performed by continuously precipitating a 10 mL TMEDA solution of acid scavenged CdSe-Cd(O$_2$CR)$_2$ with 40 mL of methyl acetate ([TMEDA]$_{\text{final}}$ = 1.33 M, [MeOAc]$_{\text{final}}$ = 10.1 M). After approximately 10 cycles, the nanocrystals undergo a drastic change in solubility and become insoluble in TMEDA (as well as pentane), indicating that the carboxylate coverage has been reduced to a surface density that cannot stabilize the particles ($\leq$ 0.5 carboxylates nm$^{-2}$). At this point, the aggregated particles can be redispersed in a 10 mL 5 M $n$-butylamine solution of toluene$^{ii}$ and continuously precipitated with 40 mL of methyl acetate ([NH$_2$C$_4$H$_9$]$_{\text{final}}$ = 0.5 M, [MeOAc]$_{\text{final}}$ = 10.1 M). The surface density of carboxylates is monitored with $^1$H NMR and UV-Vis spectroscopies, which shows a complete absence of oleate species after a total of 15-20 washing cycles. This is the same number of wash cycles we have reported previously, but on a scale that is $\geq$ 5 times larger.

The storage of CdSe-NH$_2$R must be done with a high amine concentration to avoid aggregation of the particles over time. Even at a ratio of ~350 $n$-butylamines per nanocrystal ([NC]

$^{ii}$ The insoluble particles have never been allowed to sit as a solid for extensive periods of time and it is unknown whether this has an effect on the reversibility of this aggregation.
= 0.746 mM, [amine] = 0.26 M), the particles will begin to aggregate over a period of months. In most cases, continuous stirring of the solution is enough to keep the particles in solution. Severely aggregated systems will appear either as a precipitated powder or as a viscous gel. To the best of my knowledge, the best way to reverse this aggregation is by the addition of additional amine and heating the sample in a sealed Strauss flask. The majority of the nanocrystals will gradually redissolve over a span of 2 hours and stay dissolved once the solution is cooled back to room temperature. The sample can then be filtered or centrifuged to remove the nanocrystals which have irreversibly aggregated. The loss of particles is on the order of 10%. At the time of writing, no method has been developed to further prevent or slow the aggregation rate of CdSe-NH$_2$R samples.

**III.2 Traditional Nanocrystal Purification: Selective Precipitation**

As stated above, the selective precipitation of nanocrystals followed by centrifugation is one of the most common methods for isolation. This section describes the surprisingly similar effectiveness of various conditions used to displace cadmium carboxylate from CdSe-Cd(O$_2$CR)$_2$ to yield stoichiometric particles. In general, the ligand systems developed and reported here stem from previous results in the lab which demonstrate the superior effectiveness of primary $n$-alkylamines and chelating diamines at removing cadmium carboxylate from CdSe nanocrystal surfaces.\textsuperscript{3, 7} Because of this, no other types of L-type ligands were investigated during the development of these various cleaning solutions.
**III.2.1 Effect of amine concentration**

\[
\begin{align*}
\text{Cd(O}_2\text{CR)}_2 & \quad + \quad n+1 \text{NH}_2\text{R} & \quad + \quad \text{MeOAc} & \quad \rightarrow & \quad \text{NH}_2\text{R} & \quad + \quad (\text{NH}_2\text{R})_n\text{Cd(O}_2\text{CR)}_2 \\
R & = \text{C}_4\text{H}_9, \quad \text{C}_8\text{H}_{17} & & & & 0.5 - 6 \text{ M}
\end{align*}
\]

**Scheme 3.2.** The effect of amine concentration on the efficiency of cadmium carboxylate removal from CdSe nanocrystal surfaces.

The concentration of primary \( n \)-alkylamine affects the amount of cadmium oleate that is displaced from the nanocrystal surface (scheme 3.2), with larger amine concentrations removing greater amounts of cadmium oleate. A similar trend is observed in the carboxylate surface coverage after each precipitation cycle. Nanocrystals precipitated from different concentrations of amine with methyl acetate were characterized by \(^1\text{H} \text{NMR}\) and \(\text{UV-Vis}\) spectroscopies and their carboxylate coverage plotted against the number of wash cycles (Figures 3.1 and 3.2). For both \( n \)-butylamine and \( n \)-alkylamine, the coverage initially decreases faster with increasing amine concentration. However, the efficiency of removing the last 10% of the carboxylate from solution is independent of the amine concentration.
**Figure 3.1.** Carboxylate coverage as a function of washing cycles for \( n \)-butylamine solutions of various concentrations in toluene (0.5 M, blue; 2.5 M, green; 4.5 M, red). For all cleaning procedures, methyl acetate was used as the antisolvent. The horizontal dashed line indicates a carboxylate coverage of 0.3 nm\(^2\), which is the lowest coverage achieved when removing cadmium carboxylate from CdSe-Cd(O\(_2\)CR\(_2\))/HO\(_2\)CR nanocrystal samples.

**Figure 3.2.** Carboxylate coverage as a function of washing cycles for \( n \)-octylamine solutions of various concentrations in toluene (3 M, blue; 4.5 M, green, purple; 6 M, red). For all cleaning procedures, methyl acetate was used as the antisolvent.
III.2.2 Effect of amine chain length

![Carboxylate coverage as a function of wash cycles for 4.5 M primary n-alkylamine solutions (n-butylamine, blue; n-octylamine, red). For all cleaning procedures, methyl acetate was used as the antisolvent. The horizontal dashed line indicates a carboxylate overage of 0.3 nm$^2$, which is the lowest coverage achieved when removing cadmium carboxylate from CdSe-Cd(O$_2$CR)$_2$/HO$_2$CR nanocrystal samples.](image)

The carboxylate coverage as a function of wash cycles for two different 4.5 M n-alkylamine cleaning solutions are plotted in figure 3.3. For both a 4.5 M n-butylamine and n-octylamine solution, the coverage decreases almost identically. This observation suggests that the chain length of the primary amine does not affect the efficiency of cadmium carboxylate removal. This result is surprising and suggests that the two different (NH$_2$C$_n$H$_{2n+1}$)-Cd(O$_2$CR)$_2$ adducts that form behave similarly in their solubility and nanocrystal surface binding affinity.
III.2.3 The effect of using chelating diamines

\[
\begin{align*}
\text{Cd(O}_2\text{CR)}_2 & \quad + \quad \text{NH}_2\text{R'} \quad + \quad \text{MeOAc} \\
& \quad \xrightarrow{\text{L}_2} \quad \text{Cd(O}_2\text{CR)}_2 \quad + \quad (\text{L}_2)\text{-Cd(O}_2\text{CR)}_2 \\
\end{align*}
\]

\(\text{L}_2 = 1,2\text{-diaminocyclohexane} \quad 3,4\text{-diaminobenzenesulfonic acid}\)

**Scheme 3.3.** The effect of chelating diamines on the efficiency of cadmium carboxylate removal from CdSe nanocrystal surfaces.

The choice of incorporating chelating diamines into the \textit{n}-alkylamine toluene solution was based off previous work which demonstrated the effectiveness of these \(\text{L}_2\) ligands in removing cadmium carboxylate from the nanocrystal surface. This increased displacement is most likely due to the extra stabilization offered from the chelation effect. Initial attempts performed with ethylenediamine as the \(\text{L}_2\) ligand proved unsuccessful as the nanocrystals immediately precipitated upon addition of the chelator. Ethylenediamine has been proposed to aid in the electronic overlap of nanocrystals for device applications, yet its small steric profile and rotational freedom can link nanocrystals together through the two nitrogen atoms. Therefore, diamines with rigid 6-member rings, such as 1,2-diaminocyclohexane, were chosen to lower their binding affinity towards the surface by hindering rotation of the NC-CN bond. Their chelating power towards cadmium carboxylate should still stabilize the removed Z-type ligand.
The choice of using 3,4-diaminobenzenesulfonic acid stems from a solubility issue that will be discussed in section III.4. We hypothesized that the sulfonic acid functional group could undergo deprotonation by a primary amine to form an ammonium sulfonate ion pair, thus increasing the corresponding cadmium carboxylate adduct’s solubility in methyl acetate (Scheme 3.3). Their corresponding coverage as a function if precipitation cycle, as well as those of other amine/diamine combinations, is presented in figure 3.4. Interestingly, the carboxylate coverage for CdSe nanocrystals treated with a 6/0.25 M octylamine/diaminobenzenesulfonic acid mixture decreases at a slower rate than those treated with n-alkylamines or n-alkylamines and diaminocyclohexane. It is possible that the ammonium sulfonate ion pair that forms can also act as a tight binding ligand to the particle surface, as low intensity broad resonances in the aromatic region appear in isolated nanocrystals. Furthermore, the addition of 1,2-diaminocyclohexane to n-alkylamine solutions does not increase the efficiency of cadmium carboxylate removal. This result is surprising and will be addressed in greater detail in section III.4. However, the presence of this diamine, while increasing the stability of the removed Z-type ligand, seems to also negatively affect the total amount removed during precipitation.
Figure 3.4. Carboxylate coverage as a function of washing cycles for various combinations of primary \( n \)-alkylamines and \( L_2 \) diame solutions in toluene. For all cleaning procedures, methyl acetate was used as the antisolvent. The horizontal dashed line indicates a carboxylate overage of 0.3 nm\(^2\), which is the lowest coverage achieved when removing cadmium carboxylate from CdSe-Cd(O\(_2\)CR)\(_2\)/HO\(_2\)CR nanocrystal samples.

III.2.4 Temperature dependent Z-type displacement

The in situ dependence of Z-type removal was briefly studied by \(^1\)H NMR spectroscopy for a 1.9 M solution of \( n \)-octylamine in toluene-\( d_8 \) heated to high temperatures (Figure 3.5). Under these conditions ([NC] = 0.3 mM, [O\(_2\)CR] = 26 mM) and upon cooling the sample back to room temperature there is a 13% increase in the amount of removed oleate after heating at 140 °C. This suggests the removal of certain cadmium oleate species from the nanocrystal surface is either an endothermic reaction or one which increases the entropy of the system. Previous studies suggest that the organic ligand shell has a temperature dependence on the structural ordering of ligands, which might also aid in their displacement upon heating.\(^43\) While only so much can be interpreted from this small collection of data, additional measurements, particularly with calorimetric
Figure 3.5. Alkene region of the $^1$H NMR spectra of CdSe-Cd(O$_2$CR)$_2$ nanocrystals ([NC] = 0.3 mM, [O$_2$CR] = 26 mM) in 1.9 M $n$-octylamine solution in toluene-$d_8$ at 25 °C (dark red) and after heating to 50 °C (green), and 140 °C (blue) for 1 hour. The inset in the upper left monitors the percent of oleate species displaced from the nanocrystal surface.
techniques, would provide quantitative information on the thermodynamics of Z-type displacement.

III.2.5 Time dependence on washing procedure

It was previously reported that L-type promoted Z-type ligand displacement is > 90% complete within a few minutes of mixing the L-type ligand with CdSe-Cd(O₂CR)₂ nanocrystals.⁷ We decided to investigate if the same displacement kinetics applied to nanocrystals which were subsequently precipitated after being exposed to n-octylamine. Figure 3.6 shows that there is no time dependence of the resulting carboxylate coverage in the range of 10 minutes to 12 hours. Thus, consecutive washing cycles can be performed in a rapid fashion without the negative effect of incompletely displacing cadmium carboxylate from the nanocrystal surface prior to precipitation.

![Figure 3.6](image)

**Figure 3.6.** Carboxylate coverage of CdSe nanocrystals treated with 5 M n-octylamine as a function of time between L-type ligand addition and precipitation with methyl acetate.
III.2.6 Zincblende vs. wurtzite crystal structure

Figure 3.7. $^{31}$P NMR spectra of wurtzite CdSe-Cd$(O_{3-n}(OH)_{n})PR_{m}$ ($n = 0,1$; $m = 1,2$) nanocrystals treated with 5 M $n$-octylamine in toluene-$d_{8}$ in situ (black) and after 5 precipitation cycles with methyl acetate (red).

As a nanocrystal is not spherical with symmetric binding sites, it is not surprising that there is a wide range of binding affinities that can exist within one particle’s surface. This difference in binding affinities of cadmium salts on different facets of CdSe nanocrystals can rationalize the growth of anisotropic materials.\textsuperscript{11,44} It is possible that a wurtzite particle with its different facets would undergo L-type promoted Z-type displacement of its surface cadmiums, typically in the
form of cadmium \( n \)-alkylphosphonates, with a different efficiency than zincblende CdSe-Cd(O\(_2\)CR\(_2\))\(_2\) samples.

The \(^{31}\)P NMR spectrum of CdSe-Cd(O\(_3\),n(OH)\(_n\)PR\(_m\))\(_n\) (n = 0,1; m = 1,2) nanocrystals exposed to a 5 M \( n \)-octylamine solution (Figure 3.7) shows displacement of both cadmium bis-monohydrogen-\( n \)-octadecylphosphonate (\( \delta = 27.2 \) ppm) and cadmium \( n \)-octadecylphosphonate (\( \delta = 18.8 \) ppm) from the nanocrystal surface, indicated by the two sharp resonances. After precipitation and 4 additional precipitation cycles, a broad resonance centered around 35 ppm remains in the \(^{31}\)P NMR spectrum. While this is not enough evidence to assign the molecular phosphorous species, it does show the utility of \(^{31}\)P NMR spectroscopy in monitoring Z-type displacement reactions. The low signal to noise of these experiments, however, warrant further investigation with more concentrated nanocrystal samples.

III.3 Isolation of CdSe-NH\(_2\)R by Column Chromatography

Chromatography is a general strategy for the purification of samples across a wide range of chemical subfields, including colloidal nanocrystals. The theoretical premise of chromatography involves the interaction of species dissolved in a mobile phase with a stationary phase. Different interactions with the stationary phase, either enthalpic or entropic, allow for elution of the species at different times. In affinity chromatography, the time a molecule spends on a column depends on the equilibrium between its free state and states interacting with the stationary phase. In applications of nanocrystals, this has been utilized to isolate bioconjugated particles using immobilized metal ion affinity chromatography or amylose-functionalized column chromatography.\(^{45}\)
The more popular chromatographic method for nanocrystal systems is size exclusion chromatography (SEC), which separates components based on their size through purely entropic factors.\textsuperscript{46} The principle that lies behind SEC is that species travel in a mobile phase through a porous stationary phase, typically cross-linked polymer gel beads. These beads typically have a size that is characterized by an effective molecular weight cutoff (MWCO) above which larger species do not enter the pores and travel quickly through the column. The length that a species travels is dependent on their hydrodynamic radius, with smaller species traversing within the pores of the stationary phase and thus eluting later than larger analytes. SEC with anhydrous mobile phases is termed gel permeation chromatography (GPC) and was originally applied to nanocrystals to improve their size distributions.\textsuperscript{47} More recent studies have shown that GPC is an effective method at purifying nanocrystal solutions. Furthermore, the various rates at which ligands and particles permeate through the column can drive ligand exchange on CdSe, InP, and Au nanocrystals.\textsuperscript{38}

The effectiveness of chromatographic methods on the separation of nanocrystals and free ligands led us to investigate them as a potential alternative to our reported precipitation and redissolution washing procedure. In the following sections, we report the efficiency of amine promoted cadmium carboxylate displacement and removal from CdSe nanocrystals through various stationary phases.

**III.3.1 Gel permeation chromatography**

For GPC studies, large CdSe-Cd(O\textsubscript{2}CR)\textsubscript{2} nanocrystals (d = 6.02 nm, 1 g of material) were employed to increase the size disparity between the particles and free cadmium oleate. For the stationary phase, Bio-Rad’s Bio-Bead S-X1 cross-linked polystyrene was chosen, as it has been
previously reported to have the correct MWCO for nanocrystal systems.\textsuperscript{38,40} The dimensions of the column were chosen so that future columns inside an inert atmosphere glove box would be practical. Using a mobile phase of 4.5 M \textit{n}-octylamine and 0.5 M diaminocyclohexane in toluene, the nanocrystals were allowed to travel through the column (Figure 3.8) and approximately 10 mL fractions were collected. The nanocrystal and carboxylate concentrations were determined by \textsuperscript{1}H NMR and UV-vis spectroscopies and are presented in figure 3.9. Under these conditions, some separation of the nanocrystals and amine-cadmium carboxylate adduct can be observed, but approximately half of the nanocrystals obtained still had a ligand coverage greater than 1 carboxylate nm\textsuperscript{2}. Thus, under practical conditions and on a scale that is comparable to our reported precipitation procedure, GPC does not provide a more efficient alternative to the synthesis of amine bound CdSe-NH\textsubscript{2}R nanocrystals.

\textbf{Figure 3.8.} Progress of GPC described in this section. (left) Nanocrystal band immediately after loading. (right) Nanocrystal band halfway through its traverse. (right) Column after the final elution of nanocrystals, where a faint yellow band of organic impurities can be seen ~2/3 down the column.
Figure 3.9. (top) CdSe nanocrystal and oleate concentrations of fractions obtained from a GPC column with a mobile phase of 4.5 M $n$-octylamine and 0.5 M 1,2-diaminocyclohexane in toluene. (bottom) The corresponding carboxylate surface density for each collected column.

There are several postulates that can help explain the failure of the above GPC method to effectively separate CdSe-$\text{NH}_2\text{R}$ and the removed cadmium carboxylate complex. Cadmium carboxylate species have diffusion coefficients, as monitored by NMR spectroscopy, which are dependent on their concentration, the solvent, and temperature. It is possible that cadmium carboxylate is not a monomer under our reported conditions, which would increase its hydrodynamic diameter and decrease its retention time on the column. Whether a large concentration gradient of amine and diamine is established through the column is also unknown, but is probable due to the different sizes of these molecules. A decreasing amine concentration down the column might affect the equilibrium of the Z-type removal process. In addition, the large
band of nanocrystals that grows as they permeate through the stationary phase indicates either a change in the hydrodynamic radius of the particles, possibly due to a change in surface ligand composition, or high polydispersity. One final chemical reasoning is that there exists oleate moieties whose binding affinity is high and moves through the column with the nanocrystal. Furthermore, it is possible that the nanocrystal loading, column length, and other parameters of the chromatographic method are not optimized. However, decreasing the loading of nanocrystals or increasing the volume of the column decreases the feasibility of this purification method in comparison to the easily scalable precipitation procedure. Thus, we conclude that size exclusion chromatography is not a viable alternative for the synthesis of amine bound CdSe nanocrystals.

### III.3.2 Interaction chromatography with silica

Silica chromatography is a widely used purification technique, particularly in small molecule chemistry. By adjusting the mobile phase of the system, usually through polarity, analytes can be resolved as a function of their interaction with the stationary silica phase. Furthermore, various functional groups can be grafted onto silica, providing further tenability of the interactions between stationary phase and molecules. In particular, silica can be functionalized with a variety of substituents, such as mercapto or amino groups, which can effectively remove metal ions in purification processes or the recycling of precious metal catalysts. This concept has been successfully used to purify nanocrystal samples, with an example being a nickel-nitrilotriacetic complex immobilized on a stationary phase that binds histidine tagged gold nanoparticles.

We hypothesized that a similar approach using a diamine-functionalized silica would aid in the removal of cadmium carboxylate from CdSe nanocrystal systems (Scheme 3.4), which could
Scheme 3.4. Proposed removal of CdX₂ (X = carboxylate) species via diamine functionalized silica.

easily be removed from the system by filtration of the silica. To test this, diamine functionalized silica (700 diamines per nanocrystal, or 3.5 diamines per Cd(O₂CR)₂) was added to a solution of CdSe-Cd(O₂CR)₂ in 5 M n-octylamine and allowed to stir for 30 minutes before filtration of the solid silica. The resulting carboxylate coverage as a function of these filtration cycles are presented in figure 3.10. The coverage decreases after each filtration, indicating that some cadmium carboxylate is removed from the system with the functionalized silica.

Figure 3.10. Carboxylate coverage of filtered CdSe nanocrystals after exposure to a 5 M n-octylamine solution slurried with diamine functionalized silica (700 diamines per nanocrystal, or 3.5 diamines per Cd(O₂CR)₂) over three cycles.
Figure 3.11. Alkenyl region of the $^1$H NMR spectra for CdSe-Cd(O$_2$CR)$_2$ nanocrystals before (blue) and after treatment with 0.2 M $n$-octylamine solution slurried in either diamine functionalized (red) or unfunctionalized (green) silica.

Surprisingly, repeating this purification method with unfunctionalized silica resulted in greater removal of cadmium carboxylate from the nanocrystal sample. Small scale (15 mg of nanocrystals) washings of CdSe-Cd(O$_2$CR)$_2$ with 0.2 M $n$-octylamine slurried in unfunctionalized silica resulted in almost quantitative removal of the oleyl species (Figure 3.11). However, larger scale silica plugs using a 5 M $n$-octylamine and 0.5 M 1,2-diaminocyclohexane solution$^{iii}$ showed no advantage in removing cadmium carboxylate from the nanocrystal sample (Figure 3.12). The use of 3,4-diaminobenzenesulfonic acid as the diamine species, which we expected to aid in the separation of the cadmium carboxylate due to its strong interaction with the polar stationary phase, did not improve the purification and led to loss of over 85% of the nanocrystals. Furthermore, large

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$^{iii}$ Greater concentrations of both the primary amine and diamine increased the amount of cadmium carboxylate removed after each step, and these concentrations were chosen so that an accurate comparison to the precipitation/centrifugation method could be made.
scale silica columns run under the same conditions in an inert atmosphere also proved an ineffective method for the synthesis of CdSe-NH₂R, also resulting in high oleate coverages and low nanocrystal yields (14%). We therefore conclude that while interaction chromatography can be used as a method to separate CdSe nanocrystals from Cd(O₂CR)₂, the similar efficiency compared to the reported precipitation method does not make this a viable alternative for preparing amine bound particles. In addition, the significantly greater difficulty in running large scale columns in an inert air environment further reduces the practicality of using chromatography in the Owen lab’s current setup.

