

CONTROLLING THE SURFACE PROCESSES OF X- AND Z-TYPE LIGANDS TO TAILOR
THE PHOTOPHYSICS OF II-VI SEMICONDUCTOR NANOCRYSTALS

By

Mersedeh Saniepay

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ABSTRACT

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II–VI colloidal semiconductor nanocrystals (NCs), such as CdSe NCs, are often plagued by efficient nonradiative recombination processes that severely limit their use in energy-conversion schemes. While these processes are now well-known to occur at the surface, a full understanding of the exact nature of surface defects and of their role in deactivating the excited states of NCs has yet to be established, which is partly due to challenges associated with the direct probing of the complex and dynamic surface of colloidal NCs. In this dissertation, we report a detailed study of the surface of cadmium-rich zinc-blende CdSe NCs. The surfaces of these cadmium-rich species are characterized by the presence of cadmium carboxylate complexes (CdX_2) that act as Lewis acid (Z- type) ligands that passivate under-coordinated selenide surface species. The systematic displacement of CdX_2 from the surface by N,N,N',N'-tetramethylethylene-1,2-diamine (TMEDA) has been studied using a combination of ^1H NMR and photoluminescence spectroscopies. We demonstrate the existence of two independent surface sites that differ strikingly in the binding affinity for CdX_2 and that are under dynamic equilibrium with each other. A model involving coupled dual equilibria allows a full characterization of the thermodynamics of surface binding (free energy, as well as enthalpic and entropic terms), showing that entropic contributions are responsible for the difference between the two surface sites. Importantly, we demonstrate that cadmium vacancies only lead to important photoluminescence quenching when created on one of

the two sites, allowing a complete picture of the surface composition to be drawn where each site is assigned to specific NC facet locale, with CdX_2 binding affinity and nonradiative recombination efficiencies that differ by up to two orders of magnitude.

To understand the effect of steric hindrance and types of functional groups in different ligands on X-type ligand exchanges, using NMR, PL and UV-Vis absorption spectroscopy, we studied X-type exchanges on CdSe NCs capped with native carboxylates, with oleic acid, oleylthiol, benzoic acid and benzenethiol ligands. We discussed the results and occurrence of undesired pathways including displacement of Z-type ligands, and suggested ligand exchange strategies that most likely lead to 100% X-type exchange.

The structural complexity of surface of CdS NCs is also discussed in this dissertation. We demonstrate presence of two different sulfur surface defects on CdS NCs with ligand binding equilibrium constants that are two orders of magnitude apart and 20-60% smaller than those of selenium on similar size CdSe NCs. We also correlated the different surface defects to the PL quenching efficiency of CdS NCs.

To My Family Who Have Always Been There for Me

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LIST OF ABBREVIATIONS

1D	One Dimensional
2D	Two Dimensional
B	Surface site
BA	Benzoate, Benzoic acid
BT	Benzenethiolate, Benzenethiol
CB	Conduction Band
CBC	Covalent Bond Classification
CBM	Charge-Balanced Model
CdS	Cadmium sulfide
CdSe	Cadmium selenide
CW	Continuous wave
DOSY	Diffusion Ordered Spectroscopy
e ⁻	Electron
eV	Electron Volt
Fc	Ferrocene
FTIR	Fourier Transformed Infrared
fwhm	Full Width at Half Maximum
GaN	Gallium Nitride
h ⁺	Hole
HOMO	Highest Occupied Molecular Orbital
ICP	Inductively Coupled Plasma
ICP-OES	Inductively Coupled Plasma-Optical Emission Spectroscopy
K _{eq}	Equilibrium Constant
LED	Light Emitting Diode
LUMO	Lowest Occupied Molecular Orbital
MA	Myristate, Myristic acid
MS	Mass Spectroscopy

NC	Nanocrystal
NIR	Near Infrared
nm	Nanometer
NMR	Nuclear Magnetic Resonance
OA	Oleate, Oleic acid
ODE	Octadecene
OT	Oleylthiolate, Oleylthiol
P	Probability
PL	Photoluminescence
PLQY	photoluminescence Quantum Yield
RI	Refractive Index
QD	Quantum Dot
TEM	Transmission Electron Microscopy
TEMPO	(2,2,6,6-Tetramethylpiperidine-1-yl)-oxy
TiO ₂	Titanium Dioxide
TMEDA	N,N,N',N-Tetramethylethylene- 1,2-diamine,
UV	Ultraviolet
VB	Valence Band
Vis	Visible
XRD	X-ray Diffraction
ZnO	Zinc Oxide
ZnS	Zinc Selenide

Chapter 1: Introduction

1.1 Semiconductor Nanocrystals

Colloidal semiconductor nanocrystals (NCs) have been the focus of studies over the past three decades due to their wide range of real-life applications and their highly tunable properties. These crystalline particles have become ubiquitous in modern society, and offer much potential for applications such as photosensing,¹⁻³ solid-state lighting,^{2,4-7} photovoltaics,^{1-3,8,9} bioimaging,¹⁰⁻¹² and photocatalytic transformations.¹³⁻¹⁹

NCs share the fascinating electronic, optical, and chemical properties that characterize crystalline semiconductor materials, but with an explicit, and often strong, dependence on the dimensionality of the crystallite.^{20,21} These chemical species can now readily be prepared efficiently through variety of solution-phase approaches.

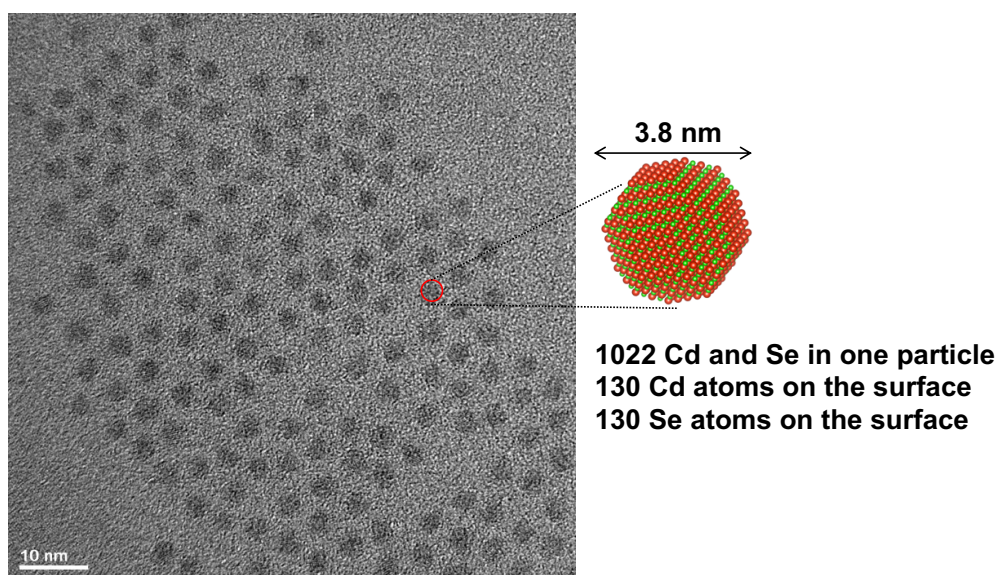
Fundamentally, a semiconductor NC is a small particle on the nanometer scale which is comprised of three important parts including core, shell and the interface between core and shell (aka known as surface).

The core, is usually composed of inorganic semiconducting materials, and can be of either one component (such as Si) or multi components (such as CdSe, InP, CuInS₂, etc). Electro-optical properties in NCs mostly stem from the core.^{22,23} Quantum size effects (Section 1.2.1), leads to discrete energy levels in the cores, which gives them unique optical and electronic properties that form a basis for a in a wide range of practical applications.²⁴

The inorganic cores are terminated with a shell of long chain organic ligands aiding in growth and colloidal stabilization of the NC, but which can also affect the optical properties of the NCs.²⁵⁻³⁰ The core of NCs can also be terminated with inorganic shells of other semiconducting materials (so-called “core-shell” NCs) to lead to new electronic properties. Among other things, these shells are known to enhance the photoluminescence quantum yield (PLQY) of the NCs.³¹

The NC interface is the region between the core and the shell. This region also known as the surface of NC, has its own properties and plays significant roles in modulating the electronic properties, and eventually the applications of NCs.³² There are not many tools available to study NCs surfaces, making this a challenging task to undertake. Nevertheless, understanding the surface chemistry of NCs is as crucial as understanding the core and shell, but traditionally this area has been understudied.