Figure 3.12. Carboxylate coverage of CdSe nanocrystals as a function of either sequential precipitation/centrifugation (blue) or silica plug (red) cycles. For each set of coverages, a 5 M n-octylamine/0.5 M 1,2-diaminocyclohexane solution in toluene was used as the solvent. The horizontal dashed line indicates a carboxylate overage of 0.3 nm², which is the lowest coverage achieved when removing cadmium carboxylate from CdSe-Cd(O₂CR)₂/HO₂CR nanocrystal samples.
In conclusion, the feasibilities of GPC and silica column chromatography to improve the synthesis of amine bound CdSe-NH$_2$R nanocrystals was investigated. While both methods show promise in being a means of separating CdSe-NH$_2$R from the displaced cadmium carboxylate, further optimization for both is required if either is to replace the current procedure of sequential precipitation cycles. Even so, the scalability of these chromatographic techniques to purify gram scale amounts of nanocrystals poses a major disadvantage compared to the easily scaled precipitation/centrifugation method.

III.4 Investigating the Solubility of L$_n$-Cd(O$_2$CR)$_2$ complexes

While the commonly used precipitation and centrifugation method allows for a rapid and practical means of purifying colloidal nanocrystals, one of its main limitations is that some impurities might be difficult to separate. Many cases report incomplete removal of excess ligands, precursors, or reaction solvents. Nozik reported the difficulty in removing InCl$_3$ from synthesized InAs nanocrystals using toluene and methanol, and Chaudret was unable to remove octadecene from the carboxylate ligand shell in InP samples. Furthermore, impurities in CdSe systems such as excess cadmium phosphonate or amides could not be removed using chloroform and methanol as a cleaning solution. While reproducibility and thorough cleaning may be reasonable culprits, similar solubilities of the nanocrystals and impurities may also explain why some species are difficult to remove. For the synthesis of CdSe-NH$_2$R nanocrystals, both solubility and high binding affinities of the cadmium carboxylate complexes are plausible causes behind the difficulty in achieving quantitative removal. While the Owen lab is not yet equipped to perform an in-depth
study of the binding affinities of cadmium salts towards CdSe surfaces, the solubility of cadmium carboxylate and its relevance to the precipitation method is the topic of this section.

III.4.1 In situ displacement of Cd(O₂CR)₂

Doubts about the solubility of the displaced cadmium carboxylate species arose upon comparing the amount displaced by amines to the amount removed after precipitation of the nanocrystals. Interestingly, ¹H NMR spectra of CdSe–Cd(O₂CR)₂ dissolved in n-octylamine (4.5 M, Figure 3.13). Alkenyl region of ¹H NMR spectra of CdSe-Cd(O₂CR)₂ in a 4.5 M octylamine solution (bottom) and in a 4.5 M octylamine / 0.5 M 1,2-diaminocyclohexane solution (top). The addition of the diamine aids in removing the cadmium oleate from the surface of the nanocrystal, however the presence of the diamine greatly decreases the solubility of the surface-displaced cadmium carboxylate adduct.

Figure 3.13. Alkenyl region of ¹H NMR spectra of CdSe-Cd(O₂CR)₂ in a 4.5 M octylamine solution (bottom) and in a 4.5 M octylamine / 0.5 M 1,2-diaminocyclohexane solution (top). The addition of the diamine aids in removing the cadmium oleate from the surface of the nanocrystal, however the presence of the diamine greatly decreases the solubility of the surface-displaced cadmium carboxylate adduct.

Calorimetric techniques may prove to be the method to quantitatively study the displacement of Z-type ligands from nanoparticle surfaces

¹iv Calorimetric techniques may prove to be the method to quantitatively study the displacement of Z-type ligands from nanoparticle surfaces
M) and toluene-$d_8$ show that as much as 90% of the oleate ligands are freely tumbling in the amine solution (Figure 3.13). However, nanocrystals precipitated from this mixture retain roughly 50% of their original carboxylate coverage, and repeated precipitation of the nanocrystals from 4.5 M $n$-alkylamine solutions was required to completely separate $n$-butylamine and $n$-octylamine bound nanocrystals (CdSe−NH$_2$R’, R’ = C$_4$H$_9$, C$_8$H$_{17}$) from cadmium carboxylate coproducts. These observations led us to believe that the precipitation process causes either the rebinding of cadmium carboxylate or its co-precipitation with the nanocrystals.

**III.4.2 Fractional precipitation studies**

In order to investigate the carboxylate-surface interaction during the precipitation process, aliquots of acetonitrile-$d_3$ were added to CdSe-Cd(O$_2$CR)$_2$ in a 4.5 M octylamine / 0.5 M 1,2-diaminocyclohexane solution and the alkenyl resonance monitored by $^1$H NMR (Figure 3.14). As acetonitrile-$d_3$ is titrated into the NMR sample, there is a gradual upfield shift of the alkenyl hydrogen’s resonance, most likely due to a solvent effect. Upon addition of 300 μL of acetonitrile-$d_3$, symmetric broadening of this resonance can be observed, which can be rationalized by faster relaxation of the hydrogens due to the presence of flocculated nanocrystals. At no point during the titration of acetonitrile-$d_3$ did a broad resonance appear downfield of the sharp alkenyl signal, which only appeared after precipitation and isolation of the nanocrystals. Integration of this resonance shows that the oleate concentration begins to decrease at an acetonitrile-$d_3$ concentration between 3-6 M (Figure 3.15), which is the same range that the nanocrystals precipitated. Thus, oleate species cannot be observed rebinding to the nanocrystal surface prior to particle flocculation.
Figure 3.14. Alkenyl region of the $^1$H NMR spectrum of CdSe-Cd(O$_2$CR)$_2$ in a 4.5 M octylamine / 0.5 M 1,2-diaminocyclohexane solution in toluene-$d_8$ (purple) with 10 (blue), 100 (green) and 300 (red) $\mu$L of acetonitrile-$d_3$. The top black spectrum is the same nanocrystal sample after precipitation and isolation of the nanocrystal sample.

Similar observations using methyl acetate as the anti-solvent were observed (Figure 3.16). While precipitation began at methyl acetate concentrations below 8 M, a large portion of particles remained in solution and additional methyl acetate was required to recover the majority of nanocrystals. These results indicate that the solubility of the nanocrystals and displaced cadmium carboxylate adducts are similar enough to cause their co-precipitation during our reported cleaning procedure.
Figure 3.15. Relative intensity of the alkenyl resonances of the $^1$H NMR spectra in Figure 3.14. The horizontal dashed line represents the relative intensity of this resonance in the isolated nanocrystal sample after one precipitation.

Figure 3.16. Relative oleate concentrations in the isolated supernatant recovered after centrifugation as a function of methyl acetate added to a solution of CdSe-Cd(O$_2$CR)$_2$ and 5 M octylamine / 0.5 M 1,2-diaminocyclohexane in toluene.
III.4.3 Solubility of Cd(O₂CR)₂ in cleaning solutions

Figure 3.17. Solubility of cadmium oleate, in mg/mL, of 20 different solutions investigated for use in preparing CdSe-NH₂R by precipitation/centrifugation. For 10 solutions containing various concentrations of n-octylamine and 1,2-diaminocyclohexane, an antisolvent choice of either methyl acetate of acetonitrile was chosen.
The observed co-precipitation of cadmium carboxylate with the nanocrystals, even in the presence of a strong L-type ligand such as \(n\)-octylamine or 1,2-diaminohexane, is surprising and warrants a further understanding of the solubility of amine-cadmium carboxylate species under our reported solvents. Figure 3.17 compares the solubility of cadmium oleate in a variety of cleaning solutions. For every solution studied, cadmium oleate has a higher solubility in methyl acetate than acetonitrile, which we attribute to both its lower polarity and concentration. In addition, it can be concluded that \(n\)-octylamine increases solubility compared to strictly toluene, THF, or methylene chloride. Surprisingly, the presence of 1,2-diaminocyclohexane decreases the solubility of cadmium oleate. While the exact reason behind this is not known, it can be rationalized that the binding of the diamine to the cadmium center lowers conformational freedoms of the carboxylate groups and increases intermolecular alkane chain interactions, leading to a lower energy barrier for crystallization. In addition to these observations, it can also be seen that the choice of methylene chloride, THF, or toluene as the organic solvent has a negligible effect on solubility. Because of the issues of photostability with methylene chloride\(^{56}\) and the potential of THF to bind the nanocrystal as an L-type ligand, we conclude that toluene is the best solvent choice for performing amine promoted cadmium carboxylate removal in CdSe nanocrystal systems.

Of particular relevance to this section is the recent report of using branched carboxylates as a method to increase the solubility of cadmium carboxylate bound nanocrystals.\(^{41, 57-58}\) The branched alkyl chain in these ligands increases rotational and bending entropy of their C-C \(\sigma\) bonds, which correlates with an increase in the solubility of the respective CdSe-Cd(O\(_2\)CR)\(_2\) nanocrystals. Preliminary studies of synthesizing CdSe-NH\(_2\)R nanocrystals starting from a branched carboxylate bound CdSe nanocrystal were not promising and will not be further
discussed in this dissertation. These results, however, hint that other factors besides solubility might be causing difficulty in the removal of cadmium carboxylate.

The concentrations of amine, diamine, toluene, and methyl acetate in the investigated cleaning solutions are identical to those used during the preparation of CdSe-NH$_2$R. Furthermore, it is known that at these concentrations, the L-type ligands can displace $> 90\%$ of cadmium carboxylate from CdSe nanocrystals. Thus, any deviation from the solubilities in figure 3.17 must be due to the presence of the nanocrystals. In figures 3.18 and 3.19, we compare the amount of cadmium oleate removed during multiple precipitation cycles to the mass expected to be removed, based off its solubility, for both a 5 M $n$-octylamine and 5 M $n$-octylamine/0.5 M 1,2-diaminocyclohexane solution with methyl acetate anti-solvent. For both systems, the number of washes required to remove cadmium oleate significant deviates from that expected based on solubility alone.

This deviation from the expected removal rate of cadmium oleate indicates a strong interaction between the displaced carboxylate species and the nanocrystal surface upon addition of anti-solvent. While the binding affinity towards the particle or intercalation with the aliphatic ligand shell may be driven by the addition of a polar solvent, our fractional precipitation results presented in figures 3.15 and 3.16 indicate otherwise. Therefore, it is likely that the rebinding of oleate species happens rapidly and coincident with nanocrystal precipitation.

One possible explanation as to why an unexpectedly high amount of oleate rebinds could be again due to the formation of ion pairs through dissocation into L-type stabilized cadmium monocarboxylate cations and carboxylate anions (Scheme 3.5). The carboxylate anion should have a strong affinity to the surface and might rebind to and precipitate with the nanocrystal. Furthermore, the cadmium cationic complex could be stabilized by sigma donation from the L-
type ligand. While only speculation at the time of writing this dissertation, this hypothesis can explain the observed trends reported in this chapter. It might be possible to observe the formation of such a molecular species spectroscopically (refer to chapter VI of this dissertation to learn about synthetic efforts into synthesizing possible nanocrystal candidates), but at this point no direct evidence exists.

Figure 3.18. Mass of cadmium oleate remaining in a CdSe nanocrystal sample ([NC]_{initial} = 2.05 mM) after precipitation cycles from a 5 mL 5 M n-octylamine solution in toluene with 45 mL of methyl acetate. The red data shows the expected amount of cadmium oleate that would remain based on its solubility in this cleaning solution.
Figure 3.19. Mass of cadmium oleate remaining in a CdSe nanocrystal sample ([NC]_{initia} = 2.95 mM) after precipitation cycles from a 5 mL 5 M n-octylamine/0.5 M 1,2-diaminocyclohexane solution in toluene with 45 mL of methyl acetate. The red data shows the expected amount of cadmium oleate that would remain based on its solubility in this cleaning solution.

Scheme 3.5. Proposed dissociation of cadmium carboxylate into an amine stabilized cadmium monocarboxylate cation and a bound carboxylate anion.
III.5 Conclusions

Gel permeation and silica affinity chromatography were investigated as alternative methods for the synthesis and purification of amine bound CdSe-NH$_2$R nanocrystals from CdSe-Cd(O$_2$CR)$_2$. While both proved successful at reducing the carboxylate surface density, they demonstrated neither improved efficiency nor practicality compared to our reported precipitation and redissolution procedure. Attempts at optimizing the cleaning solution composition for the precipitation method also proved ineffective at improving the isolation of pure CdSe-NH$_2$R material. Additional studies of the synthetic procedure show discrepancies between the amount of cadmium carboxylate displaced by amine ligands and the amount removed from the system post precipitation. Solubility studies of cadmium oleate in our reported cleaning solution conclude that there are additional driving forces besides co-precipitation of the Z-type ligand and nanocrystal that result in rebinding.

The importance of understanding the surface chemistry occurring during L-type promoted Z-type displacement and precipitation of the nanocrystals is crucial towards developing a large scale and practical synthesis of amine bound CdSe-NH$_2$R nanocrystals. Our current method allows for the production of this material on a multi-gram scale, allowing for both additional surface chemistry studies and device fabrication to be realized and studied in systemic and reproducible manners. However, lingering questions concerning the binding affinity of low carboxylate coverage CdSe-Cd(O$_2$CR)$_2$ samples and the exact binding motif of Z-type ligands in the presence of various L-type ligands warrant further investigation into this synthesis. Finding answers to these problems will not only aid in improving the preparation of CdSe-NH$_2$R, but will also provide valuable insight pertaining to the molecular interactions between Z-type ligands and nanocrystal surfaces.
III.6 Experimental

Quantitative washes of CdSe-Cd(O2CR)2. For each cleaning solution studied in section III.2, CdSe-Cd(O2CR)2 was dissolved in the appropriate concentrations of amine, diamine, and toluene and allowed to stir for 30 minutes, after which the solution was transferred to a 50 mL centrifuge tube and precipitated with methyl acetate. The tube was centrifuged a 7000 rpm for 10 minutes, and the supernatant discarded. The solid red nanocrystals were transferred to a 20 mL vial and dried for \( \leq 1\) hour under vacuum, then dissolved in either benzene-\(d_6\) or toluene-\(d_8\) for analysis by \(^1H\) NMR and UV-vis spectroscopies.

Synthesis of 3,4-diaminobenzenesulfonic acid. The synthesis of 3,4-diaminobenzenesulfonic acid was adapted from a previously reported method.\(^{59}\) In a 250 mL round bottom flask equipped with a stir bar and a reflux condenser, 90 mL of concentrated sulfuric acid was cooled to -30 °C using an o-xylene/CO\(_2\) bath while under flowing argon. o-Phenylenediamine (20 g, 185 mmol), which had been previously purified through sublimation, was added to the sulfuric acid solution at -30 °C. Upon addition the reaction turned a dark green. The reaction was immediately placed back under argon and allowed to stir at low temperature for 45 minutes, after which the flask was removed from a cooling bath and warmed to room temperature. The solution was then heated to 137 °C and allowed to stir for 24 hours, during which time a white precipitate could be seen forming. Note that if the o-phenylenediamine is not sublimed prior to addition to the sulfuric acid, the majority product is blue instead of white, possibly due to sulfonation of polymer species. The reaction was cooled to room temperature and the remaining product was precipitated with 200 mL of ice cold water added dropwise. The white solid was collected by filtration and washed with an additional 50 mL of ice cold water and 500 mL of cold ethanol. The product was recrystallized
from boiling water. Yield 29 %. \(^1\)H NMR (D\(_2\)O, 300 MHz): \(\delta = 6.91\) (d, \(^3J_{HH} = 9\) Hz), 7.17 (s, 1H), 7.32 (d, \(^3J_{HH} = 9\) Hz), 7.37 (b, 1H). \(^{13}\)C\(\{^1\)H\}(D\(_2\)O, 500 MHz): \(\delta = 119.6, 120.4, 121.8, 124.7, 135.5, 137.3\) ppm.

**Temperature dependent displacement of cadmium carboxylate from CdSe-Cd(O\(_2\)CR)\(_2\).** A 8 mL toluene-\(d_8\) solution consisting of \(n\)-octylamine (1.9 M) and CdSe-Cd(O\(_2\)CR)\(_2\) ([NC] = 0.3 mM, [O\(_2\)CR] = 26 mM) was placed in a 3 neck round bottom flask fitted with a stir bar, thermocouple adapter, and rubber septum was placed under argon and stirred for one hour at 25, 40, and 140 °C. For each temperature, a 50 \(\mu\)L aliquot of the solution was taken and diluted with 600 \(\mu\)L of toluene-\(d_8\) ([NC] = .0225 mM, [amine] = 0.1746 M, [O\(_2\)CR] = 2 mM) for analysis by \(^1\)H NMR spectroscopy.

**Synthesis of wurtzite CdSe-Cd(O\(_3\)n(OH)\(_n\)PR)\(_m\) (n = 0,1; m = 1,2).** Wurtzite CdSe nanocrystals were prepared according to a previous report.\(^6\) After isolation and purification, phosponic acid impurities were removed according to the procedure described for zincblende CdSe-Cd(O\(_2\)CR)\(_2\)/HO\(_2\)CR nanocrystals (see Reaction of CdSe–Cd(O\(_2\)CR)\(_2\)/HO\(_2\)CR with CdMe\(_2\) or ZnEt\(_2\), section II.9).

**\(n\)-Alkylamine promoted cadmium phosphonate displacement from wurtzite CdSe-Cd(O\(_3\)n(OH)\(_n\)PR)\(_m\) (n = 0,1; m = 1,2).** A solution of \(n\)-octylamine in toluene (5 mL, 4.5 M) was added to a stock solution of CdSe nanocrystals ([nanocrystals] = 0.22 mM, [phosphonate] = 15.8 mM) and the red solution stirred for 10 min. Methyl acetate (25 mL) was added and the precipitate isolated by centrifugation. This process was repeated 5 times. After the final centrifugation, the
nanocrystals were dissolved in toluene, dried under vacuum, and characterized by $^{31}$P NMR and UV–visible absorption spectroscopies.

**Gel permeation chromatography of CdSe-Cd(O$_2$CR)$_2$.** GPC on CdSe-Cd(O$_2$CR)$_2$ was adapted from a previously reported method.$^{40}$ Briefly, 10 g of Bio-Rad Bio-Bead S-X1 support were allowed to soak in toluene overnight. The beads were then used to fill a 50 cm x 1 cm glass column, and toluene was flushed through the column until no free polystyrene (monitored by its absorbance at 300 nm with a UV-Vis spectrometer) eluted from the bottom of the column. Then, 100 mL of a 4.5 M $n$-octylamine/0.5 M diaminocyclohexane toluene solution was flushed through the column. It was assumed that 100 mL was enough to establish a constant concentration gradient of the cleaning solution across the column. After, 1 mL of a CdSe-Cd(O$_2$CR)$_2$ solution in 4.5 M $n$-octylamine/0.5 M 1,2-diaminocyclohexane toluene solution ($d = 6$ nm, [nanocrystals] = 1.22 mM, [O$_2$CR] = 0.9 M) was loaded onto the column and allowed to traverse through it. A 4.5 M $n$-octylamine/0.5 M diaminocyclohexane toluene solution was used as the mobile phase. A low pressure stream of nitrogen gas was applied to the top of the column to both aid in the progress of the analytes and prevent $n$-octylcarbamate formation. Approximately halfway down the column a yellow band, presumably organic impurities, appeared above the red band of nanocrystals. A total of 14 fractions, 10 mL in volume, were collected throughout the column process. Each fraction was placed under vacuum until only a residue of nanocrystals remained, and these were dissolved in toluene-$d_8$ for subsequent analysis by $^1$H NMR and UV-Vis spectroscopies.

**Cd(O$_2$CR)$_2$ removal with diamine functionalized silica.** To a 2.5 mL, 5 M $n$-octylamine solution of CdSe-Cd(O$_2$CR)$_2$ ([NC] = 0.4 mM, [O$_2$CR] = 80 mM) was added 0.5 g of diamine functionalized
silica (1.4 mmol diamine/gram of silica, 0.7 mmol, 700 di­amines per nanocrystal, 3.5 di­amines per \( \text{Cd(O}_2\text{CR)}_2 \)) and allowed to stir overnight. The solution was then filtered, dried under vacuum, and redissolved in 0.5 mL of benzene-\( \text{d}_6 \) for analysis by \( ^1\text{H} \) NMR and UV-Vis spectroscopies. This process was repeated two additional times.

**Large scale silica plugs with CdSe-Cd(O\(_2\text{CR)}_2 \).** In an inert air glove box, approximately 80 mL of silica was added to a 100 mL fritted glass filter fit with a side arm Erlenmeyer flask and rubber vacuum adapter. The silica was washed with 200 mL of a 5 M \( n \)-octylamine/0.5 M 1,2-diaminocyclohexane toluene solution. Then, 4 g of CdSe-Cd(O\(_2\text{CR)}_2 \) dissolved in a 4 mL 5 M \( n \)-octylamine/0.5 M 1,2-diaminocyclohexane toluene solution was loaded onto the silica bed and washed through the frit with the same solution. Approximately 20 mL of a clear red solution was collected, transferred to a 40 mL vial, and placed under vacuum until only a red residue of nanocrystals remained, which was redissolved in 5 mL of benzene-\( \text{d}_6 \) for analysis by \( ^1\text{H} \) NMR and UV-Vis spectroscopies. This processed was repeated 4 additional times with fresh silica.

**Large scale silica column chromatography on CdSe-Cd(O\(_2\text{CR)}_2 \).** Silica interaction chromatography was performed in an inert air glove box on 4 g of CdSe-Cd(O\(_2\text{CR)}_2 \) nanocrystals using a 5 M \( n \)-octylamine/0.5 M 1,2-diaminocyclohexane toluene solution as the mobile phase. A 50 cm x 1 cm glass column was used for this procedure, and was fit with a side arm Erlenmeyer flask and rubber vacuum adapter to aid in the slow movement of analyte. The clear red nanocrystal solution that eluted was collected until the eluent was colorless, and this was dried under vacuum and redissolved in 5 mL benzene-\( \text{d}_6 \) for analysis by \( ^1\text{H} \) NMR and UV-Vis spectroscopies.
Fractional precipitation with acetonitrile-$d_3$. In a J Young NMR tube, a 4.5 M $n$-butylamine/0.5 M 1,2-diaminocyclohexane solution of CdSe-Cd(O$_2$CR)$_2$ ([nanocrystals] = 0.24 mM, [O$_2$CR] = 50.3 mM) in toluene-$d_8$ was made. To this was added 10, 100 and 300 μL of acetonitrile-$d_3$ and after each titration a $^1$H NMR spectrum was acquired. After the third titration, the nanocrystals were transferred to a 15 mL centrifuge tube and precipitated with 14 mL of acetonitrile, then centrifuged at 7000 rpm for 5 minutes. The recovered red solid was redissolved in toluene, dried under vacuum, and subsequently redissolved in toluene-$d_8$ for subsequent analysis by $^1$H NMR.

Fractional precipitation with methyl acetate. 0.5 mL of a CdSe-Cd(O$_2$CR)$_2$ sample ([nanocrystals] = 1.44 mM, [O$_2$CR] = 0.3 M) was dried under vacuum and redissolved in 5 mL of a 4.5 M $n$-butylamine solution in toluene. The solution was allowed to stir at room temperature for 30 minutes, then transferred to a 50 mL centrifuge tube. To the solution was added 2.5 mL of methyl acetate, after which the tube was centrifuged at 7000 rpm for 10 minutes. Afterwards, a 50 μL aliquot of clear red supernatant was taken and dried under vacuum for 1 hour. The red solid was redissolved in 600 μL of toluene-$d_8$ for $^1$H NMR analysis. This process was repeated for total methyl acetate volumes of 10 and 15 mL.

Quantitative solubility measurements of Z-type displacement L-type solutions. For each cleaning solution studied according to figure 3.17, 0.5 mL of the solution was added to cadmium oleate ([Cd(O$_2$CR)$_2$] = 0.1 M) and shaken until the solid completely dissolved. Then, 4.5 mL of either methyl acetate or acetonitrile was added to the solution and centrifuged at 7000 rpm for 10 minutes. The supernatant was filtered through a 0.2 μm syringe, and 2 mL of the solution was
taken and removed under vacuum. The resulting off white solid was dissolved in 1 mL of benzene-$d_6$ for $^1$H NMR analysis.

III.7 References


CHAPTER IV: THE EFFECT OF ION-PAIRS ON THE THIN FILM STRUCTURE AND DEVICE PERFORMANCE OF CdSe NANOCRYSTALS

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Scientific Abstract

The solid state structure of thin films made from $n$-butylamine bound CdSe nanocrystals (CdSe-$\text{NH}_2\text{C}_4\text{H}_9$) annealed at various temperatures (25 to 300 °C) at $10^{-4}$ torr was investigated. Diffuse reflectance infrared Fourier transform, nuclear magnetic resonance, and UV-vis transmission spectroscopies were used to characterize the ligand shell before, during and after thermal annealing and indicate that > 99% of the $n$-butylamine is desorbed from the nanocrystal surface with a minute amount of non-volatile organics (< 1 aliphatic chain per 20 nanocrystals) remaining. Small changes in the absorbance spectrum can be seen below an annealing temperature of 150 °C, while more dramatic changes appear if the films are annealed above 200 °C. Pair distribution function analysis and scanning electron microscopy show that these thin films do not undergo a significant change in domain size under these annealing conditions, in stark contrast to cadmium chloride and tri-$n$-butylphosphine bound CdSe nanocrystals (CdSe-CdCl$_2$/PBu$_3$) which undergo significant grain growth. Thin film transistors of CdSe-$\text{NH}_2\text{C}_4\text{H}_9$ fabricated on thermally grown silicon dioxide gate dielectrics produce field-effect transistors with an average electron mobility of $12 \pm 1$ cm$^2$ V$^{-1}$s$^{-1}$, a low threshold voltage hysteresis (4.0 ± 0.6 V$_{th}$), and an on/off ratio of $8 \times 10^4$.

Plain English Abstract

The amine bound nanocrystals discussed in chapter II were fabricated into thin film transistors to study their electrical transport properties. These samples have completely exposed surfaces and do not grow upon thermal annealing, both of which have been thought to cause poor device characteristics. Despite these structural properties these nanocrystals behave like high quality transistors.
IV.1 The importance of ligand composition in II-VI nanocrystal thin film applications

One of the benefits of colloidal nanocrystals compared to their bulk counterparts is the ability to employ solution processing in the fabrication of optical and electronic devices. Since the inception of colloidal semiconductor synthesis, a major goal in the development of their surface chemistry has been to replace the native insulating shell, typically metal carboxylates (ME-M(O₂CR)₂)¹ and phosphonates (ME-M(O₃PR)₂)² with shorter molecular complexes that allow for more efficient charge transport in thin film devices.³⁻¹⁷ Exchange of aliphatic ligands with smaller ones leads to denser packing of the particles causing stronger electronic coupling in thin film applications. Early work focused on synthesizing CdSe nanocrystals bound solely by neutral species such as pyridine and primary n-alkylamines that could readily be removed from thin films through thermal annealing processes.¹⁸⁻¹⁹ While conductance of these thin films was higher compared to alkylphosphonate and alkylcarboxylate-bound samples, difficulties in achieving complete exchange of the initial insulating ligand shell remained a limiting challenge in achieving higher carrier mobility.²⁰

The majority of new exchange methods have therefore focused on X-type ligands, replacing native insulating species with shorter anions such as inorganic metal chalcogenides,¹⁰,¹³⁻¹⁷,²¹⁻²² halides,¹,²³⁻²⁷ or thiocyanates⁹ (Table IV.1). Such ligand exchanges have led to rapid improvements in the quality of electrical devices fabricated from colloidal nanocrystals, including successful integration of circuits on flexible plastic substrates.²⁸ In addition, inorganic metal chalcogenide ligands have been shown to act as molecular “solders”, acting as a bridge to fuse single particles into large domains, resulting in thin films with mobilities approaching those of bulk cadmium selenide.¹³,¹⁷ n-Type doping of thin films with indium has also been shown to increase carrier mobility by 2 orders of magnitude.⁷ While these advances have greatly improved
Table IV.1. Reported carrier mobilities of selected semiconductor nanocrystal materials.

<table>
<thead>
<tr>
<th>core-ligand</th>
<th>reported mobility (cm² V⁻¹ s⁻¹)</th>
<th>reference(s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CdSe-NH₂(CH₂)₇NH₂/pyridine</td>
<td>1x10⁻⁶ — 1</td>
<td>19</td>
</tr>
<tr>
<td>CdSe-Cd(O,CMe)₇/In</td>
<td>0.03</td>
<td>7</td>
</tr>
<tr>
<td>CdSe-[SCN][NH₄]⁺</td>
<td>0.01—0.1</td>
<td>3</td>
</tr>
<tr>
<td>CdSe-[SCN][NH₄]⁺,In</td>
<td>27</td>
<td>3</td>
</tr>
<tr>
<td>CdSe-[S⁺][NH₄]₂</td>
<td>0.4</td>
<td>15</td>
</tr>
<tr>
<td>CdSe/CdS-GaI₇/NH₂C₄H₆</td>
<td>2</td>
<td>24</td>
</tr>
<tr>
<td>PbSe-[S⁺][Na]⁺₂/Al₂O₃</td>
<td>7</td>
<td>21</td>
</tr>
<tr>
<td>CdSe-NH₂C₄H₆</td>
<td>12</td>
<td>this work</td>
</tr>
<tr>
<td>CdSe-[In₃Se₄]⁺[N₂H₄]⁺₂</td>
<td>16</td>
<td>10</td>
</tr>
<tr>
<td>CdSe-CdCl₂</td>
<td>25</td>
<td>1</td>
</tr>
<tr>
<td>CdSe-[Cd₂Se₃]⁺[Na]⁺₂</td>
<td>≥ 300</td>
<td>13,17</td>
</tr>
</tbody>
</table>

the value of colloidal nanocrystals for optoelectronic applications, the presence of impurities and sintering makes it difficult to study the inherent transport properties of quantum confined cadmium selenide. Thus, there remains an interest in understanding the fundamental connections between ligand composition and its effect on thin film structure and electrical performance. In particular, the thin film performance of bare cadmium selenide nanocrystals without any ligands remains unknown.

It is possible that the reason why such a fundamental thin film sample has yet to be studied is the difficulty in synthesizing a pure sample. While neutral ligands have been used in various exchanges on nanocrystal surfaces, the process is complicated by a variety of dynamics occurring simultaneously. These include L-type promoted Z-type removal and ion-pair generation. Chapter II discussed how ammonium carboxylate, phosphonate, and carbamate ion-pairs can exist as subtle yet important molecular species that bind tightly to the surface of CdSe nanocrystals. Their presence, while increasing colloidal stability, also have undesirable effects on transport properties and are likely to be the cause of variability in the performance of nanocrystalline thin
film devices. The reasons for these are twofold: the anions typically consist of aliphatic carbon structures which insulate charge, and the presence of mobile ions can also interact with carriers and cause hysteretic behavior. This has been particularly the case for charge transport in perovskite materials. Ion-pairs are difficult to remove once made, and preventing their formation requires the removal of tenacious acidic impurities that are common in established synthetic methods. Using powerful organometallic reagents and rigorously prepared anhydrous solvents, amine-bound cadmium selenide (CdSe-NH$_2$R, R = C$_4$H$_9$, C$_8$H$_{17}$, C$_{12}$H$_{25}$) can be prepared, which are free of any carboxylate or phosphonate species (see chapters II and III for detailed discussions of this synthesis). With this sample in hand, we decided to explore both the solid state structure and electrical transport properties of their thin films, and devices fabricated from them, in the absence of any non-volatile ligands.

**IV.2 Characterization of CdSe-NH$_2$R thin films**

**IV.2.1 Spectroscopic Characterization of CdSe thin films**

$n$-Octylamine bound CdSe nanocrystals, CdSe-NH$_2$C$_8$H$_{17}$, were synthesized through $Z$-type displacement of acid-scavenged CdSe-Cd(O$_2$CR)$_2$ particles (refer to chapters II and III). The resulting neutral ligand shell can be exchanged for the more volatile $n$-butylamine. This solution of CdSe-NH$_2$C$_4$H$_9$ nanocrystals is indefinitely stable in a 10% (v/v) $n$-butylamine solution of toluene and can be used for solution processing. Thin films of CdSe-NH$_2$C$_4$H$_9$ were fabricated by spin coating this nanocrystal stock solution ([NC] = 0.4 mM) onto a Si/SiO$_2$ substrate, followed by annealing under vacuum ($10^{-4}$ torr) at various temperatures for 2 hours. This process produces
Figure IV.1. (A) AFM image of CdSe-NH$_2$C$_4$H$_9$ spin coated onto Si/SiO$_2$ and (B) Z-height of three traces (red, green, blue) showing an average film height of ~50 nm.

CdSe thin films that are 50 nm thick, as characterized by AFM (Figure IV.1). These annealing conditions can be simulated in situ using diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) to monitor the thermal desorption of $n$-butylamine. CdSe-NH$_2$C$_4$H$_9$ slurried in an anhydrous potassium bromide matrix (5 wt %) gave an infrared reflection spectrum that matches that of a previously reported spectrum of CdSe-NH$_2$C$_8$H$_{17}$ obtained in a liquid cell (Figure IV.2).$^{30}$

As the sample is heated and placed under vacuum ($10^{-4}$ torr), surface coordinated $n$-butylamine ($\nu$(N-H) = 3000 – 3400 cm$^{-1}$) was observed desorbing from the nanocrystal surface (Figure IV.2). No signal from $n$-butylamine was observed after annealing above 200 °C for 2 hours. This is in line with previous work on chloride-terminated CdSe nanocrystals, where $n$-butylamine completely desorbs under identical annealing conditions.$^{1}$ The use of volatile $n$-butylamine as the neutral ligand was essential to yield pure films containing bare stoichiometric CdSe. Attempts to quantitatively remove $n$-octylamine from CdSe nanocrystals could not be achieved, as the $\nu$(N-H) resonance could still be observed even after annealing under vacuum at 250 °C for 20 hours (Figure IV.3). In annealed CdSe-NH$_2$C$_4$H$_9$ films, remaining C-H resonances
can still be observed, which persists even if the sample is heated above 300 °C. Within the detection limit of the measurement, EDS confirmed that all nitrogen is removed after two hours of annealing at 250 °C and 10^{-4} torr. These observations allow us to conclude that the greater majority (> 99%) of the organic ligand shell of these thin films consist of $n$-butylamine, whose complete desorption from the nanocrystal surface leaves a pristine CdSe thin film with no amine or carboxylate species present.

Figure IV.2. (A) DRIFTS spectra of a CdSe-NH$_2$C$_4$H$_9$ (5 wt %) sample dispersed in a KBr matrix, under an evacuated atmosphere (10^{-4} torr) and annealed at temperatures ranging from 25 to 250 °C for 2 hours; (B) Zoomed in region of the $\nu_{\text{N-H}}$ resonance of the DRIFTS spectra in (A); (C) Percent of the original $\nu_{\text{C-H}}$ and $\nu_{\text{N-H}}$ intensities remaining as a function of the annealing temperature
Figure IV.3. \(\nu(\text{N-H})\) and \(\nu(\text{C-H})\) region of the DRIFTS spectra of a CdSe-NH$_2$C$_8$H$_{17}$ (5 wt %) sample dispersed in a KBr matrix, under ambient temperature and pressure (blue) and after being exposed to an evacuated atmosphere (10$^{-4}$ torr) and annealed at 250 °C for 20 hours (red).

While our DRIFTS spectra indicate that 10% of the C-H signal remains after annealing at 250 °C, more quantitative measurements point to the number of residual organics being much less. $^1$H NMR spectra of acid digested CdSe-NH$_2$C$_4$H$_9$ samples annealed at lower temperatures indicate that primary amines completely desorb from the nanocrystal surface at 180 °C, in line with our DRIFTS analysis, but with only a trace amount of non-volatile aliphatics (< 1 per 20 nanocrystals) remaining. The discrepancy of the remaining \(\nu_{\text{C-H}}\) intensity in the DRIFTS spectra may not be due to a high amount of aliphatics, but to errors within the DRIFTS measurement itself, possibly due to a difference in the extinction coefficient of vibrational transitions in N-H and C-H bonds, or changes in the roughness of the KBr pellet surface upon heating.

Digestion of multiple CdSe-NH$_2$C$_8$H$_{17}$ stock samples using DCl and $^1$H NMR analysis of the remaining organic species shows only a trace amount of non-volatile aliphatics (< 1 per 20
Figure IV.4. $^1$H NMR spectrum of an acid digested CdSe-NH$_2$C$_4$H$_9$ sample after annealing at 20 mtorr and 180 °C for two hours. The shaded blue region was integrated against an internal pyridine standard ($\delta = 7.34 – 8.57$ ppm, not shown) to get an estimate for the organic species that remain in the sample after annealing. Residual acetone solvent, trace water, and the $\alpha$ and $\beta$ proton resonances of the $n$-butylammonium species present after digestion are labelled.

nanocrystals), as reported in our previous work$^{30}$ and reproduced here with a sample of CdSe-NH$_2$C$_4$H$_9$ annealed at 180 °C for 2 hours (Figure IV.4). Mass Spectrometry ASAP analysis of the remaining organics after acid digestion shows a peak at 282.27 m/z, which corresponds well to a C$_{18}$ carbon fragment. It is possible that this trace fragment is due to remaining oleyl species, as well as possible oxidized products resulting from 1-octadecene and selenium dioxide from the original nanocrystal synthesis.$^{35}$

Within the thin film state, structural transformations can be seen with scanning electron microscopy (SEM). Surprisingly, thin films fabricated from CdSe-NH$_2$C$_4$H$_9$ show little grain growth, even when annealed at 250 °C (Figure IV.5). This behavior is similar to our previously reported study on CdSe-CdCl$_2$/NH$_2$C$_4$H$_9$ and can be attributed to the absence of a grain growth catalyst such as cadmium chloride.$^{1,23,36-37}$ However, a decrease in grain contrast might indicate the beginning of a sintering process upon removal of the $n$-butylamine ligands. Additional insight can be obtained from UV-vis transmission measurements. Annealing these thin films causes their
Figure IV.5. (A) UV-Vis transmission spectra of CdSe-NH$_2$C$_4$H$_9$ films on quartz substrates annealed at temperatures ranging from 25 to 250 °C under vacuum ($10^{-4}$) torr. (B) SEM image of a CdSe-NH$_2$C$_4$H$_9$ thin film on 100 nm thermally grown silicon oxide, after annealing at 250 °C and $10^{-4}$ torr. The scale bar is 200 nm.

optical absorption spectra to red shift and broaden as the $n$-butylamine ligands desorb (Figure IV.5). These changes are gradual below 150 °C and become more dramatic at higher annealing temperatures. Thin films annealed above 200 °C exhibit an absorption onset that corresponds to
the bulk CdSe band gap of 1.74 eV and lack narrow features usually resulting from quantum confinement. Redissolution of the thin films with \( n \)-butylamine can only be achieved if the nanocrystals are annealed at or below 150 °C; annealing the samples at higher temperatures causes the particles to become insoluble (Figure IV.6). Thus, the small changes in the absorption spectrum occurring at or below 150 °C likely reflect a decrease in inter-nanocrystal distance during ligand loss, while the more dramatic and irreversible changes at 200 °C result from a distinct structural change that further increases the coupling between nanocrystals. These changes in absorption onset correlate with the desorption of \( n \)-butylamine from the nanocrystal surface. Thus, it is likely that the removal of \( n \)-butylamine exposes enough of the nanocrystal surface to allow for attachment of neighboring particles.

**Figure IV.6.** (A) UV-Vis absorption spectra of CdSe-\( \text{NH}_2\text{C}_4\text{H}_9 \) thin films annealed under vacuum at (i) 25 °C, (ii) 150 °C, and (iii) 250 °C. (B) UV-Vis absorption spectra of (i) a CdSe-\( \text{NH}_2\text{C}_4\text{H}_9 \) thin film, (ii) annealed under vacuum at 150 °C, and (iii) of a solution of these particles redissolved in toluene after annealing.
**IV.2.2 Pair Distribution Function analysis of CdSe-NH$_2$C$_6$H$_9$ thin films**

**Scheme IV.1.** Stacking sequence along the same structural direction for the zincblende (left) and wurtzite (right) crystal structures.

Pair distribution function analysis (PDF) analysis was used to further interrogate the effect that ligand composition has on the nanocrystal sintering process. Unlike single crystal X-Ray diffraction measurements, the PDF of a material includes analysis of the Fourier transform of the entire scattering intensity and not just the Bragg peaks. By collecting scattering patterns with a high energy X-Ray source, information about the deviation from average bond lengths is not lost. Thus, the Fourier transformed scattering pattern in PDF analysis provides a histogram of interatomic distances that can be modelled with powerful computing methods to determine the structure of amorphous materials, making it a useful tool for studying nanomaterials.$^{38-40}$ As this dissertation aims to focus on the synthesis of CdSe nanocrystals, readers interested in learning more about the pair distribution function method are referred to textbooks and previous dissertations from our lab.$^{41-44}$

II-VI semiconductor alloys crystallize in either the cubic zincblende structure or the hexagonal wurtzite crystal structure. While both wurtzite and zincblende crystal structures derive from local tetrahedral bonding, they differ in their stacking sequence; for wurzite the stacking sequence is ABA along [001] while the stacking of zincblende is ABC along the same structural
direction [111] in the cubic unit cell (Scheme IV.1). Previous PDF studies on the local atomic structure of CdSe nanocrystals have concluded that they possess a disordered atomic structure intermediate between wurzite and zincblende, with a high stacking fault density as compared to the bulk semiconductor. We consider single phase wurtzite and zincblende models of $G(r)$ of CdSe-CdCl$_2$/PBU$_3$ and CdSe-NH$_2$C$_6$H$_5$ thin films to explore how annealing effects the crystal phase as well as the grain size, in addition to mixed phase models consisting of both wurtzite and zincblende components. Free parameters optimized using least squares refinement used in fitting these models to the data are independent lattice parameters, isotropic thermal parameters for each element, a quadratic correction factor for correlated atomic motion, a spherical envelope function diameter for finite nanocrystal size, and a scale factor for the data. Details of the fitting are described in the experimental section IV.6.

**Figure IV.7.** Raw PDF diffraction patterns and tables of best fit parameters for CdSe-NH$_2$C$_6$H$_5$ (A) and CdSe-CdCl$_2$/PBU$_3$ (B) annealed at 50 (B, i), 60 (A, i), 150 (ii), 200 (iii), 250 (iv), 275 (v), and 300 °C (vi) under vacuum (20 mtorr).
The experimental $G(r)$ of CdSe-CdCl$_2$/PBu$_3$ and CdSe-NH$_2$C$_4$H$_9$ thin films at annealing temperatures from 50 to 300 °C are shown in figure IV.7. Upon annealing above 200 °C, peaks at larger pair distances are seen suggesting grain growth in both films; however, this effect is much more pronounced for thin films containing Z type CdCl$_2$ surface passivation. Fitting single phase models of the PDF as described above to wurzite and zincblende models reveals dramatic differences in thin film structure and grain size for samples prepared from nanocrystals with different surface ligand coverage (Figure IV.8). To quantify the goodness of fits for each of these single-phase models we compare the residual fit function $R_w$ for both single phase fits defined as

$$R_w = \sqrt{\frac{\sum_{i=1}^{n}(G_{obs}(r_i)-G_{calc}(r_i))^2}{\sum_{i=1}^{n}G_{obs}(r_i)^2}}$$  \hspace{1cm} (IV.1).$$

Based on this analysis it can be seen that the CdSe-NH$_2$C$_4$H$_9$ thin films are generally well described by a zincblende crystal structure throughout the annealing process, while for CdSe-CdCl$_2$/PBu$_3$ a zincblende to wurzite phase transition is seen at higher annealing temperatures (Figure IV.8). This phase transition is also correlated with significantly larger grain growth in CdSe-CdCl$_2$/PBu$_3$ compared to CdSe-NH$_2$C$_4$H$_9$, which is modeled by refining the diameter of a spherical envelope function which accounts for finite size effects on the pair distribution function of nanomaterials.  