A schematic of a typical NC system we chose to work with is depicted in Scheme 1.1. As the scheme shows, these zinc-blende CdSe NCs have a diameter of 3.6 nm. On average, each NC contains about 1000 Cd and Se atoms (total), with about 260 of them located on the surface of CdSe NC (assuming a spherical symmetry), Although this number directly depends on the shape of NCs and the nature of facets exposed. NCs offer enormous potential in terms of real-life applications, but there are immense challenges that must be overcome to realize their underlying utility. Therefore, a deep understanding of NCs distinctive properties is of great importance.



Scheme 1.1. Composition of core and shell for 3.8 ± 0.2 nm CdSe NCs with zinc-blende crystalline structure

1.2 Photophysical Properties of NCs

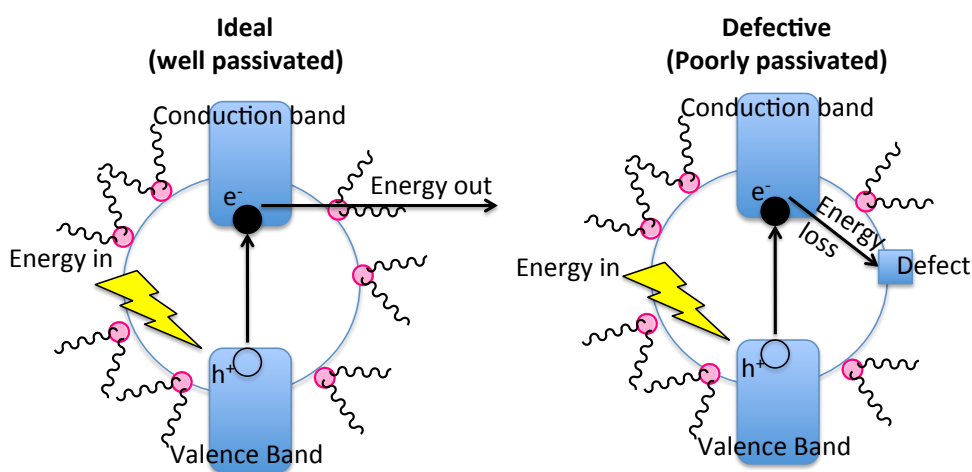
1.2.1 Quantum-size Effect

In semiconductors, the excitation of a valence-band electron into the conduction band,³³ leads to an electron –hole pair, also known as *exciton*,^{34,35} which is delocalized over a delimited volume of space, characterized by a dimension known as the *Bohr radius*, which depends on parameters such as the effective masses of each charge carrier, and the dielectric constant of the material. The Bohr

radius of bulk semiconductors is typically on the order of a few nanometer, and therefore confinement effects in bulk semiconductors are negligible. Quantum confinement occurs when the exciton is confined to a volume smaller than the volume defined by the Bohr radius. The confinement of electrons strongly perturbs the motion of electrons in NCs compared to bulk, specifically by increasing both their kinetic and coulombic energies; this typically leads to increased energies required to excite electrons across the bandgap. Because Bohr radius depends on the material, different materials experience quantum confinement at different sizes.²⁴

1.2.2 Surface Chemistry

Because of the high ratio of surface to volume in NCs, their properties are mostly dictated by their surfaces.^{36,37} Most of the applications of NCs rely on the extraction of work, of one form or another, from electronically-excited NCs. Such energy-conversion schemes necessarily require control over the energetic configuration of NC electronic structure as well as the ability to limit undesired excited-state relaxation pathways that lead to direct energetic losses by rapid excitonic recombination.



Scheme 1.2. Defects at the surface of NCs result in charge carrier traps

Unlike bulk semiconductors, where nonradiative processes generally occur at localized lattice defects (vacancies, impurity doping, dislocations, etc.)³⁸ that are often not found in NCs due to unfavorable energies of formation,³⁹ nonradiative relaxation in NCs generally originates at the surface of the crystal.^{40,41} At least from a structural point of view, the molecular objects that we refer to as “nanocrystals” are as much characterized by those atoms that are regularly organized in space (the so-called core atoms), as by those found on their surfaces which often amount to a significant part of the total mass of a single NC. Importantly, surfaces can significantly impact the desirable electronic properties associated with the NC core atoms, most notoriously by providing low-lying electronic states that lead to efficient non-radiative excitonic recombination pathways.^{20,32,40,42-47} One approach to circumvent these processes consists in growing inorganic shells properly chosen so as to electronically-insulate the NC core from its surface,⁴⁸⁻⁵² but this “potential barrier” approach, which has proven extremely powerful in the utilization of NCs for photoemission applications, cannot be easily extended to instances where charge-carriers need to be exchanged across the NC surface.

1.3 Real-life Applications of NCs

Over the last decade, progress in applications of NCs in different technologies has been nothing short than outstanding. Below are a few examples of technologies that utilize NCs.

1.3.1 NCs in Displays and Lighting

One of the interesting applications of NCs is in lighting. Various types of light emitting devices (LED) have been established that utilizes colloidal NCs.⁴⁻⁶ Semiconductor NCs LEDs, also known as QD-LEDs, have narrow emission bands leading to high color purity. They have also shown

long-term stability against photochemical degradation. II-VI semiconductor NCs such as CdSe NCs are among popular materials for manufacturing QD-LEDs. CdSe NCs can cover the visible spectrum of 480 to 650 nm. To achieve a high PL quantum yield, NCs can be coated with a shell of few monolayers of another semiconducting material (core-shell NCs) to avoid the nonradiative pathways. Among the most commonly used core-shell NCs are CdS/ZnS and CdSe/CdS.

There are two categories of QD-LEDs; the first category is based on photo-excited QDs (PL QD-LEDs) and the second category relies on electro-excited QDs (electroluminescence QD-LEDs). The most frequently utilized type of QD-LEDs are PL QD-LEDs. QD-LEDs hold the promise of being utilized as the emissive components of the next-generation solid-state lighting through accurate control of color and an improved color-rendering index.⁵³

1.3.2 NCs in Bioimaging

Since NCs have tunable photoluminescence properties, narrow-width emission light across visible and near-infrared (NIR) spectrum can be generated from them. NCs have varying emission wavelengths which can be excited with one broadband excitation source allowing for multicolor images as multiple narrow-band emissions can be distinguished after excitation with a single light source.⁵³ This property is unique for bioimaging as typical organic fluorophores emit a broad visible emission with narrow Stokes shifts, which can overlap.⁵⁴ NCs are also highly resistant to photobleaching and due to their high surface to volume ratio, they are suitable for modifications to have biological functions aka biofunctionalization. The surface of the NCs can be tailored to interact with biological molecules through electrostatic, hydrogen-bonding, or specific ligand-receptor interactions.⁵⁵ There are several ways to make NCs more biocompatible. For example,

the surface of CdSe/ZnS NCs as one of the best candidates for almost all biological applications^{48,56} can be modified with dihydrolipoic acid to make them water-soluble.⁵⁷

NCs as fluorescent probes have been studied extensively by Alivisatos *et.al.* In of their initial studies, to establish the utility of NCs for biological staining, they fluorescently labeled 3T3 mouse fibroblast cells using CdSe/CdS core-shell nanocrystals and studied biological staining and diagnostics in mouse fibroblasts.⁵⁸ More recently, Fluorescent Au NCs were successfully used for in-vitro fluorescence bioimaging of human cervical cancer cells by Dal-Hee *et. al.*⁵⁹

Rojas and co-workers presented an approach to make biocompatible and photoluminescent hybrid materials comprised of carbon quantum dots and TEMPO-oxidized cellulose nanocrystals to improve cytocompatibility when interacting with human HeLa cells for bioimaging.⁶⁰

Overall, it's fair to say that the recent developments in NCs synthesis and modifications has opened up new possibilities for scientists to leverage the unique properties of NCs in interesting biological applications.¹²