Finally, two-phase models of wurzite and zincblende were used to extract the phase composition of the nanocrystal thin-films (Figure IV.9). Consistent with the analysis above, the phase composition is largely constant in zincblende for the CdSe-NH$_2$C$_4$H$_9$ thin films as a function of annealing temperature, while for the CdSe-CdCl$_2$/PBu$_3$ thin films the phase composition changes as a function of annealing temperature.
Figure IV.8. SEF diameter obtained from selected single-phase models for (A) CdSe-CdCl₂/PBu₃ and (B) CdSe-NH₂C₄H₉ for both the wurtzite and zincblende phases; Residual fit function $R_m$ as a function of annealing temperature for single-phase (wurtzite and zincblende) fits of the experimental $G(r)$ for (C) CdSe-CdCl₂/PBu₃ and (D) CdSe-NH₂C₄H₉.
Figure IV.9. Wurtzite fraction obtained from a two-phase fit model of the experimental $G(r)$ of CdSe-NH$_2$C$_4$H$_9$ and CdSe-CdCl$_2$/PBu$_3$ samples annealed at various temperatures.

IV.3 Electronic transport measurements of CdSe-NH$_2$R thin films

Transistors prepared by evaporating aluminum top contacts (100 µm channel lengths, W/L = 30) onto thermally annealed Si/SiO$_2$ CdSe-NH$_2$C$_4$H$_9$ thin films showed significant conductivity when annealed above 200 °C (Figure IV.10). This is the temperature where SEM, UV-vis spectroscopy, and PDF indicate irreversible sintering begins. Transconductance could not be observed for films annealed below 200 °C. Its onset correlates qualitatively with the broadening and red-shifting in the absorption spectrum along with the irreversible sintering of the thin film. These optical changes also coincide with the desorption of $n$-butylamine from the nanocrystal surface. These observations provide enough evidence to conclude that the electrical performance of these thin-film transistors is correlated with complete (> 99%) removal of the organic ligand shell and subsequent electronic coupling between the nanocrystals.
**Figure IV.10.** (A) Output characteristics for CdSe-NH$_2$C$_4$H$_9$ TFTs with $V_{GS}$ increasing from 0 (teal) to +40 V (dark red) in 10 V steps. (B) Transfer characteristics representative of CdSe-NH$_2$C$_4$H$_9$ TFTs, which show a low threshold voltage ($4.0 \pm 0.6 \ V_{th}$) and an on/off ratio of $8 \times 10^4$.

Stoichiometric films are intrinsic semiconductors with significant conductivity ($> 10^{-4}$ S/cm) after films are annealed at 250 °C for 2 hours. Across 6 devices prepared from 2 separate syntheses of CdSe-NH$_2$C$_4$H$_9$ annealed at 250 °C, an average field effect mobility of $12 \pm 1 \ cm^2\ V^{-1}\ s^{-1}$ was extracted from the linear region. This, in addition to the low threshold voltage hysteresis ($4.0 \pm 0.6 \ V_{th}$) and on/off ratio of $8 \times 10^4$, indicate that films made from CdSe-NH$_2$C$_4$H$_9$ are high-quality semiconductor materials with few mobile ions. These values are significantly higher than previously reported transistors fabricated from CdSe-L ($\mu = 1 \times 10^{-6} - 1 \ cm^2\ V^{-1}\ s^{-1}$). In these examples, it is likely that acidic impurities in the as-synthesized nanocrystals led to the formation of tightly bound ion pairs. The removal of these carboxylate anions under typical annealing conditions does not happen, which leads to lower quality devices due to both the insulating nature of the carboxylate and the presence of mobile ion-pairs.
The high quality of thin film transistors made from these samples is remarkably different than previously reported devices synthesized from CdSe-L. It is likely that trace amounts of organic ion-pairs were present in these devices, hindering transport by the mechanisms postulated above. While it is intuitive that insulating ion-pairs would lower the performance of semiconductor devices, it is surprising that the thin films from CdSe-NH₂C₄H₉ exhibit such high mobilities even after removal of the n-butylamine and exposure of the nanocrystal surface states. Previous theoretical work on PbS nanocrystals concluded that stoichiometric quantum dots can be free from midgap states even without ligand passivation. More recently, density functional theory calculations concluded that X- and L-type ligands do not influence the nanocrystal electronic structure and therefore to not contribute to trap states. Amine bound, CdSe-NH₂R nanocrystals could provide an ideal model to experimentally investigate these claims.

Methods to achieve highly conductive films from stoichiometric CdSe and PbE nanocrystals are well documented, but the thin films made from CdSe-NH₂C₄H₉ are the first where neither organic nor inorganic ligands are present to passivate electronic surface states. Thus, the high performance of nanocrystalline, stoichiometric CdSe demonstrates that the passivation of traps states with ligands is not necessary to achieve high mobilities. While the state-of-the-art devices fabricated from colloidal nanocrystal solutions have indeed been accompanied by an increase in grain size, the nanocrystalline nature of the films reported here may imply that surfaces might also play an important role for transport in these materials.

**IV.4 The role of ligands in CdSe monolayer formation**

This chapter has investigated the role of ligand composition on the solid state structure and transport properties of CdSe thin films. In addition, electronic coupling between nanocrystals gives
rise to the band structure in nanocrystal solids. This can be thought of as a molecular orbital interaction where two wavefunctions on adjacent dots interact to change the energy levels of the valence and conduction bands. Electronic coupling determines the local density of states (LDOS) of the bulk material, which is of utmost importance for charge transport between nanocrystals.\textsuperscript{49} Being able to understand how the LDOS are affected by interactions between dots will provide quantitative data to help connect observed n-type and p-type transport characteristics of nanocrystals with their surface chemistry.

Scanning tunneling spectroscopy (STS), when coupled with well-defined surface chemistry, can be a powerful tool for connecting the attractive properties of colloidal nanocrystals with fundamental principles of electronic interactions.\textsuperscript{50-51} Electronic coupling between nanocrystals will result in a change in the band gap energy of the material, and has been shown to vary with interparticle spacing.\textsuperscript{52} The Vanmaekelbergh group has studied the orbital coupling of PbSe quantum dot solids using STS, showing delocalization of electrons and holes that was highly dependent on the local interparticle geometry.\textsuperscript{53} In addition, STS and STM can be combined to map the wavefunction of the bands of semiconducting particles, which has been reported for InP.\textsuperscript{54} By gathering STS data on carious CdSe nanocrystals, we expect to find trends in electronic coupling dependent upon the electronegativity, size, and binding affinity of the bound ligands. Ultimately, the knowledge obtained could give rationale to some of the interesting properties of nanocrystalline semiconductors, which will help in the development of higher quality thin films for energy and device applications. To this end, we studied the formation of CdSe-CdCl\textsubscript{2}/NH\textsubscript{2}C\textsubscript{6}H\textsubscript{9} monolayers on highly ordered pyrolytic graphite (HOPG) and their electronic structure using tunneling spectroscopy.
Chloride terminated CdSe-CdCl$_2$/NH$_2$C$_8$H$_{17}$ nanocrystals ([nanocrystal] = 4 μM) can be prepared by dropcasting a prepared solution onto HOPG. After evaporation, the sample was annealed under vacuum at 150 ºC to remove the $n$-octylamine ligands, leaving behind a layer of CdSe-CdCl$_2$ nanocrystal samples. Atomic force microscopy (AFM) and scanning electron microscopy (SEM) images show large monolayers approximately 1 μm$^2$ in area (Figure IV.11). These monolayers can be studied using a scanning tunneling microscope, providing interesting information about the topology and electronic levels of the nanocrystal film. The spectra obtained from STS measurements are consistent across multiple locations of the sample, indicating a monolayer made from high quality monodisperse CdSe nanocrystals. Unfortunately, certain reactions such as removal of CdCl$_2$ by amine resulted in monolayers with large CdCl$_2$ clusters which complicated measurements (Figure IV.12). Moving forward, we attempted to obtain organized monolayers of CdSe-NH$_2$R for additional STM/STS measurements. Such a sample, especially with complete removal of the $n$-alkylamine, provides a unique particle completely unpassivated with ligands. In addition, the lack of cadmium salts would circumvent issues of
contamination in the monolayer. A nanocrystal sample free of surface species has never studied before by tunneling spectroscopy and would provide important insight on the LDOS of these materials.

Unfortunately, achieving ordered monolayers of CdSe-NH$_2$R species has proven to be a difficult challenge, as the colloidal instability and tendency of the particles caused aggregation. While monolayers of CdSe-NH$_2$C$_8$H$_{17}$ on HOPG can be achieved ([NC] = 10 μM), most the nanocrystals aggregate on the substrate (Figure IV.13). Current efforts in the Owen lab are aimed at controlling the monolayer formation of colloidal nanocrystals using ion pair ligands. In particular, both ammonium acetate and carbamate ion pairs might provide stabilization of the monolayers. Their formation should be reversed under temperature and vacuum, removing neutral HX and L species and leaving behind a bare CdSe nanocrystal layer (Scheme IV.2). It is interesting that the presence of bound CdCl$_2$ in chloride terminated CdSe nanocrystals stabilizes the monolayers and prevents aggregation. This observation of the stabilizing effect of Z-type ligands will be investigated further in chapter VI.
Figure IV.13. AFM images of CdSe-NH$_2$C$_8$H$_{17}$ films on HOPG. Scale bars for each image are 100 nm.

Scheme IV.2. Proposed monolayer formation using ME (M = Cd, Pb; E = S, Se) nanocrystals bound with ion pair ligands whose neutral HX and L forms can be removed under heat and vacuum.

IV.5 Conclusion

The solid state structure of temperature annealed thin films made from CdSe-NH$_2$C$_8$H$_9$ were characterized using UV-vis, DRIFTS, SEM, and PDF. Using these methods allows us to conclude that complete removal of the volatile ligand shell can be achieved under vacuum and mild temperature ($10^{-4}$ torr and 200 °C) with negligible amounts of organic material remaining, affording films composed exclusively of bare cadmium selenide nanoparticles. The removal of the primary amine ligand shell corresponds to red shifts in the UV-vis transmission spectra of these
annealed films, as well as the onset of conductance in thin film transistors fabricated from these samples. Both SEM and PDF indicate that very little grain growth occurs during the annealing of CdSe-NH$_2$C$_6$H$_9$, which is in stark contrast to films prepared with CdSe-CdCl$_2$/PBu$_3$ nanocrystals, whose annealed films consist of domains that are > 180 nm in size. Despite a completely unpassivated surface and small grain size, thin film transistors fabricated from CdSe-NH$_2$C$_6$H$_9$ exhibit high electron mobility with no hysteretic behavior. Such observations lead to two significant findings. The first is that nanocrystalline thin films can still exhibit high conductivity despite a high density of surface trap states. The second is that these samples contain no mobile ion-pair species, a feat which has proven to be synthetically challenging. All of this indicates that CdSe-NH$_2$C$_6$H$_9$ nanocrystals are an ideal nanocrystal system to study the fundamental effects of particle surfaces on the electrical transport of semiconductor materials.

Additional work to further understand the electronics of thin films using STM and STS is currently underway. Our current findings suggest that a systematic study of CdSe monolayers using tunneling spectroscopy will allow us to investigate the correlation between the chemical properties of the ligands and the electronic structure of nanocrystalline solids. Ideally, future endeavors will utilize the synthetic approaches outlined in this dissertation to prepare samples with well defined nanocrystal and ligand composition.
IV.6 Experimental

**Synthesis of CdSe-NH$_2$C$_4$H$_9$** Amine bound CdSe nanocrystals were synthesized from acid-free CdSe-Cd(O$_2$CR)$_2$ using a previously reported procedure.$^{30}$

**Synthesis of CdSe-CdCl$_2$/PBu$_3$** Chloride and phosphine-bound CdSe nanocrystals were synthesized from acid-free CdSe-Cd(O$_2$CR)$_2$ using a previously reported procedure.$^{1,55}$

**Formation CdSe-NH$_2$C$_4$H$_9$ thin films for UV-vis transmission spectroscopy** Thin films were fabricated on quartz substrates by dropcasting 50 µL of a CdSe-NH$_2$C$_4$H$_9$ stock solution ([NC] = 0.4 mM) in a nitrogen-filled glove box. The films were annealed under vacuum (10$^{-5}$ torr) at 25, 100, 125, 150, 175, 200, 225, and 250 °C for 2 hours. The annealing chamber was cooled for 10 minutes under an atmosphere of nitrogen and then immediately characterized by UV-vis transmission spectroscopy.

**Monitoring desorption of NH$_2$C$_4$H$_9$ from CdSe-NH$_2$C$_4$H$_9$ using DRIFTS** In a nitrogen-filled glove box, a 10 µL aliquot of a CdSe-NH$_2$C$_4$H$_9$ stock solution ([NC] = 1-3 mM) was added to 250 mg of anhydrous potassium bromide in a ceramic mortar. Using a pestle, the sample was ground for roughly 30 seconds, then the solvent was allowed to evaporate for 10 minutes under a dynamic flow of nitrogen. The sample was then ground for an additional minute, at which time the matrix was a homogenous light red powder. The powder was then transferred to the DRIFTS sample chamber. DRIFTS measurements under 1 atm and at room temperature were performed without any modulation with the temperature controller or pressure. In order to evacuate the DRIFTS chamber, a needle valve was gradually opened to expose the sample matrix to vacuum until the...
pressure of the entire closed system increased from $1 \times 10^{-5}$ torr to 0.1 torr. At this point the needle valve was kept at its position until the total pressure of the system fell below $10 \times 10^{-5}$ torr, at which time the needle valve was opened slightly until the pressure again read 0.1 torr. This process was repeated until the needle valve was completely open to the DRIFTS sample chamber, and the pressure again reached $1 \times 10^{-5}$ torr. **NOTE:** Exposing the DRIFTS sample chamber to vacuum to rapidly will cause the nanocrystal/KBr matrix to blow out of the pellet holder. It is best to expose the chamber to dynamic vacuum very gradually to ensure a smooth sample surface. Low pressure DRIFTS spectra were collected after the nanocrystal sample was under full dynamic vacuum for 10 minutes.

High temperature, low pressure DRIFTS measurements were performed in a similar fashion. Upon achieving a sample chamber pressure of $1 \times 10^{-5}$ torr, the temperature of the sample chamber was raised to the desired temperature simulating thin film annealing conditions. Once the temperature reached the desired value, DRIFTS spectra were collected every 15 minutes for 2 hours.

For each temperature studied, a KBr blank was prepared and measured in an identical manner. All data was processed by the Kubelka-Munk transformation so that the spectral intensity was proportional to concentration.

**Digestion of CdSe-NH$_2$C$_4$H$_9$.** A 200 µL aliquot of a CdSe-NH$_2$C$_4$H$_9$ stock solution ([nanocrystal] = 3.01 mM) was placed in a J-Young NMR tube. The tube was taken out of the glove box and placed on a Schlenk link equipped with a J-Young tube vacuum adapter. The nanocrystal sample was then placed under vacuum and the solvent was carefully removed (over a period of 10 minutes) so that none of the nanocrystal residue was above the oil bath described in the next step. Once the
solvent was removed, the J-Young tube was submerged in an oil bath that was previously heated to 180 °C and allowed to anneal for 2 hours. After annealing the nanocrystal residue was cooled to room temperature and placed under flowing argon. A 600 µL solution of 50/50 (v/v %) HCl and methanol was added to the J-Young tube and the nanocrystals visibly dissolved over two hours. The resulting solution was placed under vacuum and the volatiles removed overnight at 40 °C to ensure removal of methanol and unreacted HCl. The white precipitate that remained behind, presumably a mixture of ammonium chloride and remaining organics, was redissolved in 600 µL of acetone-$d_6$ and 20 µL of an internal pyridine standard. The sample was then characterized by $^1$H NMR.

**Thin Film Formation and Annealing** Silicon wafers were cut into 2.5 cm$^2$ squares, washed with isopropyl alcohol, sonicated in isopropyl alcohol for 15 minutes, air dried under nitrogen, and placed in a 160 °C oven before being brought into a nitrogen-filled glove box. The silicon chips were then placed on the spin-coater and washed with 3 mL of toluene (filtered through 0.2 µm syringe) while rotating at 1700 rpm for 45 seconds. Immediately after this toluene wash, A 200 µL aliquot of a CdSe-$\text{NH}_2\text{C}_4\text{H}_9$ stock solution ([nanocrystal] = 0.4 mM) in a 10% $n$-butylamine solution of toluene was dropped onto the silicon substrate and allowed to wet the entire surface. The substrate was then spun at 600-1700 rpm over a period of 45 seconds to form nanocrystal films that were 50 nm in thickness.

To anneal these films, the substrates were transferred to an oven connected to the nitrogen glove box, which had been equilibrating at the desired annealing temperature for 30 minutes. The samples were placed under vacuum for 2 hours, after which time the oven was refilled with
nitrogen and the temperature cooled to room temperature. The samples were removed from the oven and stored in the nitrogen glove box.

**Transistor Fabrication** Evaporation of aluminum electrodes was performed using a shadow mask in an Angstrom Engineering thermal evaporator system. Typical device dimensions were 50-75 nm of CdSe nanocrystals on highly p-doped Si wafers with 200 nm of dry thermal oxide dielectric and 100 nm thick Al electrodes, with a channel length of 100 µm and a W/L ratio of 30.

**Modeling Device Data** Transfer curves were modeled using nonlinear least-squares fitting to ideal MOSFET models for both transfer and output characteristics. Modeling was performed using the Enthought Python Distribution with the Python Data Analysis Library (pandas), Numeric Python (NumPy), Science Python (SciPy), and Matplotlib, as we have reported previously.\(^1\) The drain current was modeled in the saturation \((V_{DS} > V_{GS} - V_t)\) and linear regimes \((V_{DS} < V_{GS} - V_t)\):

\[
I_{d,sat} = \frac{W}{2L} \mu C_{ox} (V_{GS} - V_t)^2
\]

\[
I_{d,lin} = \frac{W}{L} \mu V_{DS} C_{ox} \left( V_{GS} - V_t - \frac{V_{DS}}{2} \right)
\]

Where \(W, L, C_{ox}, \mu, V_t, V_{GS},\) and \(V_{DS}\) are the channel width, channel length, oxide capacitance, field-effect mobility, threshold voltage, gate-source bias, and drain-source bias, respectively. The width and length of the channel were measured using SEM after each measurement, while \(C_{ox}\) was computed from the thickness and dielectric constant of the oxide layer. We define hysteresis as the absolute value of the difference between threshold voltage when reversing a transfer sweep. Conductivity was extracted from the \(V_{GS} = 0\) output characteristics by taking the slope about \(V_{DS} =\)
0, assuming the contact resistance was negligible. Carrier concentration was computed by dividing the conductivity by the elementary charge and $\langle \mu \rangle$.

**Pair distribution function experiments** X-ray scattering experiments of annealed thin films fabricated from CdSe-CdCl$_2$/PBu$_3$ and CdSe-NH$_2$C$_4$H$_9$ were taken at X9 beamline at the National Synchotron Light Source at Brookhaven National Laboratory. 2D detector integration and G(r) were generated using the xPDFsuite of programs. A Qmax of 20 Å$^{-1}$ was chosen in the fourier transform to minimize signal to noise and avoid large termination effects. Qdamp and Qbroad experimental resolution parameters were obtained by fitting the recorded Pair Distribution Function of FCC Ni.

**Pair distribution function modeling** Optimized parameter values for calculating the model PDF are obtained using least squares refinement in PDFgui. For single phase fits, one independent lattice parameter is refined for the zincblende phase and two independent lattice parameters are refined for the wurtzite phase in order to preserve space group symmetry for each phase. Isotropic thermal displacement parameters are refined for Cd and Se atoms in the unit cell of each phase. To account for nanoscale finite size effects on the PDF we refine a diameter of a spherical envelope function. Correlated atomic motion was treated by optimizing an empirical quadratic correlated atomic motion correction factor. An overall scale factor for the data is also optimized for the fit.

For two phase fits, lattice parameters are refined independently, identical isotropic thermal displacement parameters are refined for Cd and Se in the unit cell of each phase, and an empirical quadratic correlated atomic motion correction factor are refined. A scale factor X was fit for the
zincblende phase which constrained the value of the wurtzite scale factor which was defined as (1-X). An overall scale factor for the data is also optimized for the fit. The refined spherical envelope diameter from the single-phase fits was used for each phase.

Details on refined parameters:

Finite q space resolution gaussian dampening factor of model PDF.\(^{57}\)

\[
B(r) = e^{-(r^2 q_{damp}^2)/2}
\]

Peak width correction factor for correlated atomic motion, and experimental resolution.\(^{57}\)

\[
\sigma_{ij} = \sigma_{ij}' \left[ 1 - \frac{\delta_{2}}{r_{ij}^2} + Q_{broad}^2 R_{ij}^2 \right]^{1/2}
\]

Spherical envelope function for finite nanocrystal size

\[
G(r, d) = G(r)_{bulk} f(r, d)
\]

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

\(h(d - r)\) is the heaviside step function which is zero for \(r\) greater than \(d\), and 1 for \(r \leq d\).\(^{45}\)

**IV.7 References**


CHAPTER V: NEUTRAL LIGAND EXCHANGE IN CdSe-L SYSTEMS

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**Scientific Abstract**

Colloidal dispersions of amine bound nanocrystals (CdSe–NH₂R’) are indefinitely stable at amine concentrations of 0.1 M or higher and slowly aggregate at lower concentrations. Diffusion NMR measurements indicate two regimes of amine ligands: a major fraction which undergoes rapid exchange and another fraction with a higher binding affinity. Dissociation and evaporation of the amine ligands in 4-ethylpyridine, tri-n-butylphosphine, or molten tri-n-octylphosphine oxide solution results in nanocrystal aggregation. Quantitative L-type ligand exchange with tri-n-alkylphosphines can be achieved with high temperatures (100 ºC) and dynamic vacuum, however the resulting CdSe-PR₃ product is highly prone to aggregation. Greater stability can be achieved using dimethyl-n-octadecylphosphine as the L-type ligand, yielding soluble CdSe-PMe₂C₁₈H₃₇ nanocrystals with a phosphine coverage of 1.8 nm². CdSe-PMe₂C₁₈H₃₇ is the first stable nanocrystal sample bound solely by neutral phosphines.