1.3.3 Solar Cells, Photovoltaic Devices

One of the well-known applications of NCs is in the photovoltaic devices or solar cells. The emergence of semiconductor NCs and their photovoltaic properties, has created new possibilities to utilize them in energy conversion applications.⁶¹⁻⁶³

There has been a tremendous amount of research on solar cells specially in the 20th century due to huge interest in renewable energies.⁶⁴⁻⁶⁶

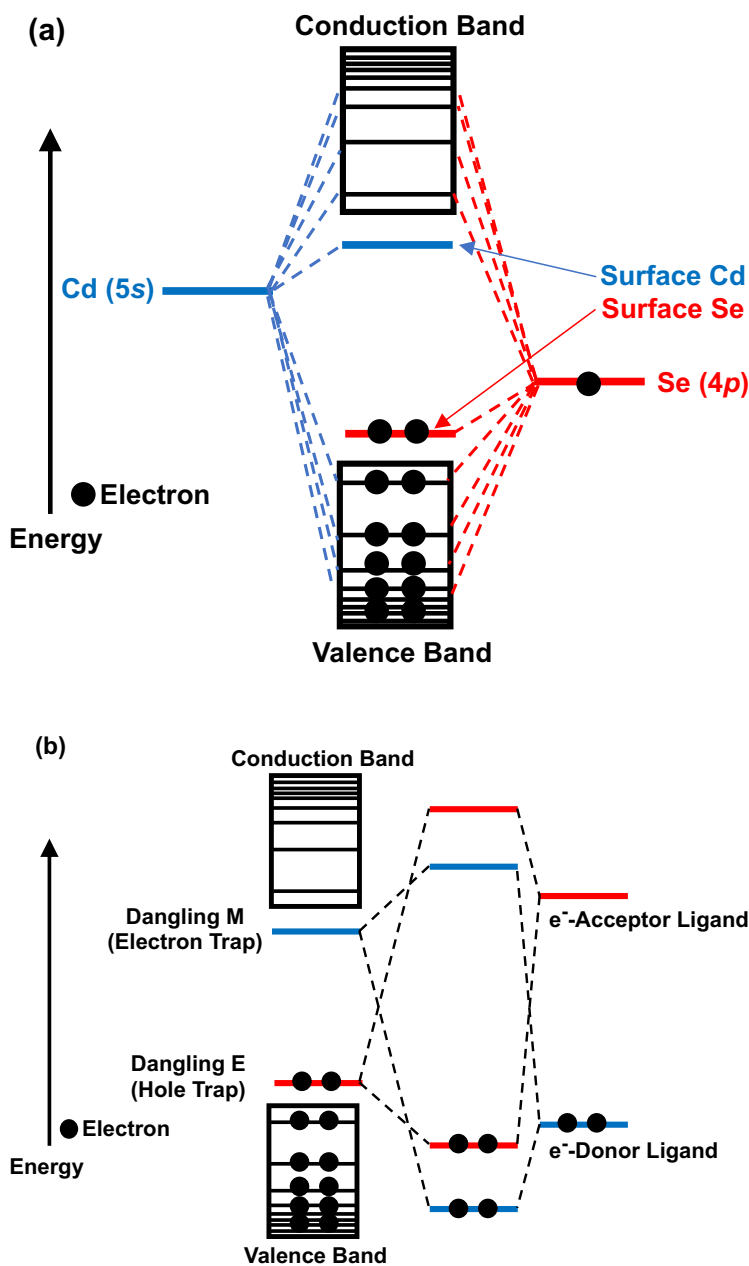
One of the major type of NC-based photovoltaic devices are quantum dot sensitized solar cells which work by injection of excited electrons from NC into a large bandgap semiconductor, such as TiO₂ or ZnO, which holes then will be scavenged by a redox couple.⁶⁶⁻⁷¹

1.4 Origin of Surface Defects: A Molecular Orbital Theory Approach

Semiconducting NCs lie between the molecules and bulk materials. They have the crystalline structure of the bulk (however more complicated due to the faceted compositing of their surface) but in a molecular dimension. Despite the complexity of NC structure, we can still use the molecular orbital theory to make a simplified model of the valence band and conduction band in NCs. Since the focus of this thesis is on II-IV semiconductor NCs, CdSe NCs which are one of the most studied materials of their class^{45,47,72-89} are discussed as an example here. The coordination number of Cd and Se (in a unit cell, zinc blende or wurtzite) is 4 and the Se atoms have a formal oxidation state of -2 and Cd has a formal oxidation state of +2. Se atoms are more electronegative and they lie lower in energy in the MO diagram compared to Cd atoms. The valence orbitals of Se (4p) form the valence bands. Because the repetition of the unit cells of NCs terminates at the surface, the atoms that are located on the surface are under-coordinated, leading to electronic states with energies that fall between the valence band and conduction band of NCs, (aka trap states). The chemistry of under-coordinated atoms depends on the structure and the coordination chemistry of the different facets.⁹⁰

In principle, the detrimental contribution of surfaces can be mitigated by providing adequate termination of the surfaces by ligating species that push the surface electronic states far from the lowest delocalized excited-state energy,^{20,32,40} (Scheme 1.3 shows the trap passivation by both e-acceptor and e-donor ligands) and indeed the literature is replete with empirical approaches that lead to various levels of improvement of the photoluminescence quantum yield (PLQY),^{32,91-96} the main metric by which the efficiency of non-radiative recombination processes is generally quantified. An important issue that severely limits the development of rational approaches to

control the behavior of NC surfaces is the complexity of their structure, which varies not only from NC to NC, but also from facet to facet or even from site to site.⁹⁷⁻¹⁰² Furthermore, surface-bound species are often labile and/or mobile, and thus exhibit complicated dynamical variations across complex free-energy landscapes with multiple nearly equivalent minima. Detailed and quantitative structural surveys of NC surfaces are consequently notoriously challenging tasks even for the simplest cases and using state-of-the-art analytical probes.^{45,72,73,95,103-112}



Scheme 1.3. Molecular orbital diagram of metal chalcogenide NCs a) without surface passivation, represents the hole and electron trap at the surface b) with surface passivation with e⁻-donor and e⁻-acceptor ligands. (adapted from ref 47)

1.5 Capping Ligands and Stoichiometry of NCs: CBM vs CBC Model

As seen in the previous section, ligands are the key concept in NCs surface chemistry as they contribute to the overall optoelectronic properties of NCs. Since the discovery of colloidal NCs,

many groups have used colloidal and organometallic chemistry to optimize the synthesis pathways of NCs and inevitably to this aim, many different ligands have been investigated as well.¹¹³⁻¹¹⁷ Trioctylphosphine was one of the first standard capping ligands.¹¹⁸ Later on, amines were realized to impact the PLQY of NCs.^{76,91,119-122} More recently, it has been concluded that carboxylic acid ligands are more efficient in capping the surface of NCs than phosphine-based ligands.^{73,111} Moreover, these ligand species need to be characterized by their type, binding modes, surface coverage, etc.¹¹⁰ Regardless of the nature of the ligands, they assure the charge neutrality of NCs which is necessary for their dispersion in non-polar solvents. There are two different notations by which we can describe the charge neutrality of NCs: the charge-orbital balance model (CBM) and the covalent bond classification (CBC). Though both models are useful for surface characterization studies, the CBM model is more applicable for doped NCs systems. (Note: these models are useful for non-stoichiometric NCs, as stoichiometric NCs have equal number of atoms and therefore are charge neutralized)

1.5.1 CBM Model

This model describes non-stoichiometric NCs by accounting for the extra ions (metal or non-metal) at the surface of NCs. It assumes that the atoms and ligands are in their thermodynamically most favorable oxidation states.¹²³ (In CdSe, +2 for Cd and -2 for Se and -1 for anionic ligands, 0 for non-ionic ligands). A formula can be derived to describe the charge balance in neutral NCs.