**Plain English Abstract**

Many reports of CdSe nanocrystals claim that the surface is coated with ligands such as amines and phosphines. However, the amine-bound CdSe nanocrystals presented in chapter II precipitate from solution easily and are even more unstable if the amines are replaced with phosphines. This major difference in our samples and previous samples is due to the presence of ion pairs, which until this dissertation had not been considered as a potential ligand in previously reported CdSe samples. In this chapter, we discuss the weak binding nature of these types of ligands and propose synthetic methods to make the first stable phosphine-bound CdSe nanocrystal.
V.1 Neutral ligand exchange in the colloidal nanocrystal field

Scheme V.1. Commonly proposed L-type exchange with CdSe-TOPO nanocrystals.

The study of neutral ligand exchanges on the surface of cadmium selenide nanocrystals has been crucial to our understanding of these systems. In fact, neutral ligand exchanges were the first employed to modify as-synthesized CdSe nanoparticles. In a landmark publication, CdSe nanocrystals incorrectly reported as bound by tri-\(n\)-octylphosphine oxide (TOPO) ligands were reported to undergo L-type exchange with the more basic pyridine ligand in quantitative yield (Scheme V.1).\(^1\)\(^2\) As our understanding of the surface landscape of II-VI semiconductor colloidal materials became more refined, it is now evident that a simple L-type exchange was insufficient to describe all the molecular interactions at the nanocrystal surface. Impurities in technical grade TOPO, such as \(n\)-alkylphosphonic acids and phosphonic anhydrides, were discovered to act as X-type ligands with a higher binding affinity to the surface compared to TOPO.\(^3\)\(^5\)

Previous work in our lab (as well as my advisor’s post-doctoral studies) further developed the surface chemistry of CdSe nanocrystal systems, showing that these X-type ligands can be viewed differently, particularly as part of a Lewis acidic Z-type ligand denoted CdX\(_2\).\(^3\)\(^6\)\(^8\) Perhaps a more accurate depiction of the pyridine exchange, then, is one similar to scheme V.2, where pyridine can act as a neutral L-type ligand to both the nanocrystal surface as well as the CdX\(_2\) Z-type ligand, or as part of an ion pair (as reported in chapter II of this dissertation).
Scheme V.2. Updated assignment of the ligand exchanges occurring for the system in scheme V.1 following publication of references 6 and 18.

While this vision of nanocrystal surface chemistry can be further refined to include different binding affinities towards various surface sites (facets, edge and corner sites, for example), it is likely that studies reporting L-for-L type ligand exchanges also included other molecular interactions. There have been multiple reports concerning the kinetics and thermodynamics of L-type exchange on CdSe nanocrystals, in particular with phosphines,9 amines,10-13 and carboxylic acid14-17 species. While their findings have been crucial towards the rational functionalization of nanocrystal surfaces, it is possible that the data they reported for certain ligand exchange processes did not account for the subtle interactions discussed above. This was the case for our CdSe-NH₂C₆H₅ nanocrystal synthesis, which generated ion pairs that prevented quantitative removal of non-volatile oleate species.18 Thus, quantifying the binding affinity of neutral donors towards nanocrystal surfaces requires using a system where only L-type ligands are present, uncomplicated by any other Z-type or ion pair interactions.

V.1.1 L-type exchange in CdSe-CdCl₂/PBu₃ systems: insight into relative ligand binding affinities

Previous work in the Owen group focused on studying L-type ligand binding affinities relative to tri-n-butylphosphine.19 Titration of various L-type ligands into CdSe-CdCl₂/PBu₃
systems and monitoring the displacement of tri-\textit{n}\textendash butylphosphine via $^{31}\textit{P}$ NMR allowed for the development of a relative binding affinity scale for CdSe nanocrystal systems. Important conclusions for this dissertation can be derived from this work and are briefly summarized in this section. The foremost conclusion from these L-type studies is that sterics are the dominating factor in determining how well certain molecules can bind and stabilize CdSe nanocrystals. Thus, while phosphines are electronically a better stabilizing ligand compared to amines (this is the second important conclusion that’s relevant to this dissertation, \textit{infra vide}), the stability and availability of primary \textit{n}\textendash alkylamines makes them the L-type ligand with the strongest binding affinity towards CdSe-CdCl$_2$ nanocrystal systems. These are general rules, but other factors such as the electron donating capability of the L-type ligand and the orbital overlap also matter. For example, butyl isocyanide doesn’t displace Bu$_3$P despite its slimmer profile. While this study has provided our lab with indispensable lessons about the factors that dictate the binding of L-type ligands to CdSe nanocrystal systems, the presence of Z-type CdCl$_2$ ligands still complicates the exchange reactions studied. Using Anderson \textit{et al.} as a starting point, we chose to study L-type exchange on a nanocrystal system free from acidic impurities (both Lewis and Bronsted acids). To this end, this chapter reports our results on L-type exchange in stoichiometric CdSe-L systems.

\textbf{V.2 \textit{n}\textendash Alkylamine exchange in CdSe-NH$_2$R nanocrystal systems}

The exchange of \textit{n}\textendash alkylamines in CdSe nanocrystals was first studied in our lab using chloride-terminated CdSe-CdCl$_2$/PBu$_3$ samples.\textsuperscript{7} It was shown that the addition of amines to these phosphine-bound particles led to the rapid displacement of phosphines and formation of CdSe-CdCl$_2$/NH$_2$R. Under ambient conditions, the system cannot revert to CdSe-CdCl$_2$/PBu$_3$ even in large excess of tri-\textit{n}\textendash butylphosphine. These observations are most likely general to the majority of
CdSe nanocrystal systems. Thus, we sought to extend our understanding of L-type exchanges past CdSe-CdCl₂/NH₂R, using CdSe-NH₂R as a starting point.

**V.2.1 Self-exchange of n-alkylamine in CdSe-NH₂R systems**

Titration of n-octylamine into a sample of CdSe-NH₂C₈H₁₇ (initial [NH₂C₈H₁₇] = 9.1 mM) causes changes to both the linewidth and position of the resonances in the ¹H NMR spectrum (Figure V.1A). As the amine concentration increases from 9 to 500 mM, each resonance corresponding to n-octylamine shifts upfield and is accompanied by line narrowing. Figures V.1D-E plots the change in chemical shift of the NH₂R and α-CH₂ resonances. Interestingly, at low amine concentrations the NH₂R resonance appears to be broadened beneath the chemical shifts of the other amine protons and only appears at higher concentrations (δ = < 0.7 to 0.54 ppm), which is important for interpreting the 1D ¹H NMR spectrum of these nanocrystals. The large broadening seen from these hydrogens at low concentrations can be rationalized by their proximity to the surface, as the nanocrystal core can provide a fast T2 relaxation mechanism.²⁰ The changes in chemical shift of the α-CH₂ hydrogens are complicated by what appears to be two resonances. One resonance centered at 3.3 ppm has a broad linewidth, whose decrease in intensity correlates with the growth of the second resonance at 2.5-2.6 ppm. It is possible that these two resonances correspond to two different chemical environments of the α-CH₂ hydrogens, with the more downfield and broader resonance corresponding to more tightly bound n-octylamine ligands.

While broad resonances in the NMR spectra of nanocrystal samples are usually indicative of surface-bound ligands, other factors such as fast exchange can also contribute to the line width of the observed chemical shift. Diffusion NMR was made possible with the development of NMR probes capable of applying magnetic pulsed field gradients. As a result, diffusion of excited nuclei,
Figure V.1. (A) $^1$H NMR spectra of CdSe-NH$_2$C$_8$H$_{17}$ ([nanocrystals] = 45 μM) with increasing (from bottom to top) concentrations of $n$-octylamine. (B) Zoomed in region of (A) focusing on the $\alpha$-CH$_2$ hydrogen resonance. (C) Zoomed in region of (A) focusing on the R-NH$_2$ hydrogen resonance. (D) and (E) plot the chemical shift of the $\alpha$-CH$_2$ (D) and R-NH$_2$ (E) resonances as a function of amine concentration. The horizontal dashed lines represent the chemical shift of the corresponding hydrogens in the absence of CdSe nanocrystals.
which itself is dependent on the hydrodynamic size of the species it belongs to, becomes an additional factor in its transverse (T2) relaxation, with smaller, faster diffusing molecules generally relaxing faster than larger and slowing diffusing ones. In nanocrystal samples, surface-bound ligands will diffuse at the same rate as the particle, yielding a smaller diffusion coefficient compared to its unbound state. For labile ligands, such as amines, diffusion oriented spectroscopy (DOSY)\textsuperscript{21-22} NMR measurements can provide complementary information about their interactions with the particle surface.\textsuperscript{23-25}

The second dimension in diffusion NMR measurements is the applied magnetic field strength $g$. For each resonance observed the signal intensity $I$ can be plotted against this field strength, and the resulting decay curve is described by the Stejskal-Tanner equation (equation V.1)\textsuperscript{26}

$$I = e^{-D\gamma_{eff}g^2\sigma^2g^2}\Delta'$$

(V.1)

$$I = \sum_{n=1}^{m} A_n I_n = \sum_{n=1}^{m} A_n e^{-D_n\gamma_{eff}g^2\sigma^2g^2}\Delta'$$

(V.2)

in which $D$ is the translational diffusion coefficient of the molecule corresponding to the measured nuclei, $\gamma_{eff}$ is the gyromagnetic ratio, $\delta$ is the duration of the applied pulse field gradient, $\sigma$ is the gradient shape factor and $\Delta'$ is the diffusion time of the sample. Fitting the observed decay to a mono- or biexponential (the latter case described by equation V.2 where $A_n$ is an average weighted prefactor), the diffusion coefficient of the molecule being studied can be extracted and used to determine the corresponding hydrodynamic diameter $d_H$ according to the Stokes-Einstein relation (equation V.3)

$$d_H = \frac{k_BT}{3\pi\eta D}$$

(V.3)
This technique was applied to a CdSe-NH₂C₇H₉ sample with minimal \( n \)-butylamine ([NH₂C₇H₉] = 0.26 M, [nanocrystal] = 0.746 mM, 348 amines per nanocrystal) to ensure colloidal stability while not unnecessarily skewing the observed diffusion coefficient towards that of free amine. The 2D plot and calculated fits of the NMR data are shown in figure V.2. The decay curve of the intensity of the –CH₃ hydrogen resonances does not fit well to a single-exponential formula, but fits a biexponential with little residual intensity. The two diffusion coefficients obtained from the fit, 116.5 and 769.7 \( \mu \text{m}^2\text{s}^{-1} \), correspond to hydrodynamic diameters of 6.35 and 0.96 nm, respectively. The larger of the diameters is consistent with that of a 3.4 nm CdSe nanocrystal with bound \( n \)-butylamine, whereas the smaller diameter is slightly larger than that calculated for \( n \)-butylamine in toluene-\( d_8 \). The result of a biexponential fit to the decay curve obtained from DOSY measurements is surprising. It is generally assumed that all amines are in fast exchange with the nanocrystal surface, which would result in a mono-exponential decay curve that yields a time averaged diffusion coefficient reflecting bound and free amine species. However, our results point to some \( n \)-butylamine tightly bound to the nanoparticle, which matches our observations of some amine being difficult to remove from samples until heated under vacuum (see sections IV.2.1 and V.2.3). These results are similar to recent reports of \( n \)-alkylamines on ZnO nanocrystals, where DOSY also supported various amine-binding strengths.¹⁰

**V.2.2 L-type exchange between different primary amines**

While the alkyl chain length does not significantly alter the binding affinity of the primary amine, the exchange of NH₂R for NH₂R' can be achieved by multiple cycles of excess NH₂R' addition (typically a 4.5 M solution in toluene), precipitation, and centrifugation. After 3 cycles, > 99% of the initial NH₂R has been removed from the system, estimated by the relative integrations
**Figure V.2.** (top) 2D contour plot of the DOSY spectrum of CdSe-NH$_2$C$_4$H$_9$. (bottom) Decay curve of the integrated intensity of the $n$-butylamine methyl peak (shaded region in the 2D plot above) as a function of gradient field strength. Displayed to the right are the parameters obtained for a bi-exponential decay, with the two diffusion coefficients obtained being 116.5 and 769.7 $\mu$m$^2$s$^{-1}$.
of the $^1$H NMR signals. Initial amine-bound nanocrystals were synthesized by Z-type displacement of cadmium carboxylate with $n$-octylamine (CdSe-$\text{NH}_2\text{C}_8\text{H}_{17}$).  While $n$-octylamine provides greater colloidal stability compared to $n$-butylamine due to its longer alkyl chain length, $n$-butylamine is more volatile and is thus a better L-type ligand for applications involving the removal of amines, such as device fabrication (Chapter IV) This difference also plays a significant factor in additional L-type exchange studies, which will be discussed in section V.3.

V.2.3 Desorption of $n$-alkylamines from CdSe-$\text{NH}_2\text{R}$ surfaces

In section IV.2.1 of this thesis, the desorption of $n$-butylamine from the surface of CdSe-$\text{NH}_2\text{C}_4\text{H}_9$ nanocrystal thin films and powders was discussed. While ~90% can be removed under vacuum at room temperature, complete desorption of the amine could only be achieved under annealing conditions of 150 °C under vacuum. Given that the boiling point of $n$-butylamine is low (B.P. = 70 °C), the high temperature required for complete desorption implies a strong binding affinity for $\text{NH}_2\text{C}_4\text{H}_9$ towards some binding sites of the CdSe nanocrystals. The binding strength of primary amines to II-VI materials has been employed to stifle the rate of nanocrystal growth on various facets, allowing for the synthesis of anisotropic materials. In addition, the binding of dodecylamine to the surfaces of ZnO nanocrystals demonstrated three separate binding regimes: strongly bound, weakly bound, and free in solution.  It is possible that different binding sites or allosteric effects can produce multiple binding affinities of $n$-alkylamines to CdSe surfaces as well. Future studies with CdSe-$\text{NH}_2\text{R}$ focused on facet-specific binding would allow for a more

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1 In this case, relative integration refers to the ratio of the intensities of the terminal CH$_3$ hydrogens to the rest of the resonances. Quantitatively reporting this exchange is quite difficult as the proton signals are broadened in spectra of CdSe-$\text{NH}_2\text{R}$. Digestion of the CdSe core using a HCl/MeOH solution and characterization of the remaining ammonium chloride product yields sharper resonances in the $^1$H NMR and provides a better method to measure the exchange between primary amines in these systems.
quantitative understanding of the binding of one of the most common ligands in the colloidal nanocrystal field.

V.3 L-type exchange in CdSe-NH₃R systems: more insight into relative ligand binding affinities

Given the propensity of CdSe–NH₃R’ to aggregate (section II.5.2), we sought to test the stability of nanocrystal dispersions solely stabilized by other canonical Lewis basic surfactants, including 4-ethylpyridine, Bu₃P, and TOPO (Scheme V.3). CdSe–NH₃R’ (where R’ = n-butyl) was added to neat Bu₃P or 4-ethylpyridine at room temperature or to molten TOPO at 50 °C, and stirred under dynamic vacuum to remove the n-butylamine ligands. In all cases, insoluble nanocrystal aggregates were obtained. While the aggregation kinetics depend on a number of factors including the nanocrystal concentration, solvent, and particle size, neither 4-ethylpyridine, Bu₃P, nor TOPO ligands stabilize a nanocrystal dispersion under neat conditions (>3 M). These results are surprising and suggest a clear difference between the nanocrystals prepared in this study and previous TOPO, Bu₃P, and pyridine stabilized dispersions. One such difference is the use of zincblende nanocrystals in this study, while CdSe nanocrystals used in early studies typically have a wurtzite structure. In addition, previous reports of nanocrystal dispersions thought to be stabilized by TOPO, Bu₃P, and amines suffer from unaccounted residual adsorbed metal surfactant complexes or carboxylate, phosphonate, or carbamate anions.
Scheme V.3. L-type exchange of 4-ethylpyridine, Bu$_3$P, or TOPO on CdSe-$\text{NH}_2\text{R'}$ results in insoluble nanocrystals.

Many have proposed that pyridine and $n$-alkylamines, TOPO, and Bu$_3$P stabilize colloidal dispersions of metal chalcogenide nanocrystals, yet the presence of undetected anions, such as octylphosphonate$^4$ and $n$-alkylcarbamate$^{29,30}$ anions complicate these claims. Reports on the stability of pyridine-capped CdSe nanocrystals are unclear and often contradictory.$^{13,31-32}$ In light of the incomplete displacement of native ligands using pyridine,$^1,33$ we speculate that the presence of adsorbed anions and pyridinium counterions may have provided the stability in those cases. By comparison, the CdSe--$\text{NH}_2\text{R'}$ isolated in this study is free from acidic impurities and adsorbed anions and aggregates in neat 4-ethylpyridine,$^{ii}$ TOPO, or Bu$_3$P. These experiments show the somewhat surprising result that canonical neutral donor ligands do not effectively support stable colloidal dispersions. Moreover, it suggests that the stability of nanocrystals reported to be bound solely by neutral donor ligands, and amine ligands in particular, may benefit from the presence of acidic impurities that lead to adsorbed ion pairs.

During the course of studying the L-type exchange reaction between CdSe-$\text{NH}_2\text{C}_4\text{H}_9$ and Bu$_3$P, it was found that diluting the nanocrystal solution, initially in 4 M (neat) Bu$_3$P, with toluene

$^{ii}$ 4-ethylpyridine was used instead of pyridine because of its higher boiling point, allowing for the removal of $n$-butylamine under vacuum.
led to soluble nanocrystal solutions. While the exact conditions in which the nanocrystals transition from insoluble aggregates to stable colloidal solutions has not been determined, we can conclude that the nanocrystals are stable under conditions of low nanocrystal concentration ([nanocrystal] = 0.322 mM) and 0.5 M Bu₃P. Two possible explanations likely contribute to this observation. First, some amount of n-butylamine could remain strongly bound even under vacuum at 25 °C and aid in stabilizing the nanocrystals. Our observations of the high temperatures required to achieve complete desorption of n-butylamine from CdSe-NH₂C₄H₉ DRIFTS samples supports this idea. Second, the aggregation kinetics of nanocrystals likely has a high-order rate law that exponentially increases with particle concentration. Thus, higher nanoparticle concentrations are more likely to rapidly aggregate.

While the aggregation kinetics of CdSe-NH₃R warrant further study, the observation of a soluble CdSe nanocrystal in the presence of tri-n-alkylphosphine offered a new synthetic challenge, namely whether there existed conditions in which colloidal CdSe-PR₃ could be obtained. Such a sample, though often erroneously described in the literature, has most likely never been synthesized based on our observations of colloidal instability. The motivation for studying CdSe-PR₃ systems stems from the phosphine ligands. The convenient $^{31}$P handle has already proven a valuable spectroscopic tool to study nanocrystal surface chemistry.⁷,¹⁹ In addition, the lability of the phosphine also provides a reporter complex to compare the binding abilities of other L-type ligands. It can also act as a reactive species for clean surface modification. As an example, sections VI.4-5 of this dissertation reports on attempts to synthesize CdSe-MX₂/PR₃ starting from phosphine bound nanocrystals.
V.3.2 CdSe-PR₃ systems

\[ \text{NH}_2\text{R} \xrightarrow{\text{PR}_3, 20 \text{ mtorr, 12h}} \text{PR}_3 \]
\[ 100 \degree \text{C}, -\text{NH}_2\text{C}_4\text{H}_9 \quad \text{R} = \text{C}_4\text{H}_9, \text{C}_8\text{H}_{17} \]

**Scheme V.4.** The use of high temperature and vacuum can drive L-type exchange between n-alkylamines and tri-n-alkylphosphine on CdSe nanocrystal surfaces.

As stated earlier, the synthesis of CdSe-CdCl₂/PBu₃ from CdSe-CdCl₂/NH₂R could not be achieved under ambient conditions. However, with the insight gained from the desorption of n-butylamine, and the observations of achieving soluble samples under certain conditions, we sought to synthesize a phosphine bound CdSe-PR₃ species by driving the L-type ligand exchange with high temperature and dynamic vacuum (Scheme V.4). Initial attempts involved stirring CdSe-NH₂C₄H₉ ([nanocrystal] = 0.322 mM) in neat Bu₃P under vacuum and 100 °C for 3 hours, resulting in a soluble red solution which turned into a solid as the tri-n-butylphosphine evaporated. Interestingly the nanocrystals, which had rapidly aggregated upon phosphine addition, became soluble again upon heating for 30 minutes. The red solid could also be redissolved in toluene, indicating that enough excess phosphine remained in the residue to stabilize the particles in solution. ¹H NMR spectroscopy indicates that some amine remains bound to the nanocrystal. Repeating this exchange at higher temperatures (120 and 150 °C) result in a nanocrystal sample that cannot be redispersed in toluene, an observation that could be explained by both a low phosphine concentration and aggregation kinetics.

In an attempt to increase the colloidal stability of the CdSe-PR₃ product, L-type exchange was performed using tri-n-octylphosphine (Oct₃P). The longer alkyl chains allow for higher
Figure V.4. $^1$H NMR of CdSe-POct$_3$. The absence of a resonance centered at 2.5 ppm, corresponding to the $\alpha$-NH$_2$CH$_2$C$_3$H$_7$ protons in $n$-butylamine, indicate that L-type exchange for Oct$_3$P can be achieved with reduced pressure and high temperature. Subsequent purification to remove residual cleaning solvents resulted in irreversible aggregation of the nanocrystals.

annealing temperatures to be achieved without a decrease in the phosphine concentration (due to evaporation), as well as greater separation between the nanocrystals (assuming little intercalation between tri-$n$-alkylphosphines bound to different particles). Reaction solutions of CdSe-NH$_2$C$_4$H$_9$ and neat 2.24 M (neat) Oct$_3$P can be heated under vacuum at 100 °C without evaporation of the phosphine. The nanocrystals behaved similarly to their reaction with Bu$_3$P, becoming soluble at high temperatures, aggregating upon cooling back to room temperature, and redispersing upon the addition of toluene. A $^1$H NMR spectrum of the crude CdSe-POct$_3$ product after one precipitation cycle from methyl acetate indicates the absence of $\alpha$-NH$_2$CH$_2$C$_3$H$_7$ proton resonances (Figure V.4). Thus, ligand exchange between $n$-butylamine and tri-$n$-octylphosphine can be driven to completion under high temperature and dynamic vacuum. Further purification of this sample, however, resulted in irreversible aggregation. In the case of both CdSe-PBu$_3$ and CdSe-POct$_3$,
titration of the corresponding phosphine into a toluene solution of these aggregated nanocrystal samples did not aid in the redispersion of the particles, even at phosphine concentrations > 0.25 M. In addition, heating of these solutions to 110 °C for up to 12 hours did not result in soluble nanocrystals.

While the observation that CdSe-PR₃ samples are quite prone to aggregation is undesirable for additional surface tailoring, it is not surprising given the already unstable nature of CdSe-NH₂C₄H₉ which requires high concentrations of amine to maintain nanocrystal solubility. Furthermore, our group has also determined that tri-ₙ-alkylphosphines exhibit a weaker binding affinity compared to primary amines due to their steric profile. While further work is required to increase our understanding of the aggregation mechanism of CdSe-PR₃, we conclude that L-type exchange on CdSe-NH₂C₄H₉ with tri-ₙ-alkylphosphines results in a nanocrystal product that is highly prone to aggregation.

V.3.3. CdSe-PMe₂C₁₈H₃₇

It is likely that the colloidal instability of CdSe-PR₃ systems is due to the tri-ₙ-alkylphosphine’s large steric profile. Previous work in our lab studying CdSe-CdCl₂/PBu₃ demonstrated that the smaller trimethylphosphine ligand could access and bind to more surface cadmium sites than tri-ₙ-butylphosphine. In addition, dimethyl-ₙ-octylphosphine’s (PMe₂C₈H₁₇) slimmer profile compared to Bu₃P allowed CdSe-CdCl₂/PMe₂C₈H₁₇ to be synthesized with a phosphine surface density of 2.8 nm⁻². The approach of limiting a phosphine ligand’s steric profile with a dimethyl-ₙ-alkylphosphine guided our efforts into synthesizing dimethyl-ₙ-octadecylphosphine (PMe₂C₁₈H₃₇). Compared to dimethyl-ₙ-octylphosphine, PMe₂C₁₈H₃₇’s higher boiling point allows for L-type ligand exchange on CdSe-NH₂C₄H₉ to be performed at 100 °C.
Dimethyl-\textit{n}-octadecylphosphine was synthesized by adapting a previously published synthesis of dimethyl-\textit{n}-octylphosphine.\textsuperscript{19,34} $^{31}$P{$^1$H} NMR spectroscopy shows a single peak at $\delta$ = -53 ppm (Figure V.5), which is similar to that reported for PMe$_2$C$_8$H$_{17}$ ($\delta$ = -55 ppm). Titration of PMe$_2$C$_{18}$H$_{37}$ into a solution of CdSe-\textsubscript{NH$_2$C$_4$H$_8$} nanocrystals showed no change in the chemical
shift or line width compared to the free ligand, even at a phosphine to amine ratio of 10:1 (Figure V.6). Thus, little to no displacement of \( n \)-butylamine seems to occur under ambient conditions. With 10 equivalents of phosphine to amine in the sample, however, a broad resonance (\( \delta = -38 \) ppm) appears in the \(^{31}\)P NMR spectrum if the sample is placed under vacuum for 1 hour (Figure V.6). Heating the sample to 50 °C under vacuum for an additional hour causes the broad peak to grow, with the surface density of bound \( \text{PMe}_2\text{C}_{18}\text{H}_{37} \), increasing from 0.6 to 1.1 \( \text{nm}^2 \). This coverage increases to 1.9 \( \text{nm}^2 \) when the sample is heated to 100 °C under vacuum for one hour. Increasing the temperature to 150 °C causes the nanocrystals to aggregate.

An increase in the amount of ligated \( \text{PMe}_2\text{C}_{18}\text{H}_{37} \) with higher reaction temperatures is indicative of a higher number of binding sites accessible to the phosphine ligand. It is intuitive that these sites arise from the dissociation of \( n \)-butylamine from surface cadmiums. This is most likely an endothermic process\(^ {35} \) as well as one with a \( \Delta S > 0 \) (assumed due to the greater degree of freedom for a free ligand compared to one bound). Raising the temperature of a CdSe-\( \text{NH}_2\text{C}_4\text{H}_9 \) solution should cause desorption of a greater amount of amine, which subsequently is removed from the system by vacuum. While the large steric profile of tri-\( n \)-alkylphosphines prevents access to these now open cadmium sites, \( \text{PMe}_2\text{C}_{18}\text{H}_{37} \) can and therefore its surface density increases.

Repeating the L-type exchange between \( \text{PMe}_2\text{C}_{18}\text{H}_{37} \) and \( \text{NH}_2\text{C}_4\text{H}_9 \) (10 equivalents of phosphine per amine) on CdSe nanocrystals on a larger scale ([nanocrystals] = 0.75 mM) at 100 °C under vacuum yields nanocrystals readily dispersed in toluene. These particles can be precipitated from toluene with the addition of methyl acetate multiple times without aggregation. \(^{31}\)P NMR spectroscopy (Figure V.7) shows peaks corresponding to bound (\( \delta = -37.7 \) ppm, \( \Delta \text{ppm} = 15 \) ppm) and free (\( \delta = -52.4 \) ppm, \( \Delta \text{ppm} = 7 \) ppm) and free phosphine. \(^1\)H NMR spectroscopy
Figure V.6. $^{31}$P NMR spectra (at room temperature and 1 atm) of CdSe-$\text{NH}_2\text{C}_n\text{H}_9$ with 10 equivalents of PMe$_2$C$_{18}$H$_{37}$ (per amine) under ambient conditions (bottom, navy blue) and upon exposure to vacuum at 25 (dark purple), 50 (violet), 100 (light red), and 150 °C (dark red). The inset in the upper left plots the surface density of bound phosphine (calculated from the ratio of the intensity of the chemical shift at -38 ppm to the total intensity) as a function of temperature at 20 mtorr.
Figure V.7. $^{31}$P NMR spectrum of CdSe-PMe$_2$C$_{18}$H$_{37}$ in benzene-$d_6$. Taking the ratio of the intensity of the resonance of bound phosphine ($\delta = -38$ ppm) and the total intensity gives a surface density of 1.8 nm$^{-2}$ (calculated by multiplying the total phosphine concentration by the above ratio).

Figure V.8. $^1$H NMR spectrum of CdSe-PMe$_2$C$_{18}$H$_{37}$ in benzene-$d_6$. Integration of the total intensity from 0.0-3.0 ppm against an internal ferrocene standard ($\delta = 4.0$ ppm) gives a total phosphine concentration of 0.047 M, or 164 per nanocrystal.
Figure V.9. Bi-exponential fit of the decay curve of the methyl species generated from the DOSY spectrum of CdSe-PMe$_2$C$_{18}$H$_{37}$ in benzene-$d_6$.

dimethyl-$n$-octadecylphosphine ligand.

Diffusion NMR spectroscopy of CdSe-PMe$_2$C$_{18}$H$_{37}$ was performed to gain additional insight into how the phosphine ligands interact with the nanocrystal surface. Figure V.9 plots the decay curve of the methyl species generated from the DOSY spectrum of CdSe-PMe$_2$C$_{18}$H$_{37}$. This decay curve fits a bi-exponential (equation V.2) with extracted diffusion coefficients of 73.9 and 361.4 $\mu$m$^2$ s$^{-1}$ that correspond to hydrodynamic diameters of 9.7 and 2.0 nm, respectively. These values imply that there exists a fraction of phosphine that either binds tightly to the nanocrystal surface or is in slow exchange (with respect to the NMR time scale), similar to the amine case noted previously.

TEM reveals that much like CdSe-NH$_2$R samples, CdSe-PMe$_2$C$_{18}$H$_{37}$ aggregates upon drying (Figure V.10). However, the UV-vis absorption spectrum of CdSe-PMe$_2$C$_{18}$H$_{37}$, shown in figure V.11, maintains a sharp first transition and doesn’t show a scattering background, implying no aggregation in solution. While the peak position of the first peak is identical to that of CdSe-
NH$_2$C$_4$H$_9$, the second electronic transition commonly seen in CdSe nanocrystals cannot be seen. At the present time, this is the broadest transition observed in a CdSe nanocrystal studied in our research group. Such a broad peak corroborates our assumption that the density of bound ligands dictates its width, possibly through lifetime broadening. The origin of this broadening warrants further study, and CdSe-PMe$_2$C$_{18}$H$_{37}$ provides an ideal nanocrystal system to aid in this direction.

![TEM image of CdSe-PMe$_2$C$_{18}$H$_{37}$](image)

**Figure V.10.** TEM image of CdSe-PMe$_2$C$_{18}$H$_{37}$. Scale bar is 50 nm.
**Figure V.11.** UV-vis absorption spectra of CdSe-NH$_2$C$_4$H$_9$ (red) and CdSe-PMe$_2$C$_{18}$H$_{37}$. Absorbances were normalized at $\lambda = 350$ nm (not shown).

**V.4 Discussion**

Post-synthesis surface functionalization of nanocrystals has made it possible to study these materials in a variety of applications and media, ranging from electronic transport in thin films to luminescent based probes in biological systems. Regardless of the specific measurement or property of the nanocrystal being exploited, understanding and controlling aggregation is crucial to the stability of the particles and therefore to their utilization in any technology. Colloidal aggregation theory identifies two distinct regimes of irreversible aggregation. The first, referred to as diffusion limited colloid aggregation, describes systems where there are little to no repulsive forces between the particles. In this regime, the aggregation rate is primarily limited by diffusion of the particles through the medium, and typically occurs very rapidly. The other regime, reaction-limited colloid aggregation, occurs more slowly over time because there exists significant repulsive forces between particles, for example because of tightly bound surfactants. Aggregation
in this scenario is limited by the thermal activation required for two particles to overcome these repulsive forces. While these regimes represent two extreme cases of aggregation, the concept\(^{17}\) has been proven to be universal for a multitude of colloidal systems including gold,\(^{38-39}\) silica,\(^{40-41}\) and latex\(^{42}\) colloids.

These concepts most likely apply to II-VI semiconductor nanocrystals, yet the variable surface chemistry and difficulty in quantitating the binding affinities of the various surfactants makes classifying their aggregations exclusively qualitative. However, it is apparent that both X and Z-type ligands provide a significantly larger barrier to aggregation compared to L-type ligands. This larger stabilization stems from the higher binding affinity of X and Z-type ligands towards the nanocrystal.\(^6, 43\) L-type ligands, on the other hand, are typically labile and undergo fast self-exchange at the particle surface. The combination of a relative lower binding affinity to the surface and fast exchange kinetics most likely attribute to CdSe-L systems being more unstable to aggregation compared to those stabilized with MX\(_2\) species.

The colloidal stability of CdSe-L systems is dependent on the binding affinity and surface density of the present L-type ligands. It is not surprising then, that these particles cannot be stabilized by weak ligands such as TOPO or 4-ethylpyridine, whose relative binding affinity has been demonstrated to be weaker than a primary amine.\(^{19}\) However, binding affinity is not the only factor in stabilizing CdSe-L, as steric limited surface densities of the ligand must also be taken into consideration. While tri-\(n\)-alkylphosphines have a higher binding affinity to the surface compared to tri-\(n\)-alkylamines, their low surface density results in unstable colloidal solutions. Decreasing the effect of the phosphine’s sterics can increase the resulting surface density, which rationalizes the higher stability of CdSe-PMe\(_2C_18H_{37}\). Unfortunately, it is difficult to differentiate between the binding affinity and steric factors when evaluating a ligand’s surface density.
One of the more surprising observations reported here is evidence (from diffusion NMR) of a fraction of ligands in both CdSe-\(\text{NH}_2\text{C}_4\text{H}_9\) and CdSe-\(\text{PMe}_2\text{C}_{18}\text{H}_{37}\) systems that diffuse as though tightly bound to the nanocrystal surface. In a fast exchanging regime, NMR is unable to differentiate between free and bound ligands. While not conclusive, this evidence supports the possibility of a fraction of these species being tightly bound to the particle. Multiple regimes of binding affinities for dodecylamine have been reported on ZnO nanoparticles, also using diffusion NMR.\(^1\) In addition, the Hens group demonstrated that primary amines bind exceptionally strong to the surface of CuInS\(_2\) nanocrystals.\(^{44}\) The instability of the CdSe-L samples discussed herein implies that the density of tightly bound L-type ligands is not enough to maintain colloidal stability. However, the existence of tightly bound species can rationalize our observations that high temperatures are required to quantitatively remove \(n\)-butylamine from both solution and solid state.

V.5 Conclusions

Amine bound CdSe-\(\text{NH}_2R\) nanocrystals are an ideal model system to study L-type ligand exchange, but they proved relatively unstable to aggregation unless the amine concentration was maintained near 0.1 M or higher. The stability worsens following exchange of the primary amine ligands for commonly used ligands such as 4-ethylpyridine, TOPO, or \(\text{Bu}_3\text{P}\). These experiments show the somewhat surprising result that canonical neutral donor ligands do not effectively support stable colloidal dispersions. Moreover, it suggests that the stability of nanocrystals reported to be bound solely by neutral donor ligands, and amine ligands in particular, may benefit from the presence of acidic impurities that lead to adsorbed ion pairs.

The difficulty synthesizing stable dispersions of CdSe-L nanocrystals stems from the observations that sterically bulky ligands such as tri-\(n\)-alkylphosphines cannot achieve the high
surface density that is required to maintain solubility. We have demonstrated that a phosphine ligand with a slimmer profile, \( \text{PMe}_2\text{C}_{18}\text{H}_{37} \), can achieve a higher ligand coverage than the commonly used tertiary alkylphosphines. The resulting CdSe-PMe\(_2\text{C}_{18}\text{H}_{37}\) nanocrystals are soluble and remain so even after removal of excess phosphine. Taking into account the presence of ion pairs and metal phosphanates in previously reported CdSe-PR\(_3\) systems, our sample of CdSe-PMe\(_2\text{C}_{18}\text{H}_{37}\) is the first stoichiometric CdSe nanocrystal sample bound solely by neutral phosphines. Previous attempts to quantify L-type exchange on nanocrystal surfaces were most likely reporting numbers that described a combination of interactions. CdSe-L systems simplify these interactions at the nanocrystal surface, lacking Z-type ligands or ion pairs, and allow for more accurate studies of neutral ligand exchange.

**V.6 Experimental**

**General Considerations**

**Diffusion NMR Experiments.** DOSY measurements were performed using a double-stimulated echo sequence. The gradient strength was varied linearly from 2% to 95% of the probe’s maximum value. The diffusion parameters consisting of the pulse length (\( \delta/2 \)) and delay (\( \Delta \)) were chosen to ensure that > 90% of the signal decayed at the highest magnetic field gradient. The resulting decay curves were fit using an Igor Pro macro developed by Jonathan De Roo, and the same macro was used to calculate the hydrodynamic diameter, which assumed a spherical shape of the nanocrystals.

**Monitoring desorption of \( \text{NH}_2\text{C}_8\text{H}_9 \) from CdSe-\( \text{NH}_2\text{C}_8\text{H}_{17} \) using DRIFTS.** DRIFTS measurements with \( n \)-octylamine bound CdSe nanocrystals were performed in a similar fashion to that of \( n \)-butylamine bound CdSe nanocrystals. Refer to the Experimental section in chapter IV.
**L-Type exchange with 4-ethylpyridine on CdSe-NH$_2$C$_4$H$_9$.** In a 20 mL vial equipped with a stir bar, 200 μL of a CdSe-NH$_2$C$_4$H$_9$ stock solution ([nanocrystals] = 3.22 mM, [amine] = 0.38 M) was added to a 1 mL solution of 4-ethylpyridine ([nanocrystals] = 0.54 mM, [amine] = 0.063 M, [4-ethylpyridine] = 7.3 M). The resulting homogeneous solution was placed under vacuum for 3 hours, and the nanocrystals precipitated within 30 minutes. After 3 hours, 1 mL of toluene was added to the resulting red residue and allowed to stir overnight. No dissolution was observed after 12 hours, and subsequent titration of 1 mL of 4-ethylpyridine into the solution did not aid in re-dissolving the particles.

**L-Type exchange with tri-$n$-octylphosphine oxide on CdSe-NH$_2$C$_4$H$_9$.** In a 25 mL Teflon sealed Schlenk tube equipped with a stir bar, 100 μL of a CdSe-NH$_2$C$_4$H$_9$ stock solution ([nanocrystals] = 3.22 mM, [amine] = 0.38 M) and 1 g (2.586 mmoles) of tri-$n$-octylphosphine oxide (TOPO) were added, and the tube was placed on a Schlenk line and heated to 60 ºC under dynamic vacuum. Within 30 minutes, the nanocrystals had aggregated from the molten TOPO solution.

**L-Type exchange with tri-$n$-butylphosphine on CdSe-NH$_2$C$_4$H$_9$.** In a 20 mL vial equipped with a stir bar, 100-200 μL of a CdSe-NH$_2$C$_4$H$_9$ stock solution ([nanocrystals] = 3.22 mM, [amine] = 0.38 M) was added to 1 mL of Bu$_3$P (4 M), which immediately caused precipitation of the nanocrystal solution. The sample was stirred under dynamic vacuum overnight. Dilution of the nanocrystals with toluene to specific concentrations of Bu$_3$P (see table below) either led to redissolution of the particles or had no effect.
<table>
<thead>
<tr>
<th>[NC] before dilution</th>
<th>[NC] after dilution</th>
<th>[PBu₃]</th>
<th>Solubility</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.322 mM</td>
<td>40.25 μM</td>
<td>0.5 M</td>
<td>soluble</td>
</tr>
<tr>
<td>0.322 mM</td>
<td>53.67 μM</td>
<td>0.67 M</td>
<td>soluble</td>
</tr>
<tr>
<td>0.966 mM</td>
<td>56.82 μM</td>
<td>0.36 M</td>
<td>insoluble</td>
</tr>
<tr>
<td>1.288 mM</td>
<td>161 μM</td>
<td>0.25 M</td>
<td>insoluble</td>
</tr>
</tbody>
</table>

**L-Type exchange with tri-\textit{n}-octylphosphine on CdSe-NH₂C₄H₉.** In a 25 mL Teflon sealed Strauss flask equipped with a stir bar, 300 μL of a CdSe-NH₂C₄H₉ stock solution ([nanocrystals] = 3.22 mM, [amine] = 0.38 M) was added to 2 mL of Oct₃P (2.24 M), causing immediate precipitation of the nanocrystal. The flask was placed on a Schlenk line and heated to 100 ºC under vacuum for 12 hours. The nanocrystals dissolved once reaching 100 ºC and then precipitated after cooling the reaction solution back to room temperature. The sample was transferred back into a nitrogen filled glove box and diluted with 2 mL of toluene, which redissolved the nanoparticles. The clear red solution was transferred to a 15 mL centrifuge tube and precipitated with 10 mL of methyl acetate, then centrifuged at 7000 rpm for 10 minutes. After removal of the colorless supernatant, the nanocrystals did not redissolve in 2 mL of toluene, and remained insoluble in Oct₃P concentrations \( \leq 1.12 \) M.

**Synthesis of dimethyl-\textit{n}-octadecylphosphine.** In a 25 mL Schlenk flask equipped with a stir bar, 0.5038 g (0.0207 moles) of crushed magnesium turnings (previously cleaned with sandpaper to expose the reactive surface) was added and the flask was evacuated and backfilled with argon three times. 7 mL of anhydrous THF was then cannula transferred to the reaction flask and allowed to stir for 10 minutes. In a separate 20 mL vial, 7.0133 g (0.021 moles) of 1-bromooc tadecane was added and the vial’s atmosphere purged with argon for 15 minutes. 7 mL of anhydrous THF was
cannula transferred to this vial to give a homogeneous solution. Under flowing argon, the 1-bromooctadecane solution was added dropwise to the magnesium slurry. The reaction was stirred at 40 °C under argon for 4.5 hours, at which point the Grignard reaction was > 97% complete (as monitored by $^1$H NMR spectroscopy). After 5 hours, the reaction was cooled to room temperature and the gray slurry was cannula transferred to an inert air fritted filter and filtered into an attached 25 mL Schlenk flask. The filter was then replaced with a rubber stopper under flowing argon and cooled to 0 °C. To this reaction flask, 2 g of chlorodimethylphosphine (0.0207 moles) was added dropwise. The solution was kept at 0 °C for 30 minutes, then warmed to room temperature and allowed to react for an additional 2 hours, after which the THF was removed under vacuum to reveal a solid white powder. The powder was recrystallized from hot, anhydrous acetonitrile and subsequently dried under vacuum overnight. $^1$H NMR (benzene-$d_6$, 300 MHz): $\delta = 0.87$ (d, 6H, P-$C\text{H}_3$, $^1J_{P-H} = 3$ Hz), $\delta = 0.92$ (t, 3H, PMe$_2$R-$\text{C\text{H}}_3$, $^2J_{H-H} = 7.5$ Hz), $\delta = 1.2 - 1.5$ (m, 34H, PMe$_2$(C$_{17}$H$_{34}$)CH$_3$). $^{31}$P{$^1$H} NMR (benzene-$d_6$, 300 MHz): $\delta = -53.2$ (s, 1P).