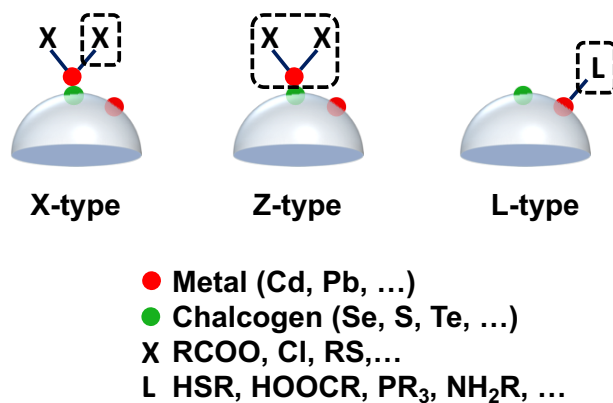
$$N_{exc} = \sum_i N_i q_i$$

where N_{exc} is the excess electrons in the valence orbitals. N_i is the number of constituent atoms or ligands of NCs and q_i is their oxidation states. For example, in a Cd rich CdSe NC with N extra Cd atoms, there would be $2N$ of anionic species such as carboxylate to maintain the charge

neutrality of the NCs ($N \times 2 + 2N \times -1 = 0$). If neutral ligands like phosphines or amines are present at the surface, they do not contribute to the equation as the charge on those ligands is 0. If $N_{exc} \neq 0$, then the NCs are doped and depending on the sign of N_{exc} , NC is n-doped ($N_{exc} > 0$) or p-doped ($N_{exc} < 0$). However, this model is more useful when the NCs are not charge balanced, as first proposed and used by Vozznyi et al. to model doped NC film.¹²³

1.5.2 CBC Model

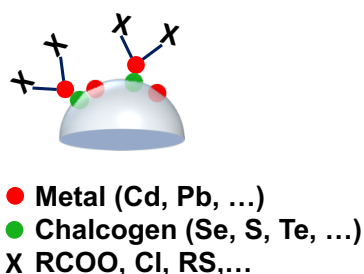
This model was first proposed by Green in 1995 and was used mainly for organometallic compounds.¹²⁴ Recently, this model was adopted for studying the surface chemistry of NCs.^{74,95,102,105,125} Within this framework, all species (that is, both the inorganic core and ligand shell) are taken as neutral. The core of NCs consists of equal number of the constituent atoms (e.g. in $[\text{Cd}_n\text{Se}_m]$, $n=m$). In this model, ligands are categorized based on the number of electrons they donate. Scheme 1.4 shows this classification. X-type ligands are one electron donors.



Scheme 1.4. Ligands used in passivation of the surface of NCs in the Covalent Bond Classification model

L-type ligands are 2-electron donors and Z-type ligands are 2-electron acceptors. In all cases, there is a covalent bond between the ligands and surface atoms where both surface atoms and ligands have each one electron. X-type ligands are often the conjugated base versions of their HX acids.

L-type ligands can be the HX form of the acid or can be phosphines, amines or thiols. Z-type ligands are less common, but the common forms are CdX_2 , ZnX_2 , etc. (Metal complex that acts as a Lewis acid). Going back to the metal rich NCs, we use the example of Cd-rich CdSe NCs; we picture a neutral core of CdSe with equal numbers of Cd and Se atoms which CdX_2 complexes act at Z-type to passivate Se surface atoms. Since the Se atoms share their electron to Z-type CdX_2 , Se atoms can be considered as Lewis base and Z-type CdX_2 ligands are considered Lewis acids. Group VI Z-type ligands at the surface of NCs are essential as they bind to under-coordinated surface atoms and heal the surface traps. For under-coordinated metal atoms at the surface, there are variety of ligands (L-type), the non-metal surface atoms can almost only be passivated with Z-type ligands. However, due to sterically hindrances, not all the surface atoms can be passivated by ligands.

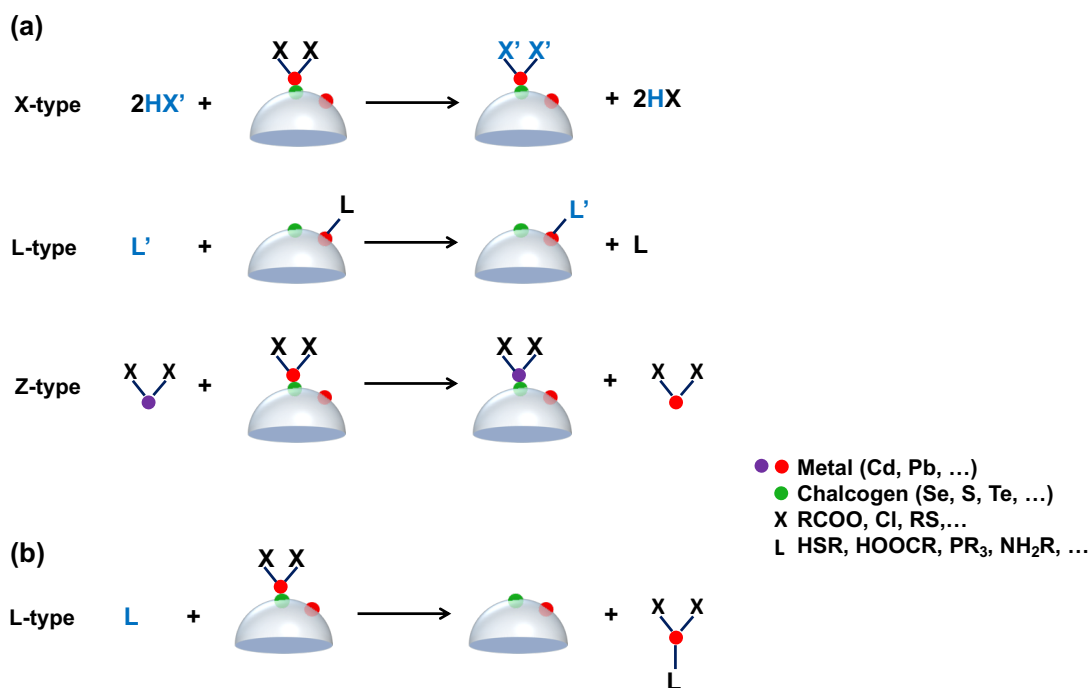


Scheme 1.5. Metal-rich metal chalcogenide NCs

1.6 Ligand Exchange and Ligand Displacement

Long chain ligands that are used in synthesis of NCs are known to lead to good size distributions by controlling the mechanism of growth and even the crystal structure of NCs. However, these ligands are not suitable for all kinds of applications and hence, need to be exchanged for more suitable ones based on specific applications. Such exchange processes also need to maintain the surface passivation to prevent charge trapping. Scheme 1.6 depicts the different types of ligand

exchanges including X-type, L-type and Z-type. These exchanges are mostly accompanied by some kind of complications including occurrence of a pathway different than the desired ligand exchange reaction. For example, a simple X-type exchange that might appear straight forward, will often be accompanied by other types of ligands exchange (discussed in detail in Chapter 4). One of the major undesired pathways is the displacement of the ligand from the surface of NCs and consequently creation of the surface defects on the surface. It has been realized that amines can etch the surface.⁸⁴ A thorough 2013 study by Anderson et al. showed that L-type ligands can facilitate the displacement of Z-type ligands and create defects on the surface.⁹⁵ Although the absence of ligands on surface sites of any NC leads to creation of surface traps, the traps that are created due to removal of Z-type ligands are known to make deep surface traps that are the most responsible for quenching of photoluminescence.^{45,47,101} Therefore, it is of great importance to study the displacement of Z-type ligands.



Scheme 1.6. a) Different type of ligand exchange and b) Ligand displacement, at the surface of NCs

1.7 Characterization Techniques: Semiconducting Core and Ligand Shell

Since the discovery of semiconductor NCs, various techniques have been used to investigate the optical properties and electronic states of NCs. By contrast, it took many years to develop techniques to directly monitor the surfaces of NCs. Common ways to characterize NCs are typically comprised of TEM, ICP and UV-Vis spectroscopy. The first method to calculate the size of NCs was proposed by Brus,³³ based on the effective mass approximation model, which fails to correctly estimate the confinement energy of the smallest NCs. Later on, empirical formulas were developed to calculate the size and concentration of cadmium chalcogenide NCs¹²⁶ from optical data. The polynomial fits directly give the size of NCs if the NCs' absorption wavelength at the lowest excitonic peak is known. In addition, other empirical formulas have been developed to assess concentration of NCs from the absorption spectrum of NC.¹²⁶ However, the original study overestimated the concentration of metal chalcogenide NCs, and in 2009, Mulvaney *et. al.* refined the empirical formula to estimate the size and concentration of CdSe NCs.¹²⁷ In this method, coupled plasma-optical emission spectroscopy (ICP-OES) was utilized and results were combined with TEM which resulted in two empirical formula, one to estimate the size and the other to estimate the extinction coefficient.