**L-Type exchange with P,P-dimethyl-$n$-octadecylphosphine on CdSe-NH$_2$C$_4$H$_9$.** To a 25 mL Teflon sealed Strauss flask equipped with a stir bar, 1 mL of a CdSe-NH$_2$C$_4$H$_9$ stock solution in toluene-$d_8$ ([nanocrystals] = 0.746 mM, [amine] = 0.26 M) and 671.3 g (2.13 mmol) of dimethyl-$n$-octadecylphosphine were added and stirred under vacuum for 10 minutes to remove toluene-$d_8$. The flask was then heated to 110 °C for 24 hours under vacuum. During this time, the nanocrystals were soluble in the molten dimethyloctadecylphosphine. The reaction solution was then cooled to room temperature, brought inside a nitrogen filled glove box, and dissolved with 2.5 mL of toluene. The red clear solution was transferred to a 15 mL centrifuge tube, precipitated with 12.5 mL of methyl acetate, and centrifuged at 7000 rpm for 5 minutes. This redissolution and precipitation
cycle was repeated twice more, and the collected red nanocrystal solid was dissolved in benzene-
$\text{d}_6$ for analysis by $^1\text{H}$ and $^{31}\text{P}$ NMR and UV-Vis spectrocopies.

V.7 References


CHAPTER VI: REBINDING OF Z-TYPE LIGANDS TO CdSe NANOCRYSTALS

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Scientific Abstract

Z-type rebinding was investigated with metal oleate species (M\(^{n+}\)(O\(_2\)CR)\(_n\), M = Cd\(^{2+}\), Zn\(^{2+}\), Pb\(^{2+}\), In\(^{3+}\)), and a relative binding affinity of these complexes can be established. Rebinding of metal oleate species at 25 °C yield lower coverages, yet can reach saturation upon heating to 100 °C. Cadmium and zinc carboxylates display the highest surface density of the studied ligands, reaching saturated coverages of 3.2 and 2.6 nm\(^2\), respectively. We show that the rebinding of cadmium chloride to aggregated CdSe-PBu\(_3\) stabilizes the particle and aids in their redissolution. The concepts reported in chapter V and here are applied to the synthesis of a new model compound passivated by dimethyl-n-octadecylphosphine and cadmium trifluoroacetate ligands, CdSe-Cd(O\(_2\)CCF\(_3\))\(_2\)/PMe\(_2\)C\(_{18}\)H\(_{37}\), which is characterized by UV-Vis, \(^1\)H, \(^{19}\)F, and \(^{31}\)P NMR spectroscopies. These results demonstrate the utility of CdSe-NH\(_2\)R as a clean nanocrystal starting reagent for the synthesis of novel CdSe-MX\(_2\)/L systems.

Plain English Abstract

In this chapter, we show that cadmium salts can bind to the surfaces of amine-bound CdSe nanocrystals, which provides experimental proof that we can use this sample as a model system to study fundamental surface chemistry. As an example, we use this synthetic procedure to make a nanocrystal terminated with ligands, including one we present in chapter V, that contain a variety of atoms that can be easily characterized with spectroscopy techniques. These sensitive atoms might help us ascertain important information about how these ligands bind to the particle surface, which would help in the design of new ligands that can be applied to biological imaging, solid state lighting, and electronic devices.
VI.1 The importance of Z-type ligands in colloidal nanocrystal systems

Lewis acids have played an essential role in the nanocrystal field. In particular, metal oleates, phosphonates, and halides have been extensively employed as both surface ligands and precursors with consequential impacts during particle synthesis and post-synthesis in device performance. For example, Liu et al have shown that nanocrystal precursor conversion can proceed through a Lewis acid cadmium phosphonate activated adduct \( (\text{CdX}_2\text{-Se}=\text{PR}_3) \). In addition, the binding affinity of the metal salts can dictate the growth rate of nanocrystals during their synthesis, and also allow for synthetic control over the anisotropy of the resulting particles. Post synthesis, the surface density of metal salts dictates crucial properties such as colloidal stability, photoluminescence, and their ability to facilitate charge transport in thin film devices. Sargent et al have shown that various metal halides can change the electronic states at the band edges of CdSe materials, passivating the surface or possibly giving rise to new trap states at various energy levels. This strategy has afforded lead halide passivated PbS quantum dot films whose power conversion efficiency exceeds 6%. Thus, the understanding of how Z-type ligands (i.e. metal salts) interact in these systems is vital for every aspect of nanocrystal research.

Several aspects of Z-type ligands remain unexplored in the current state of colloidal nanocrystal research. For example, substitution of the first layer of metal cations in II-VI materials, which could serve as interesting models for studying electronic surface states or strain at core-shell interfaces, has not been reported for CdSe quantum dots. In addition, the manner in which \( \text{MX}_2 \) species bind to the nanocrystal surface is still not well understood. It is generally assumed that they bind through an intuitive dative interaction with a surface chalcogenide atom, yet recent DFT studies show that anionic chloride species can act as a \( \mu_2 \) bridging ligand between two surface metals. We speculate \( \text{MX}_2 \) ligands might dissociate into \([\text{MX}]^+ [\text{X}]^-\) species with the anion acting...
as a multidentate or bridging ligand at the particle surface (Scheme 6.1). In chapter II, we proposed this as a possible binding motif of ammonium carboxylate, carbamate, and phosphonate ion pairs. We additionally speculated in chapter III that the formation of carboxylate ion pairs from cadmium carboxylate species might increase the binding affinity of Cd(O₂CR)₂. Furthermore, previous work done by our lab on CdSe-CdCl₂/PR₃ nanocrystals have demonstrated similar difficulties in removing PR₃/CdCl₂, which might be stabilized by binding μ₂ through a chloride anion whose charge is balanced by a phosphine stabilized cadmium monochloride cation. A nanocrystal model which can be spectroscopically characterized as having [X][LₙMX]⁺ species would provide more direct evidence for the existence of these rather unintuitive binding modes.

Scheme 6.1. Proposed binding motifs of CdX₂ Z-type ligands to CdSe nanocrystal surfaces.

In chapters II and III of this dissertation, we discussed the synthesis of CdSe-NH₂R systems from CdSe-Cd(O₂CR)₂ through L-type promoted Z-type displacement. Chapter V presented how we utilized this stoichiometric nanocrystal to synthesize phosphine bound nanocrystals. In this chapter, we discuss using CdSe-L systems as a starting point for the synthesis of CdSe-MX₂/L nanocrystals via Z-type rebinding. We show that CdSe-L systems can be utilized as a synthetic intermediate for the formation of these novel compounds, and that the identity of the Z and L-type
ligands can be modified to allow for a more detailed spectroscopic characterization of the chemical environments in which these surface moieties exist.

VI.2 Rebinding of metal oleates to CdSe-NH₂R

Amine bound CdSe-NH₂R is an ideal material for preparing nanocrystals with novel ligands designed to passivate or functionalize nanocrystal surfaces. As a proof-of-concept demonstration, we studied the addition of several metal oleates to amine bound CdSe nanocrystals. ¹H NMR spectroscopy was used to monitor the binding over a range over metal oleate concentrations while keeping the concentration of nanocrystals and n-butylamine ligands constant. The alkenyl region of the spectrum provides a convenient means of measuring bound and free metal oleate. Broad resonances correspond to ligands bound to the nanocrystal surface, while sharp peaks are due to metal oleate free in solution. Integrating the broad region thus provides a measurement of metal oleate bound to the nanocrystal depending on the concentration of added metal oleate.

Figure 6.1 shows the metal oleate coverage of CdSe nanocrystals over a range of concentrations for zinc, cadmium, and lead oleate. In all three cases, surface density increases with increasing concentration of metal oleate. Cadmium oleate consistently results in greater coverage than lead oleate at a given concentration of M(O₂CR)₂, with both reaching saturation at a maximum coverage of 0.4 nm² and 0.25 nm², respectively. These results imply that a Cd²⁺ cation has a higher affinity for surface selenides than Pb²⁺. The case of zinc oleate rebinding is more complicated. The coverage of zinc oleate is lower than both Pb and Cd at metal oleate concentrations below 15 mM, yet surpasses both at higher concentrations (25 mM).
Figure 6.1. Dependence of M(O_2CR)_2 coverage on M(O_2CR)_2 concentration for stoichiometric CdSe nanocrystals \((d = 3.4 \text{ nm})\). The coverage of Cd(O_2CR)_2 (red circles), Zn(O_2CR)_2 (blue squares), and Pb(O_2CR)_2 (green triangles) was measured by \(^1\)H NMR spectroscopy over a range of M(O_2CR)_2 concentrations while keeping the concentration of nanocrystals (0.13 mM) and \(n\)-butylamine ligands (11.5 mM) constant. See experimental for additional details.

The lower binding affinity of zinc can be rationalized by a mismatch in orbital overlap between the soft selenide base and hard Zn\(^{2+}\) acid. This observation also supports our finding that Zn(O_2CR)_2 formed during treatment of CdSe-Cd(O_2CR)_2 nanocrystals with diethyl zinc does not tightly bind the nanocrystal surface.\(^6\) The higher coverage at 25 mM is much more surprising as it implies a larger number of surface binding sites for zinc oleate than cadmium or lead oleates. The packing density of alkyl chains in the crystal structure of oleic acid is 5.4 nm\(^2\), which sterically limits the saturation of the nanocrystal surface to 2.7 M(O_2CR)_2 nm\(^2\). All of the metal oleates studied here failed to reach these coverages at room temperature. In addition, cadmium carboxylates have been recently shown to bind almost exclusively to (100) facets.\(^{16-17}\) It is possible
that zinc carboxylates have a higher binding affinity to the other major facets (111) and (-1-1-1), which would explain its higher surface density. It is important to note that because of the stability of a surface displaced L-MX₂ complex, the extent of Z-type binding will depend on the concentration of both metal oleate and amine (11.5 mM). The polymeric nature of metal oleates will also alter their ability to bind the nanocrystal surface. Interestingly, carboxylate species bind to cadmium and lead in a bidentate fashion, yet monodentate with zinc carboxylates. These structural differences in the metal oleates may account for the apparent ability of zinc oleate to achieve relatively high surface densities at room temperature.

The identity of the metal salt in CdSe-M''(O₂CR)ₙ samples causes slight changes in the UV-vis absorption spectra of these materials (Figure 6.2).

With rebound cadmium oleate, the spectrum resembles that of the original CdSe-Cd(O₂CR)₂ nanocrystals, where the first electronic transition is positioned at 560 nm. The same is true for particles with rebound zinc and indium oleate salts. CdSe-Pb(O₂CR)₂, on the other hand, shows a more dramatic blue shift in the first transition to 550 nm. However, the spectrum is complicated by scattering, as these particles in particular remained unstable to aggregation upon dilution to UV-vis concentrations, which can partially explain the more dramatic shift. All UV-vis spectra did not contain sharp second electronic transitions, and all samples had low PLQY of < 2%. This is most likely due to the low surface density of the metal oleates.

Previous work has been performed on CdSe and CdS quantum belts, which exhibited more dramatic absorption changes in CdSe-NH₂R, CdSe-Cd(O₂CR)₂, and CdSe-Zn(O₂CR)₂ materials. While it is likely that these quantum belts have a mixture of Z and L-type ligands, it is possible that there might be a greater affect on the optical properties of anisotropic CdSe samples compared to quantum dots upon Z-type exchange. The small changes in the UV-vis spectra from Z-type
Figure 6.2. UV-Vis absorption spectra of CdSe-NH₂C₄H₉ (black), CdSe-Cd(O₂CR)₂ (red), CdSe-Zn(O₂R)₂ (blue), CdSe-In(O₂CR)₃ (purple), and CdSe-Pb(O₂CR)₂ (green). All spectra are normalized at $\lambda = 350$ nm (not shown) and offset for clarity.

Rebinding in our samples differs greatly from what has been reported for thermodynamically stable CdSe clusters, which exhibit red shifts of 240 meV upon the addition of cadmium benzoate.¹⁹
We sought to reach higher coverages of the added Z-type ligand by both heating the sample in the presence of excess metal oleate and removing the n-butylamine. Previously, cadmium oleate coverages of 1.7 nm$^{-2}$ were achieved by heating CdSe nanocrystals to 240 °C in the presence of excess cadmium oleate. After removing n-butylamine from stoichiometric CdSe nanocrystals under vacuum, we were able to synthesize new nanocrystal materials of the generic formula CdSe-M$^{n+}$(O$_2$CR)$_n$ by heating CdSe nanocrystals in the presence of the desired M$^{n+}$(O$_2$CR)$_n$ at 100 °C. The Z-type ligand coverages for rebound CdSe-Cd(O$_2$CR)$_2$, CdSe-Zn(O$_2$CR)$_2$, CdSe-Pb(O$_2$CR)$_2$, and CdSe-In(O$_2$CR)$_3$ are summarized in Table 6.1. Under these conditions, cadmium oleate achieves the highest surface coverage, followed closely by zinc. The low coverage of indium oleate most likely stems from both its larger steric profile as well as its tendency to bind in a polymeric fashion to nanocrystal surfaces.

Table 6.1. Oleate surface coverages (nm$^{-2}$) of various metal oleates after Z-type rebinding to CdSe-NH$_2$C$_4$H$_9$ at 100 °C.

<table>
<thead>
<tr>
<th>Metal oleate</th>
<th>Cd(O$_2$CR)$_2$</th>
<th>Zn(O$_2$CR)$_2$</th>
<th>Pb(O$_2$CR)$_2$</th>
<th>In(O$_2$CR)$_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>olate surface coverage (nm$^{-2}$)</td>
<td>3.2</td>
<td>2.6</td>
<td>0.8</td>
<td>1.4</td>
</tr>
</tbody>
</table>

VI.3 Temperature dependence of metal oleate rebinding

The requirements to achieve maximum Z-type rebinding led us to study the rebinding of cadmium, zinc, and lead oleate as a function of temperature. Figure 6.3 plots the in situ metal carboxylate coverage on 5.3 nm CdSe-NH$_2$R nanocrystal samples, obtained from $^1$H NMR, as the samples were heated from 25 °C to 200 °C. The surface coverage of all metal oleates increases, saturating above 100 °C. Thus, it does not seem necessary to heat CdSe-NH$_2$R and metal oleate solutions back to reaction temperatures (240 °C) to achieve maximum Z-type rebinding, as previously reported by us. While lead oleate still maintains the lowest coverage (1.2 nm$^{-2}$), at
higher temperatures cadmium oleate reaches the highest surface density (1.6 nm\(^2\)) out of the three metals. This contrasts with the coverages we observed at room temperature, where zinc oleate achieved higher binding densities than cadmium oleate. A variety of factors can attribute to this change at higher temperatures. For example, reconstruction of the surface atoms at high temperature might expose binding sites that preferentially bind cadmium over zinc. A change in the structure of cadmium oleate from bidentate to monodentate might allow for more efficient packing of the carboxylates on the nanocrystal surface. In addition, it is possible that binding affinities for all three metal oleates are nanocrystal-size dependent, as more of the metal salts could
reach a higher surface density on 5.3 nm CdSe particles versus those 3.5 nm in diameter. All of these factors could play a role in the resulting surface coverage of the metal oleates.

The results in this section imply that Z-type ligand binding can be achieved with metal salts other than cadmium, adding synthetic value to CdSe-NH$_2$C$_4$H$_9$ as a possible synthon for the synthesis of CdSe-MX$_2$ samples whose Z-type ligands are more tailored towards specific applications. In addition, they might prove to be useful model systems to study interfaces in CdSe/ME core/shell materials. Furthermore, binding of a heavy metal center, such as mercury via HgX$_2$, could be an ideal system to study metal cation diffusion using high energy X-Ray scattering methods (EXAFS, PDF, etc.).

VI.4 Proof of concept: an alternate synthesis of CdSe-CdCl$_2$/PBu$_3$

Scheme 6.2. L-Type exchange and Z-Type rebinding allows for the synthesis of CdSe-CdCl$_2$/PBu$_3$ from CdSe-NH$_2$R.

The rebinding of Z-Type ligands to the surface of CdSe-NH$_2$R nanocrystals has the potential to offer a new route for the synthesis of novel CdSe-MX$_2$ and CdSe-MX$_2$/L samples that might be difficult to accomplish using techniques such as X-type exchange (Scheme 6.2). To demonstrate this concept, chloride terminated CdSe-CdCl$_2$/PBu$_3$ nanocrystals were synthesized.
from CdSe-PBu₃ (for discussion on the synthesis of phosphine bound CdSe-PR₃ samples, please refer to chapter V).¹

CdSe-PBu₃ particles were synthesized by L-type ligand exchange from CdSe-NH₂C₄H₉. At nanocrystal concentrations of 0.16 mM and a Bu₃P concentration of 0.25 M in toluene, CdSe-PBu₃ is insoluble and remains aggregated even after stirring for 24 hours. Upon the addition of excess CdCl₂ (775 per nanocrystal), the nanocrystals slowly dissolved over 2 hours. This observation that cadmium chloride helps stabilizes CdSe-PBu₃ in solution indicates that CdCl₂ is binding the nanocrystal surface.

CdSe-CdCl₂/PBu₃ prepared in this manner can be precipitated from a toluene solution (and purified by centrifugation) multiple times without difficulty in redissolving the nanocrystals, another major difference from CdSe-PR₃ samples. Their UV-vis, ¹H and ³¹P NMR spectra resemble those of CdSe-CdCl₂/PBu₃ particles synthesized by X-type ligand exchange with bistrimethylsilyl chloride (Figures 6.4-6.6).² The position of the first electronic transition in the UV-vis absorption spectrum does not change with respect to the original CdSe-NH₂C₄H₉ sample, an observation also seen when comparing CdSe-Cd(O₂CR)₂ species with decreasing Z-type ligand coverage.³ However, the second feature still remains broad, which is in stark contrast to a sharp peak previously observed in CdSe-CdCl₂/PBu₃ systems. We speculate that this difference is due to a lower cadmium chloride surface coverage in the nanocrystals reported here. This is in line with our observation that Z-type rebinding needs high temperatures to achieve Z-type ligand coverages that are on the order of as synthesized CdSe-Cd(O₂CR)₂ samples (~1.6 CdX₂ nm⁻²).

¹ It was mentioned that CdSe-PBu₃ is not colloidally stable in chapter V, thus the starting sample for the reactions in this section are aggregates and not a solution.
Integration of the $^1$H NMR resonances against an internal ferrocene standard gives a total Bu$_3$P concentration that corresponds to 118 per nanocrystal. Comparing the relative ratios of the total peak areas of bound and free phosphine in the $^{31}$P NMR spectrum, we conclude that the coverage of bound phosphine is 0.46 nm$^2$. This coverage is very similar to that previously reported by our lab (0.5 Bu$_3$P nm$^2$). Interestingly, the $^{31}$P NMR spectrum reported here lacks a resonance corresponding to (Bu$_3$P)$_n$CdCl$_2$ species. While it is possible that this species was removed during purification, it is also possible that trace amounts of primary amine preferentially bind to CdCl$_2$.

![Figure 6.4](image)

**Figure 6.4.** $^1$H NMR spectrum of CdSe-CdCl$_2$/PBu$_3$. Integration of the $^1$H NMR resonances against an internal ferrocene standard gives a total Bu$_3$P coverage of 3.26 nm$^2$. 
Figure 6.5. $^{31}$P NMR spectrum of CdSe-CdCl$_2$/PBu$_3$.

Figure 6.6. UV-visible absorbance spectrum of CdSe-CdCl$_2$/PBu$_3$.

over Bu$_3$P, leading to the formation of (RNH$_2$)$_n$CdCl$_2$ adducts that would not exhibit a resonance in $^{31}$P NMR spectroscopy.
The specific molecular interactions that occur when CdCl\textsubscript{2} binds and stabilizes phosphine-bound CdSe nanocrystals are still unclear, yet we speculate that this effect stems from two possible sources. The first is that binding of CdCl\textsubscript{2} most likely occurs with a surface selenide, thereby reducing the number of exposed lone pairs at the nanocrystal surface. It is possible that these lone pairs raise the surface energy of the particle, and that in the absence of Z-type ligands the nanocrystal forms aggregates to lower this energy. Addition of CdCl\textsubscript{2} to aggregated CdSe-PBu\textsubscript{3} seems to reverse this process. A second rationale could be the ionization of CdCl\textsubscript{2}, forming a tightly bound [(Bu\textsubscript{3}P)\textsubscript{n}CdCl]+[Cl\textsuperscript{-}] ion pair which could also help stabilize the nanocrystals in solution.

Spectroscopically, it is difficult to distinguish a neutral (Bu\textsubscript{3}P)\textsubscript{n}CdCl\textsubscript{2} species from a [(Bu\textsubscript{3}P)\textsubscript{n}CdCl]\textsuperscript{+}[Cl\textsuperscript{-}] ion pair. Currently our group is investigating if these two species can be distinguished with \textsuperscript{111/113}Cd NMR spectroscopy techniques, both of which have not been successful at the time of the preparation of this dissertation. NMR spectroscopy, nevertheless, is acutely sensitive to the nuclei’s chemical environment and may still provide the means of observing ionization of MX\textsubscript{2} salts in the presence of CdSe nanocrystals. To this end, we set out on using our newly developed synthetic tools to develop nanocrystal model systems that might be sensitive enough to differentiate these structurally identical molecules.

\textbf{VI.5 CdSe-Cd(O\textsubscript{2}CCF\textsubscript{3})\textsubscript{2}/PR\textsubscript{3}:} a new model system to study molecular interactions at nanocrystal surfaces

CdSe nanocrystals bound by both cadmium trifluoroacetate and phosphine ligands offer a variety of nuclei (\textsuperscript{111/113}Cd, \textsuperscript{77}Se, \textsuperscript{31}P, \textsuperscript{19}NMR, \textsuperscript{13}C, and \textsuperscript{1}H) which can be characterized using 1 and 2D NMR spectroscopy. In addition, many of these NMR active nuclei are located within close proximity to the particle surface and could provide valuable information about the various binding
sites. Furthermore, both $^{19}$F and $^{31}$P nuclei are highly sensitive to their chemical environment and can potentially act as useful probes for different binding motifs.\textsuperscript{21} Using the L-type exchange methods presented in chapter V and the Z-type rebinding insight discussed in this chapter, we sought to synthesize CdSe-Cd(O$_2$CCF)$_3$/PR$_3$ using a similar approach to that of CdSe-CdCl$_2$/PBu$_3$.

Beginning with an aggregated CdSe-PBu$_3$ sample in toluene ([nanocrystals] = 0.16 mM, [Bu$_3$P] = 0.25 M), addition of cadmium trifluoroacetate (100 equivalents per nanocrystal) causes the dissolution of the particles over a few minutes. This rapid change in solubility of the nanocrystals is drastically different than that observed during the synthesis of CdSe-CdCl$_2$/PBu$_3$, and is likely due to the rate at which the different cadmium salts dissolve in 0.25 M solution of phosphine in toluene. An in situ $^{19}$F NMR spectrum of this reaction shows two resonances corresponding to bound and free Cd(O$_2$CCF)$_3$, as indicated by their difference in line width (Figure 6.7). Upon precipitation and purification of the particles, only one broad resonance ($\delta = -72.9$ ppm, $\Delta$ppm = 4 ppm remains in the $^{19}$F NMR spectrum, indicating that the majority of the cadmium trifluoroacetate is surface-bound. Integration of this resonance against an internal C$_6$F$_6$ standard ($\delta = -162.1$ ppm, not shown) quantifies the Cd(O$_2$CCF)$_3$ coverage at 15 per nanocrystal. This is a lower surface density compared to the CdCl$_2$ surface coverage in CdSe-CdCl$_2$/PBu$_3$ samples (99 per nanocrystal), which could be explained by both the size of the X-type ligand and the Lewis acidity of the CdX$_2$ species. Since chlorides have smaller steric profile than trifluoroacetate, and CdCl$_2$ is a stronger acid than Cd(O$_2$CCF)$_3$, it is logical that cadmium trifluoroacetate does not achieve a coverage as high as cadmium chloride.
Figure 6.7. \(^{19}\text{F}\) NMR spectra of CdSe-PBu\(_3\) with added Cd(O\(_2\)CCF\(_3\))\(_2\) (100 equivalents per nanocrystal) (top) and isolated CdSe-Cd(O\(_2\)CCF\(_3\))\(_2\)/PBu\(_3\) (bottom).

The \(^{31}\text{P}\) NMR spectrum is similar to that of CdSe-PR\(_3\) samples, showing only two resonances corresponding to bound (\(\delta = -17.9\) ppm, \(\Delta\text{ppm} = 20\) ppm) and free Bu\(_3\)P (\(\delta = -32\) ppm, \(\Delta\text{ppm} = 2.1\) ppm) (Figure 6.8). The absence of a resonance corresponding to a (Bu\(_3\)P)\(_n\)Cd(O\(_2\)CCF\(_3\))\(_2\) adduct can be explained either by the presence of trace (NH\(_2\)R)\(_n\)Cd(O\(_2\)CCF\(_3\))\(_2\) adducts, or a weak binding affinity, and hence easy removal of, L\(_n\)-Cd(O\(_2\)CCF\(_3\))\(_2\) species towards the nanocrystal surface. The \(^1\text{H}\) NMR spectrum looks like that of CdSe-PBu\(_3\), albeit with a small broad resonance centered at 3.18 ppm corresponding to bound \(\alpha\)-NH\(_2\)\(CH\(_2\)C\(_3\)H\(_7\)\) hydrogens (Figure 6.9). Repeating the synthesis by heating CdSe-NH\(_2\)C\(_9\)H\(_9\), PBu\(_3\), and Cd(O\(_2\)CCF\(_3\))\(_2\) to 100 °C under vacuum in 1-
octadecene for 12 hours removes the tenacious amine, giving a $^1$H NMR spectrum without this resonance (Figure 6.9). The UV-vis absorption spectrum of CdSe-Cd(O$_2$CCF$_3$)$_2$/PBu$_3$ resembles that of CdSe-CdCl$_2$/PBu$_3$ synthesized from CdSe-NH$_2$C$_4$H$_9$. In particular, the position of the first transition remains constant, and the second transition remains broad, which we again attribute to a low surface density of the Z-type ligand.

![Figure 6.8. $^{31}$P NMR spectrum of CdSe-Cd(O$_2$CCF$_3$)$_2$/PBu$_3$.](image)

Figure 6.8. $^{31}$P NMR spectrum of CdSe-Cd(O$_2$CCF$_3$)$_2$/PBu$_3$. 
Figure 6.9. $^1$H NMR spectrum of CdSe-Cd(O$_2$CCF$_3$)$_2$/PBu$_3$ synthesized by annealing $n$-butylamine from the reaction solution at room temperature (black) and at 100 °C (red). The impurities in the alkenyl region of the red spectrum are terminal alkene resonances from the 1-octadecene reaction solvent.

While CdSe-Cd(O$_2$CCF$_3$)$_2$/PBu$_3$ samples have resonances in NMR studies that indicate bound cadmium salts and phosphine, they are still unstable to aggregation and fail to redisperse in various organic solvents (toluene, methylene chloride, benzene-$d_6$, diethyl ether, 1-octadecene, or diphenyl ether) after additional purification cycles. We speculate that the instability of these particles originate from the low surface density of the tri-$n$-butylphosphine ligands, which in turn stems from their large steric profile. Substituting tri-$n$-octylphosphine as the L-type ligand also yields colloidally unstable CdSe-Cd(O$_2$CCF$_3$)$_2$/PR$_3$ products. Even with the presence of a stabilizing Z-type ligand, the choice of ligands for this nanocrystal system does not provide enough stabilization to prevent aggregation after removal of the large excess of tri-$n$-alkylphosphine.
Figure 6.10. $^{31}$P NMR spectra of CdSe-PMe$_2$C$_{18}$H$_{37}$ (i) before and (ii) after the addition of 100 equivalents (per nanocrystal) of Cd(O$_2$CCF$_3$)$_2$, and (iii) isolated and purified CdSe-Cd(O$_2$CCF$_3$)$_2$/PMe$_2$C$_{18}$H$_{37}$.

As presented in section V.3.1.2, a phosphine ligand with a smaller steric profile such as PMe$_2$C$_{18}$H$_{37}$ provides greater stabilization for the nanocrystals. Synthesis of CdSe-Cd(O$_2$CCF$_3$)$_2$/PMe$_2$C$_{18}$H$_{37}$ was achieved by the addition of 100 equivalents (per nanocrystal) of Cd(O$_2$CCF$_3$)$_2$ to CdSe-PMe$_2$C$_{18}$H$_{37}$. Upon addition of a cadmium trifluoroacetate solution in 90/10% benzene-$d_6$/THF-$d_8$ (v/v), there is significant downfield shifts in the $^{31}$P NMR resonances.
compared to those of CdSe-PMe₂C₁₈H₃₇ (Figure 6.10). In addition, a broad peak across the entire spectrum can be observed. The origins of these chemical shifts are yet unknown, but could be due to new phosphorous chemical environments, solvent effects (from the 1.67% by volume THF-d₈ in the reaction solution), or fast exchange processes at the phosphorous nuclei.

These nanocrystals can be precipitated and redispersed multiple times without any decrease in observed colloidal stability, supporting our claim that dimethyl-n-octadecylphosphine can stabilize a CdSe nanocrystal surface better than tri-n-alkylphosphines. The phosphorous NMR spectrum (Figure 6.10) only shows one resonance centered at -35.6 ppm (Δppm ~ 22.9 ppm). This resonance is further downfield than those observed in CdSe-PMe₂C₁₈H₃₇ samples, which potentially infers a new chemical environment of the phosphorous ligand. Additional work is required to understand the exact molecular nature of these environments, yet such observations are promising and point towards the power of solution ³¹P NMR spectroscopy in discerning ligand-surface interactions in colloidal nanocrystal systems. It is also interesting that a ³¹P NMR spectrum with one broad peak could be obtained with CdSe-PMe₂C₁₈H₃₇/Cd(O₂CCF₃)₂, whereas a sharper resonance was always observed in spectra of CdSe-Cd(O₂CCF₃)₂/PBu₃. This is possibly due to the higher surface density that can be achieved by dimethyl-n-octadecylphosphine compared to tri-n-butylphosphine, which might require Bu₃P to be present in a greater excess to maintain colloidal stability of the nanocrystals. The product was also characterized by ¹H and ¹⁹F spectroscopies (Figures 6.11 and 6.12). Integrating the region of the ¹H NMR spectrum from 0.0-4.0 ppm (and correcting for the residual toluene at 2.08 ppm) against an internal ferrocene standard allows us to calculate a phosphine coverage of 1.8 nm², which matches the coverage reported from CdSe-PMe₂C₁₈H₃₇. The broad resonance in the ¹⁹F NMR spectrum (δ = -72.8 ppm, ΔHz ~ 2250 Hz, Δppm ~ 4.5 ppm) indicates that cadmium trifluoroacetate is bound to the nanocrystal surface.
Figure 6.11. $^1$H NMR spectrum of CdSe-Cd(O$_2$CCF$_3$)$_2$/PMe$_2$C$_{18}$H$_{37}$.

Figure 6.12. $^{19}$F NMR spectrum of CdSe-Cd(O$_2$CCF$_3$)$_2$/PMe$_2$C$_{18}$H$_{37}$. 
Figure 6.13. Mono-exponential fit of the decay curve of the methyl species generated from the DOSY spectrum of CdSe-Cd(O$_2$CCF$_3$)$_2$/PMe$_2$C$_{18}$H$_{37}$ in benzene-$d_6$.

Diffusion NMR measurements were performed on CdSe-Cd(O$_2$CCF$_3$)$_2$/PMe$_2$C$_{18}$H$_{37}$. The decay curve in Figure 6.13 can be fit with a mono-exponential function with little error, implying that the majority of phosphine in the nanocrystal sample moves with a diffusion coefficient of 87.7 $\mu$m$^2$ s$^{-1}$. This corresponds to a hydrodynamic diameter of 8.2 nm and implies that PMe$_2$C$_{18}$H$_{37}$ diffuses as though it is bound to the nanocrystal. These results further support the claim that dimethyl-$n$-octadecylphosphine can stabilize a CdSe nanocrystal surface without a large concentration of free phosphine in solution.

TEM images of CdSe-Cd(O$_2$CCF$_3$)$_2$/PMe$_2$C$_{18}$H$_{37}$ do not show an improvement in the stability of the particles upon evaporation of the solvent (Figure 6.14). UV-vis spectroscopy, while indicating the particles remain monodisperse and unaggregated in solution, shows no change in the second electronic transition, commonly seen with the rebinding of Z-type ligands to CdSe (Figure 6.15). This is rationalized by a low surface coverage of Cd(O$_2$CCF$_3$)$_2$, whose surface density might be increased upon performing the rebinding chemistry at higher temperatures.
Figure 6.14. TEM images of CdSe-Cd(O₂CCF₃)₂/PMe₂C₁₈H₃₇. The scale bars for the images are 50 (left) and 20 nm (right).

Figure 6.15. UV-vis absorbance spectra of CdSe-NH₂C₄H₉ (red), CdSe-PMe₂C₁₈H₃₇ (blue), and CdSe-Cd(O₂CCF₃)₂/PMe₂C₁₈H₃₇ (green). The spectra are offset for clarity.
VI.6 Conclusions

Using CdSe-NH$_2$C$_4$H$_8$ nanocrystals as a starting material, cadmium, zinc, lead, and indium oleate were all demonstrated to rebind as Z-type ligands, demonstrating the reversibility of the binding of metal salts. The extent of rebinding is temperature dependent with a higher surface density of metal oleate being achieved at higher reaction temperatures. Z-type rebinding was further explored with CdSe-PBu$_3$ and CdSe-PMe$_2$C$_{18}$H$_{37}$ nanocrystals, through which both chloride and trifluoroacetate bound particles could be obtained. Of particular interest is CdSe-Cd(O$_2$CCF$_3$)$_2$/PMe$_2$C$_{18}$H$_{37}$, whose NMR spectra indicate various chemical environments of the Z-type ligand. The results in this dissertation demonstrate the novelty of Z-type rebinding for the synthesis of novel nanocrystal materials. Moving forward, this synthetic motif can aid in the preparation of CdSe-MX$_2$/L systems to study core-shell interfaces, surface cation diffusion into the nanocrystal core, and other unique samples to further understand binding motifs in these materials.

While NMR has proved invaluable throughout the course of this dissertation, additional techniques would be complementary to the results presented here. The spectra obtained using NMR have been useful in characterizing the ligand composition of various CdSe nanocrystals, and have also provided some insight into exchanges at their surface. However, discerning between binding affinity and steric encumbrance of a variety of ligands has always proven to be challenging. Isothermal titration calorimetry can provide thermodynamic information on the removal and rebinding of Z-type ligands.\(^\text{ii}\) I highly encourage future endeavors in the surface

\(^\text{ii}\) and yet no biology group who has calorimeters to study their aqueous systems would allow for me to use their machines to titrate in organic solutions of strong Lewis bases.
chemistry of the Owen lab to incorporate calorimetric methods to study the surface chemistry developed by myself and previous graduate students. Such measurements would allow for an even deeper understanding of binding affinities, and might even afford insight on the binding energies of various binding sites which are difficult to distinguish in solution NMR spectroscopy.

VI.7 Experimental

Synthesis of $\text{M}($C$_{18}$H$_{33}$O$_2$)$_2$ ($\text{M} = \text{Cd, Zn}$). Cadmium oleate and zinc oleate were prepared on a 25 mmol scale from a modified procedure for the synthesis of cadmium myristate reported previously using oleic acid and the respective metal nitrate.$^{22}$

Synthesis of $\text{Pb}($C$_{18}$H$_{33}$O$_2$)$_2$. Lead oleate was prepared using a method reported previously by Hendricks et al.$^{23}$

Synthesis of $\text{In}($C$_{18}$H$_{33}$O$_2$)$_3$. A 2 mL aliquot of a 0.156 M InMe$_3$ solution in toluene was added dropwise to a stirring 2mL oleic acid solution in toluene (0.469 M). This solution was allowed to stir for 4 hours. The toluene was removed under vacuum for 10 hours, after which a clear, colorless, viscous, oily-like substance remained, which was dissolved in 1 mL toluene-$d_8$ and used as a 0.223 M stock solution for future experiments.

Titration of $\text{M}($C$_{18}$H$_{33}$O$_2$)$_2$ ($\text{M} = \text{Cd, Zn, Pb}$) to CdSe-$\text{NH}_2\text{C}_4\text{H}_9$. A 10 mL toluene-$d_8$ stock solution of CdSe-$\text{NH}_2\text{C}_4\text{H}_9$ ([nanocrystals] = 0.128 mM, [amine] = 11.5 mM) and ferrocene (0.43 mM) was prepared. For the titration experiment, this stock solution acted as the sample with zero
equivalents of added metal oleate. The amount of metal oleate in the stock and subsequent samples was monitored by $^1$H NMR spectroscopy and analyzed using the fitting procedure described in the next section. A 1 mL aliquot of this stock solution was added to the metal oleate to make the most concentrated metal oleate sample (24 mM). A 500 μL aliquot of this sample was added to 500 μL of the stock solution, thereby keeping the concentrations of all species except the metal oleate constant. This dilution procedure was repeated in a similar manner to make the other samples with decreasing metal oleate concentration.

To achieve endpoints for the titration, a 0.1 mM solution of CdSe-nBuNH$_2$ with a free amine concentration of 1.15 mM and a metal oleate concentration of 150 mM was prepared in toluene-$d_8$. These solutions were allowed to stir overnight, and the amount of bound and free metal oleate was monitored by $^1$H NMR spectroscopy.

**Binding saturation studies of M$^{n+}$($C_{18}H_{33}O_2$)$_n$ at elevated temperatures.** In order to achieve saturated carboxylate coverage compared to their coverage at room temperature, a 0.1 mM solution of CdSe-nBuNH$_2$ with a free amine concentration of 1.15 mM was prepared in toluene with a total volume of 1mL. The amine and toluene were removed under reduced pressure (20 mtorr) at 100 °C for 6 hours. The reaction flask was brought into the glove box and a 150 mM slurry of the desired metal oleate in 2 mL toluene was added to the flask. Upon stirring the solution became clear (except for zinc oleate, which only completely dissolved at elevated temperatures). The flask was then heated to 100 °C for 2 hours, after which the toluene was removed under reduced pressure. The flask was then transferred into a glove box and cleaned using a previously reported procedure. The solid sample was re-dissolved in 1 mL pentane and subsequently precipitated from solution by the addition of 20 mL of methyl acetate. The sample was centrifuged at 7000 rpm for
10 minutes. This cleaning procedure was repeated three times. Upon the final dissolution of the sample into pentanes, the sample was dried overnight under vacuum and re-dissolved into a stock solution of toluene-$d_8$ for subsequent studies. This stock solution was used to measure the concentration of bound metal oleate by the $^1$H NMR and UV-Vis experiments described in the previous section of the experimental.

**Synthesis of CdSe-CdCl$_2$/PBu$_3$ from CdSe-NH$_2$C$_4$H$_9$.** In a 20 mL vial equipped with a stir bar, 200 $\mu$L of a CdSe-NH$_2$C$_4$H$_9$ ([nanocrystals] = 3.22 mM, [amine] = 0.38 M) was added to 0.5 mL of Bu$_3$P. The nanocrystals immediately precipitated from solution, and the slurry was allowed to stir under vacuum overnight. The slurry was then diluted with 7.5 mL of toluene and allowed to stir for 30 minutes. Afterwards, 8.4 mg of CdCl$_2$ was added to the solution, and the nanocrystals gradually dissolved within 2 hours. The homogeneous solution was split into two 45 mL centrifuge tubes and precipitated with 30 mL of methyl acetate which caused the precipitation of nanocrystals. The tubes were centrifuged at 7000 rpm for 10 minutes. The solid was cleaned twice more by precipitating the nanocrystals from 2 mL of toluene with 30 mL of methyl acetate. The nanocrystals were dried under vacuum for 2 hours, then redissolved in benzene-$d_6$ for analysis by $^1$H and $^{31}$P NMR and UV-Vis spectroscopies.

**Synthesis of CdSe-Cd(O$_2$CCF$_3$)$_2$/PMe$_2$C$_{18}$H$_{37}$ from CdSe-PMe$_2$C$_{18}$H$_{37}$.** In a J-Young NMR tube, 500 $\mu$L of CdSe-PMe$_2$C$_{18}$H$_{37}$ ([nanocrystals] = 0.285 mM) in toluene-$d_8$ was added. To this solution was added 100 $\mu$L of a 34.3 mM solution of Cd(O$_2$CCF$_3$)$_2$ in toluene-$d_8$, and the sample was analyzed by $^1$H NMR spectroscopy. Afterwards, the solution was transferred to a 15 mL centrifuge tube and precipitated with 10 mL of methyl acetate. The nanocrystals were cleaned two additional
times by precipitating the particles from 1 mL of toluene with 9 mL of methyl acetate. The purified nanocrystals were then dried under vacuum for 2 hours before being redissolved in benzene-\textit{d}_6 for analysis by \textsuperscript{1}H, \textsuperscript{19}F, and \textsuperscript{31}P NMR and UV-Vis analysis.

**Diffusion NMR Experiments.** DOSY measurements were performed using a double-stimulated echo sequence. The gradient strength was varied linearly from 2\% to 95\% of the probe’s maximum value. The diffusion parameters consisting of the pulse length (\(\delta/2\)) and delay (\(\Delta\)) were chosen to ensure that >90\% of the signal decayed at the highest magnetic field gradient. The resulting decay curves were fit using an Igor Pro macro developed by Jonathan De Roo, and the same macro was used to calculate the hydrodynamic diameter, which assumed a spherical shape of the nanocrystals.

**VI.8 References**


CONCLUSION

The chemistry reported in this dissertation focuses on the molecular interactions at the surfaces of cadmium selenide nanocrystals. The role that ion pairs play in the fundamental properties of these systems has been investigated. Synthetic control over their formation and subsequent binding can be achieved by removing acidic impurities. Through L-type promoted Z-type displacement, CdSe nanocrystals bound exclusively by primary amines can be obtained, allowing for the first time access to these samples free from X-type impurities.

Ion pairs are a double-edged sword for CdSe nanocrystal systems. On one end, they hinder charge transport and act as local charges in thin films. However, they are also indispensable for the colloidal stability of these particles. In this dissertation, it has been shown that the absence of ion pairs allow for the fabrication of high quality devices. Unfortunately, the same nanocrystal samples are highly unstable and aggregate over time. We have shown that ion pairs bind tightly to CdSe, potentially offering a novel design scaffold for surface modification to produce particles with static ligand shells.

The simplicity and lability of the ligand shell in CdSe nanocrystal systems bound by amines makes these systems ideal candidates to study fundamental surface interactions. Using the concepts from previous L-type exchanges, the synthesis of nanocrystals bound exclusively by phosphines has been reported. Taking into account the presence of ion pairs, these samples are likely the first of its kind despite being present in the literature since the field’s beginnings. They also act as clean starting materials for the binding of various Z-type ligands, providing access to novel CdSe-MX₂/L nanocrystal samples for use in either fundamental studies or practical applications.
The results discussed above improve the ligand model that the Owen lab consistently tunes and modifies for colloidal nanocrystal materials. It is likely that the molecular interactions studied in this dissertation apply to other II-VI materials as well as IV-VI and III-V semiconductor nanocrystals. Metal and metal oxide particles also share similar motifs. Hopefully, these findings will allow for future endeavors to investigate the fundamental driving forces behind ligand exchange and their effect on optoelectronic properties. In turn, this will lead to improved bottom-up engineering of nanocrystal materials for a variety of applications.

Finally, these findings point to the ever important idea that many complicated and heterogeneous systems can be broken down into its fundamental and molecular interactions. Ligands binding to nanocrystals are, in a simplistic model, just dative interactions with nanocrystal surface atoms. Understanding basic principles of chemistry and how it applies to these systems is a powerful way to design and understand ligand exchange reactions and should not be overlooked despite the hundreds or thousands of binding sites. The power that chemists can bring to the nanocrystal field through their chemical intuition should not be underestimated, and can hopefully help move this and related fields to the point where significant and positive impacts on our society can be achieved.