For surface chemistry studies require that the concentration of NCs for surface coverage measurements is known accurately. Therefore, it is important to choose the most accurate model to calculate concentrations of NCs.

In order to directly look at the surface of NCs, XPS and XRD are used to get information about stoichiometry, oxidation states and crystalline structure of NCs respectively.¹²⁸ IR can provide information on ligand bindings. For example, the shift of ligands IR peaks to lower energies is indicative of surface binding.⁸⁶ In some NCs with air-sensitive surfaces such as Si NCs, IR can

detect the oxidation of surface (Si-O bond). However, IR measurements are mostly qualitative and do not account for the number of ligands. Photoluminescence measurements and adsorption isotherm methods have been used to estimate the number of adsorbed ligands on the surface of NCs Indirectly but they are not accurate as the change in photoluminescence could be due to several different parameters.^{26,129} ^1H NMR techniques have been used to study the NCs surface ligands,^{130,131} but the high power and applicability of NMR was not realized till early 2000.^{106,132} Free ligands have much faster tumbling rates than the bound ligands attached to the surface. This is the key point to distinguish the bound from free ligands using NMR. Not only signals from the bound and free ligands are much different from each other,^{133,134} (free ligand = sharp and bound ligands = broad), but the chemical shift of the bound ligands is also shifted downfield as the electrons are being deshielded. This phenomenon is more prominent in the signal of the atom closest to the surface. For example, in ^1H NMR of oleate-capped CdSe NCs, the alpha protons of oleic acid are shifted downfield more so than the terminal methyl peaks.⁷⁷ Other useful NMR techniques include 2D NMR spectroscopies.¹⁰⁶ Diffusion order spectroscopy (DOSY) can be used to distinguish between bound and free ligands based on the magnitude of their diffusion. One drawback of NMR spectroscopy is the need for high concentration of NCs for acceptable signal to noise. Although this can be overcome by scaling-up the synthesis, the cleaning processes are time consuming. The other problem in characterizing NCs is combining NMR data created from high concentrations of NCs with optical spectroscopy data which is obtained using almost two orders of magnitude lower concentrations. Although dilution of NCs affect their inter-particle space and the viscosity of the suspension, these changes are usually neglected. Other than ^1H NMR, P, Cl and F NMR techniques can also be used to study surface ligands. In some cases, Cd and Se solid state NMR techniques can also be used,¹⁰³ but these techniques are less popular due to the need

for significantly more material compared to ^1H NMR, and their long relaxation times, leading to long experiment times.

Given all the methods discussed above, combination of NMR techniques with optical spectroscopy, TEM and IR have facilitated the study of surface chemistry of NCs. Changes in optical properties can be directly correlated to the changes in surface, whether it occurs due to healing or creating a defect, the changes in ligands indirectly but accurately provide information about surface defects.

1.8 Thesis Structure

The prime objective of this study is to gain insight on the complexity of the surface chemistry of II-VI semiconductor NCs and the effect of NCs surface chemistry on the optical properties of NCs. To clarify “the why” and “the how” of this objective, this thesis is structured as follows:

after our brief discussion on the history, importance, and interesting applications of NCs, along with fundamentals and theories behind their chemistry and function in this Chapter, we discuss our experiments and findings in Chapters 2 to 5 following by concluding remarks in Chapter 6.

In Chapter 2, the equilibria from Z-type ligand displacement on the surface of CdSe NCs was investigated using NMR which revealed presence of two types of surface defects. In Chapter 3, these surface defects were correlated to PL quenching efficiency of NCs.

In Chapter 4, we discuss the undesired pathways that occur during X-type ligand exchange experiments by studying X-type ligand exchanges on CdSe NCs and various types of ligands with different sterics and functional groups.

We also investigated surface defects on CdS NCs to compare our findings with those of CdSe. Similar to Chapter 2 and 3, in Chapter 5, we studied the equilibria from Z-type ligand displacement on the surface of CdS NCs using NMR and PL.

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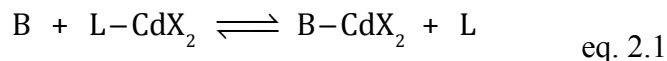
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**Chapter 2: Insights Into the Structural Complexity of the Colloidal NCs
Surfaces: Studying the Stability of Z-Type Ligands on the Surface of NCs**

2.1 Introduction

Studying charge trapping processes is of great importance as the existence of charge traps at the surface of semiconductor NCs causes energy losses. As it has been realized by a few groups, the removal of Z-type ligands from the surface of NCs leads to the creation of surface hole trap.^{1,2} We present here a detailed investigation of the surface of CdSe NCs, one of the most studied materials of its class.¹⁻²¹ We specifically focused our attention to zinc-blende (cubic) CdSe NCs obtained from carboxylate precursors; these materials have a nonstoichiometric cadmium-rich composition, which arises from the presence of neutral cadmium carboxylate (CdX_2) complexes on the NC surfaces. A valuable model to describe the surface of these NCs has been formulated by Owen and collaborators,²¹⁻²⁴ whereby these CdX_2 complexes are considered as Lewis acid acceptors that bind unpassivated surface selenide sites (Se^{2-}), yielding stable surfaces and likely playing an important role in favoring the zinc-blende morphology during the growth process. These surface-bound CdX_2 complexes can be displaced by simple (Lewis) acid/base exchange reactions taking the following general form:



where B represents a generic Lewis-basic site at the surface of the CdSe NCs (sometimes referred to as a Se^{2-} “dangling bond”) and L is a soluble Lewis base. The displacement of CdX_2 from the surface is associated with a strong reduction of the PLQY, betokening enhanced nonradiative relaxation to surface states that have been associated with hole-trapping processes.^{1,2} In this Chapter, we studied the Z-type exchange process on the surface of CdSe NCs. We created traps on the surface of CdSe NCs by displacing the CdX_2 groups and monitored this process using ^1H NMR spectroscopy. Then a model was developed to describe these Z-type displacement process.

Moreover, we studied the thermodynamics of surface binding to these Z-type ligands using temperature dependent ^1H NMR spectroscopy.

2.2 Experimental Details

2.2.3 Chemicals

Cadmium nitrate tetrahydrate ($\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, 98%), oleic acid (90%), octadecene (ODE, 90%), N,N,N',N',-tetramethylethylene-1,2-diamine (TMEDA, 99%), myristic acid (>99%), selenium dioxide (SeO_2 , %99.9), and ferrocene (Fc, 98%) were purchased from Sigma Aldrich. Ethyl acetate (HPLC grade), toluene (ACS grade), sodium hydroxide (>98%), anhydrous methanol (HPLC grade) were purchased from Macron Fine Chemicals. Pentane was purchased from Fisher Chemical, and *d*-toluene was purchased from Cambridge Isotope Laboratories (CIL). Ethyl acetate was degassed by bubbling nitrogen for 2 h and dried over molecular sieves for at least two days prior to use. Oleic acid was degassed through 3 cycles of vacuum/purge with nitrogen and kept under nitrogen atmosphere just prior to use. Ferrocene was recrystallized from methanol solutions. Toluene and pentane were dried using an alumina distill columns. TMEDA was stored in the glovebox and taken out for sample preparation. Other chemicals were used as received.

2.2.4 Synthesis of Cadmium Myristate

Cadmium myristate was prepared by adapting a literature protocol.²⁵ 4.63 g (15 mmol) cadmium nitrate tetrahydrate is weighed and transferred to a 500 mL beaker with 150 mL anhydrous methanol. The mixture was sonicated until all cadmium nitrate was dissolved, and the solution was transferred to a 250 mL addition funnel. Separately, 1.2 g (30 mmol) crushed NaOH, 6.85 g (30 mmol) myristic acid and 1.5 L anhydrous methanol were added to a 2 L flask; the mixture was

heated in a water bath at 40 °C for 2 min, then sonicated until a single-phase solution of sodium myristate is formed in about 10 minutes. The solution was then transferred to a 2 L round bottom flask with a stir bar, and positioned over a magnetic stirrer. The cadmium nitrate solution was then added dropwise to the sodium myristate solution over the course of 3 h, under stirring. The resulting cadmium myristate was then filtered and washed five times with anhydrous methanol (200 mL) and air-dried for 24 h, then crushed and transferred to a 250 mL round bottom flask, and finally sealed and dried under vacuum (50-70 mTorr) for 24 h at 50 °C. The yield was typically 82%. The product was characterized using melting point, ¹H NMR and FTIR spectroscopies. ¹H NMR (500 MHz, CDCl₃): δ= 0.89 (6H, -CH₃, m), δ= 1.27(32H, -CH₂, b), δ= 2.36 (4H, α-CH₂, t), δ= 1.56 (4H, β-CH₂, m). FTIR: ν= 1384 cm⁻¹ (s, CO₂ sym), 1560cm⁻¹ (s, CO₂ assym), 2852 cm⁻¹ (s, C-H assym), 2920 cm⁻¹ (s, C-H, sym).

2.2.5 Synthesis and Purification of CdSe NCs

Cadmium selenide was prepared following a literature protocol.²⁶ 5.67 g (10 mmol) cadmium myristate, 1.11 g (10 mmol) selenium dioxide powder and 630 mL octadecene were placed in a 1 L three-neck round bottom flask equipped with a water condenser. The flask was degassed in three cycles of 20 min each, then heated to 240 °C over 7 min. Heat was maintained until the desired size was reached, which was checked by taking the absorption of a diluted aliquot of the reaction suspension (*vide infra*). Heat was consequently removed and 10 mL (32 mmol) of degassed oleic acid were injected via a syringe over 20 min while the flask was allowed to cool down back to room temperature, followed by continuous stirring for 15 h under nitrogen flow. Octadecene was then removed by vacuum (50-70 mTorr) distillation at 130 °C, after which 20 mL dry toluene was added to the dark red concentrated and impure NCs suspension, which was finally

transferred into four test tubes and centrifuged for 20 min at 6000 rpm. This step precipitated the unreacted precursors. The supernatant was then transferred in 1 mL portions into test tubes, and 10 mL ethyl acetate was added to each tube to precipitate the NCs. After centrifugation at 6000 rpm, the supernatant was removed and the NCs resuspended in 1 mL of pentane; the entire cleaning cycle was repeated four times. Finally, 10 mL ethyl acetate was added to each test tube (with only the pellet of particles), followed by sonication for 15 s. The test tubes were then centrifuged (6000 rpm) and the supernatant removed. The NCs were dried over nitrogen for 24 h, and then suspended in enough *d*-toluene to make a 85.8 μ M stock solution of NCs, as assessed by UV-Vis spectroscopy, following the empirical calibration curve established by Mulvaney et al.²⁷

2.2.6 Optical Spectroscopy

Absorption spectra were collected on an OLIS17 UV/vis/NIR spectrometer in 1 nm increments, using 1 cm pathlength quartz cuvettes. Spectra were measured in toluene after the toluene background was subtracted. Continuous wave (CW) photoluminescence (PL) measurements were performed using a 0.55 m focal length spectrometer (iHR550, f/6.4, 150 grooves/mm grating blazed at 500 nm) equipped with a CCD detector (Horiba Symphony II nitrogen cooled deep depleted CCD), and exciting at 450 nm using a tungsten lamp coupled to a 0.32 m focal length monochromator (Horiba iHR320, f/4.1, 600 grooves/mm grating blazed at 500 nm). PLQY were measured with an absolute PL quantum yield spectrometer (Hamamatsu Quantaurus, C11347), using toluene suspensions prepared as described below and exciting at 400 nm.

2.2.7 Diffusion Ordered Spectroscopy (DOSY) on the Mixture of CdSe NCs and TMEDA

All diffusion experiments were run with the DBPPSTE pulse sequence. A total of 15 gradient values were used for diffusion measurement. Gradient levels were chosen such that signal intensity for the highest power gradient was 10% of that for the lowest power. The deuterium lock settings were carefully optimized to minimize artifacts. 232 scans per each gradient value were used to obtain sufficient signal to noise. Gaussian apodization of 1.3 Hz was applied to the raw fids prior to Fourier transform. Zero filling and baseline correction were applied to all spectra prior to DOSY transform. (see Appendix, SI 2.16)

2.2.8 Powder X-ray Diffraction

XRD data was collected on a Bruker D8 DaVinci diffractometer equipped with Cu K α radiation (0.15406 nm) line source operating at 40 kV and 40 mA. Samples were placed in a PVMA sample holder with zero-background silica plates by drop-casting concentrated (~86 μ M) CdSe suspensions in hexane. The sample was scanned from 20° - 70° using 10 s/scan. Diffraction lines are compared to the JCPDS card number: 00- 019-0191. (see Appendix, SI 2.11)

2.2.9 Transmission Electron Microscopy (TEM)

TEM images were recorded on a JEOL 2200 FS microscope operating at 200 keV. Formvar-coated copper grids (Ted Pella, 01824) were used as nanocrystal supports for TEM. Toluene suspensions of CdSe NCs were drop-casted on the TEM grid prior to the measurements. Images were analyzed using ImageJ. (see Appendix, SI 2.10)

2.2.10 Fourier Transform Infrared (FTIR) Spectroscopy.

FTIR spectra were obtained from a Mattson Galaxy 3020 in the 4000 to 400 cm^{-1} range at a resolution of 4 cm^{-1} for 16 scans. Background spectra were measured on a clean potassium bromide disk (KBr, 2.5mm $\times$ 4mm, International Crystal Laboratories, no. 0002C-74). Samples were drop-cast on the KBr disk after the background subtraction. (see Appendix, SI 2.14)

2.2.11 Reaction of CdSe NCs with Diethylzinc

As previously shown by Chen, Owen and co-workers,⁴ the addition of diethylzinc to NCs displaces ethane, which is indicative of the presence of protons which have been associated with the presence of residual carboxylic acid ligands at the surface of the NCs. Following the same procedure, concentrated solutions of NCs (0.5-1 mM in NCs and 100-300 mM in carboxylate/carboxylic acid) in *d*-benzene (dried over calcium hydride and distilled, degassed) were prepared in a glovebox under dimmed light conditions. 10 μL of each sample was taken and diluted to measure the concentration of NCs. Vials are then covered with black tapes to keep the sample in the dark. 40 μL of ferrocene (19 mM in *d*-benzene) was added as internal standard. For each size of NCs, neat diethylzinc (roughly double the equivalent amount of ligands) was added in a closed system and the mixture was allowed to stir for 10 minutes and then the mixture was transferred to a J-Young NMR tube and NMR spectra were measured. A sharp singlet peak at $\delta = 0.8$ arises from solubilized ethane released from the reaction of diethylzinc and carboxylic acid. This peak and ferrocene were fitted using Gaussian fits for the quantitative analysis of the amount of ethane. (see Appendix, SI 2.14)

2.2.12 Sample Preparation for ^1H NMR

Toluene solutions of TMEDA were prepared to cover a range of concentrations from 0.01 M to 6.7 M (neat TMEDA). Mixtures of CdSe NCs and TMEDA in *d*-toluene were prepared, each containing 600 μL of 85.8 μM CdSe NCs ($[\text{CdSe NC}] = 78 \mu\text{M}$), 30 μL of a given TMEDA solution ($[\text{TMEDA}]$ varying from 0.1 mM to 273 mM, or about 1:1 to 1:3500 CdSe NC:TMEDA ratios) and 30 μL of 4.2 mM ferrocene solution ($[\text{Fc}] = 0.19 \text{ mM}$); each sample was allowed to equilibrate after mixing by waiting 30 min prior to measurements.²² ^1H NMR spectra were collected on an Agilent DDR2 500 MHz NMR spectrometer equipped with 7600AS 96 sample auto-sampler running VnmrJ 3.2A, using a 45° pulse angle / 10 s relaxation time sequence and 32 scans (See Appendix, Sections SI 2.1 and 2.2). Spectra were analyzed using MestreNova (Mestrelab Research S.L.) and Igor Pro 7.05 (Wavemetrics).

2.2.13 Ligand Concentration and Surface Coverage Calculations

The integration of terminal methyl ($-\text{CH}_3$) peak at 1 ppm in ^1H NMR each spectrum was recorded and referenced to the integration of the ferrocene protons at 4 ppm, allowing for the calculation of the total concentration of carboxylate ligands. From charge compensation considerations, the number of cadmium carboxylate complexes (CdX_2) is half that of the carboxylate ligands. The ligand coverage was then calculated from the number of cadmium carboxylate ligands per NC (concentration of ligands divided by concentration of NC) and the surface area of the NC, assuming spherical shape (as confirmed by TEM). Although the surface coverage involves a mixture of both oleate and myristate species, both types of ligands behave identically with regard to exchange reactions,²⁸ which we further confirmed by NMR by monitoring terminal methyl protons (which account for both types of carboxylates) as well as vinylic protons (which belong only to oleate

ligands). Specific ligand exchange reactions were monitored subsequently by monitoring exclusively the vinylic peaks. Residual protonated carboxylates (oleic or myristic acid) were observed by displacement of ethane with diethyl zinc added to isolated and cleaned NC samples (assuming there are no other sources of protons); the integration of the ethane ^1H NMR peak suggested that these species form at most 10% of the total carboxylate population, which is consistent with values reported by Chen *et al.*⁴ This puts at ~5% the overestimation of the cadmium coverage values reported herein. Further details are given in the Appendix SI 2.3.

2.3 CdX_2 Displacement from CdSe NCs

The absorption and photoluminescence spectra of a clean suspension (that is, without free ligands; *vide infra*) of 3.8 nm CdSe NCs are shown in Figure 2.1.

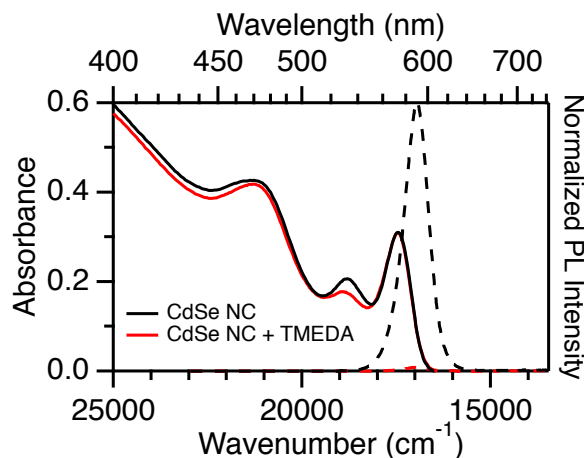


Figure 2.1. Absorption (solid) and photoluminescence (dashed) of 3.8 nm CdSe NCs ($1 \pm 0.1 \mu\text{M}$) before (black) and after (red) addition of TMEDA (3.6 mM), illustrating the impact of displacing CdX_2 complexes from the surface of CdSe NCs.

Upon addition of 3,500 equivalents of TMEDA per NC, the PLQY drops by more than two orders of magnitude, from 10% to <0.1%, which is associated with the displacement of CdX_2 complexes in solution (eq. 2.1), which can be quantified by ^1H NMR.²² The overall ^1H NMR spectra of 3.8 nm

CdSe NCs, with and without TMEDA, are presented in Figure 2.2(a). Given the nature of these colloidal NCs (zinc blende CdSe NCs capped with oleate/myristate surfactants – see Experimental Section and Appendix, SI 2.3 and 2.4 for more details), these spectra give a detailed account of the surfactants bound to the surface of the NCs, as well as of any organic species freely diffusing in solution. Of particular interest are the integrated intensities of bands associated with specific ligands, as they allow a direct evaluation of the NC surface densities of these species to be evaluated. Direct comparison of the integrated intensity of terminal methyl ($-\text{CH}_3$) groups, located at 1 ppm in Figure 2.2(a), with an internal standard (ferrocene), yields a value of 190 ± 4 carboxylate (X^-) ligands per NC, corresponding to 95 ± 2 CdX_2 complexes per NC for the 3.8 nm CdSe NCs sample shown in Figure 2.3. This value corresponds to a surface coverage of 4.2 ± 0.6 carboxylate $\cdot\text{nm}^{-2}$, or, equivalently, 2.1 ± 0.3 CdX_2 nm^{-2} , a value close to the largest coverage of CdSe NC by carboxylates reported in the literature.²⁹⁻³¹

Furthermore, the ^1H NMR spectrum of as-prepared CdSe NCs indicates that, prior to the addition of TMEDA, all carboxylate species are quantitatively bound to the surface, without any measurable trace of unbound carboxylate species. This is indicated by the single broad feature around 5.7 ppm, better seen in the zoomed-in perspective of Figure 2.2(b), which is assigned to the vinylic protons of surface-bound oleate ligands. Upon addition of TMEDA to the CdSe NCs suspension, the integrated intensity of this broad feature decreases, concomitantly with the increase of a sharp feature at 5.47 ppm, which is readily assigned to carboxylate species that are unbound from the surface of CdSe NCs (hereby labeled “free”).³¹⁻³³ Importantly, as shown in Figure 2.3, the decrease in intensity from the broad band is exactly matched by the increase in the integrated intensity of the sharp band, consistent with the assignment of a single species (the carboxylate ligands) being exchanged dynamically under the influence of the TMEDA species. The nature of

this equilibrium was discussed in great details previously²² as a L-type ligand-induced displacement of surface-bound cadmium carboxylates (CdX_2) complexes into solution, as shown in a general form by eq. 2.1, where the soluble Lewis base (L) was chosen here to be N,N,N',N'-tetramethylethylenediamine, TMEDA, shown in Scheme 2.1 (we note that formally TMEDA, a bidentate donor, would be referred to as a L_2 ligand and the resulting free complex as CdL_2X_2 in the CBC;³⁴ we use the shortcut notation throughout here). The CdX_2 complex behaves as a Lewis acid (Z-type ligand) and eq. 2.1 thus describes the Lewis acid/base exchange of a Z-type ligand (the cadmium carboxylate complex) between two Lewis base groups: (i) the surface of the NC (B) and (ii) TMEDA (L).

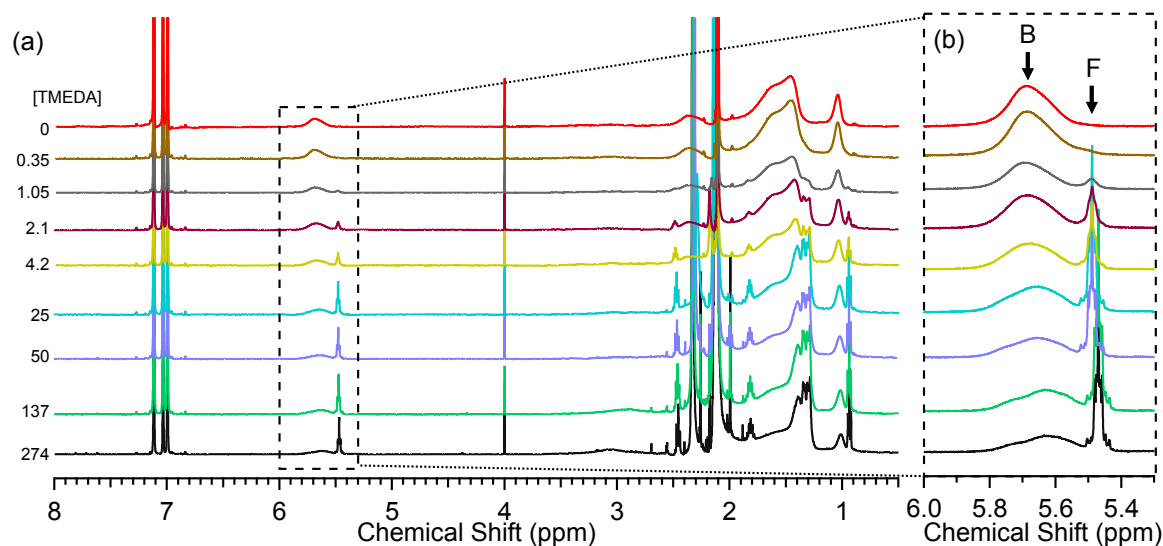


Figure 2.2. a) ^1H NMR Spectra of 3.8 nm CdSe NCs (78 μM in d-toluene) in presence of different concentrations of TMEDA (10 points are selected, values in mM listed on the right-hand side). b) Zoomed-in spectra (from panel (a)) between 5 and 6 ppm showing the bound (B) and free (F) cadmium carboxylates (CdX_2).

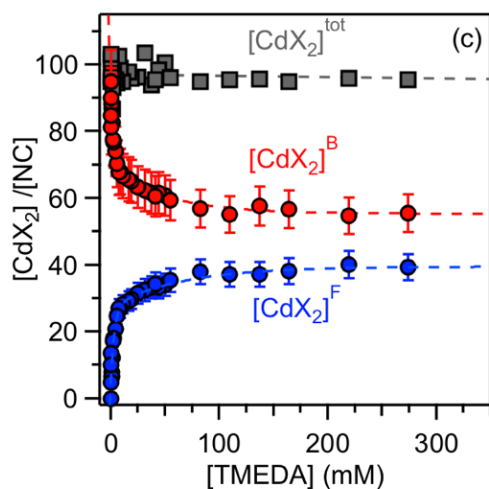
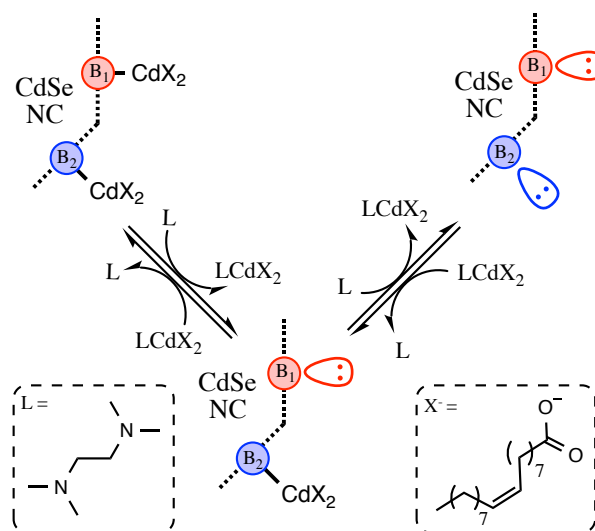


Figure 2.3. Total number of CdX_2 units per CdSe NC (gray squares), number of CdX_2 units bound to the surface of CdSe NCs (red circles), and number of CdX_2 units displaced by TMEDA from the surface of CdSe NCs (blue circles).

Interestingly, the trends in Figure 2.3 suggest that the simple relation given by eq. 2.1 cannot account fully for this dynamical exchange: whereas almost a third of the surface-bound CdX_2 can

be displaced upon addition of 10 mM of TMEDA (about 125 equivalents per NC here), the further addition of over 250 mM of TMEDA has a much-reduced impact overall, bringing the total CdX_2 displacement to 40% of the initial value. This general feature is observed for all samples we investigated, irrespective of the NC size (see Appendix, SI 2.6). We show below that this behavior can be readily explained by invoking the existence of two separate CdX_2 binding sites at the NC surface, each with their own free energy of binding and role in deactivating the excited state of CdSe NCs.



Scheme 2.1. Surface exchange processes involving two Lewis-basic surface sites, B_1 and B_2 , with different binding affinities to a generic CdX_2 Lewis-acidic moiety.

2.4 Analysis of the Ligand-Exchange Equilibrium

We begin by describing quantitatively the equilibrium involving a single type of surface sites (B), which can be either open (vacant) or occupied by a CdX_2 complex, itself being involved in a dynamic exchange between the free Lewis base (L) and the Lewis-acidic surface site (B), as given by eq. 2.1 above. The equilibrium constant for this equilibrium is given by:

$$K_{eq} = \frac{[B-CdX_2][L]}{[B][L-CdX_2]} = \frac{[B-CdX_2]}{[B]} \phi \quad \text{eq. 2.2}$$

where as an approximation molarities are invoked instead of activities. We note that eq.2.1 describes the binding of the CdX_2 complex onto the NC surface, which is the reversal of the displacement process monitored in Figure 2.2; as shown below, this form yields simpler equations to describe quantitatively the equilibrium process; this convention will be kept throughout the study, where larger equilibrium constants are associated with stronger NC- CdX_2 bonds (*i.e.* less easily displaced by TMEDA). The parameter ϕ in eq. 2.3 designates the ratio of unbound (“free”) vs. bound TMEDA:

$$\phi = \frac{[L]}{[L-CdX_2]} = \frac{[L]_0}{[L-CdX_2]} - 1 \quad \text{eq. 2.3}$$

and is a quantity directly obtainable from NMR data such as that presented in Figure 2.2 ($[L]_0$ is the total concentration of TMEDA). The total number of binding sites per NC, N , is given by the sum of occupied and vacant (open) sites:

$$N = \frac{[B-CdX_2] + [B]}{[NC]} \quad \text{eq. 2.4}$$

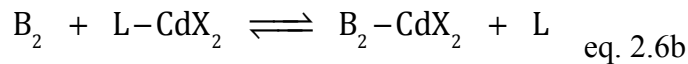
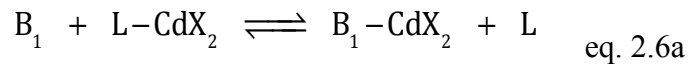
Combining eqs. 2.2 and 2.4 yields an equation to describe the equilibrium process in terms of directly measurable quantities:

$$\frac{[NC]}{[B-CdX_2]} = \frac{1}{N} + \frac{1}{N \cdot K_{eq}} \phi \quad \text{eq. 2.5}$$

Eq. 2.5 shows that a plot of $[NC]/[B-CdX_2]$ (the inverse of the number of bound CdX_2 complexes per NC, directly obtained from the NMR data in Figure 2.2(b)) vs. ϕ should yield a line of slope

$(N \cdot K_{eq})^{-1}$ and intercept N^{-1} . Figure 2.4(a) reports the same data shown in Figure 2.3 for the 3.8 nm CdSe NCs using the formalism of eq. 2.5. Consistent with the conclusion drawn above in Section 2.3, the data shows two different regimes, each converging to linear trends in the limits of small and large TMEDA concentrations. Obviously, the assumption of a single binding site is too restrictive, and a more sophisticated equilibrium model involving two types of surface sites is needed to describe the data in Figure 2.4(a). We note that the two equilibria are not well separated, which implies that both equilibrium regimes are coupled to each other (at least in the intermediate region) and need to be considered simultaneously.

As above, we define these exchange reactions as being associative in terms of the CdX_2 complex, and use the labels B_1 / B_2 and $B_1\text{-CdX}_2 / B_2\text{-CdX}_2$ to distinguish the two types of open (vacant) and occupied surface sites, respectively:



The equilibrium constants for each exchange reaction are given by:

$$K_1 = \frac{[B_1\text{-CdX}_2][\text{L}]}{[B_1][\text{L-CdX}_2]} = \frac{[B_1\text{-CdX}_2]}{[B_1]} \phi \quad \text{eq. 2.7a}$$

$$K_2 = \frac{[B_2\text{-CdX}_2][\text{L}]}{[B_2][\text{L-CdX}_2]} = \frac{[B_2\text{-CdX}_2]}{[B_2]} \phi \quad \text{eq. 2.7b}$$

The analysis of ^1H NMR does not allow us to distinguish between the two types of sites (B_1 and B_2), as the deconvolution of free and bound cadmium carboxylates peaks yields only the total concentration of TMEDA-bound CdX_2 species, $[\text{L-CdX}_2]$, as well as the total concentration of surface-bound CdX_2 species, $[\text{B-CdX}_2]$:

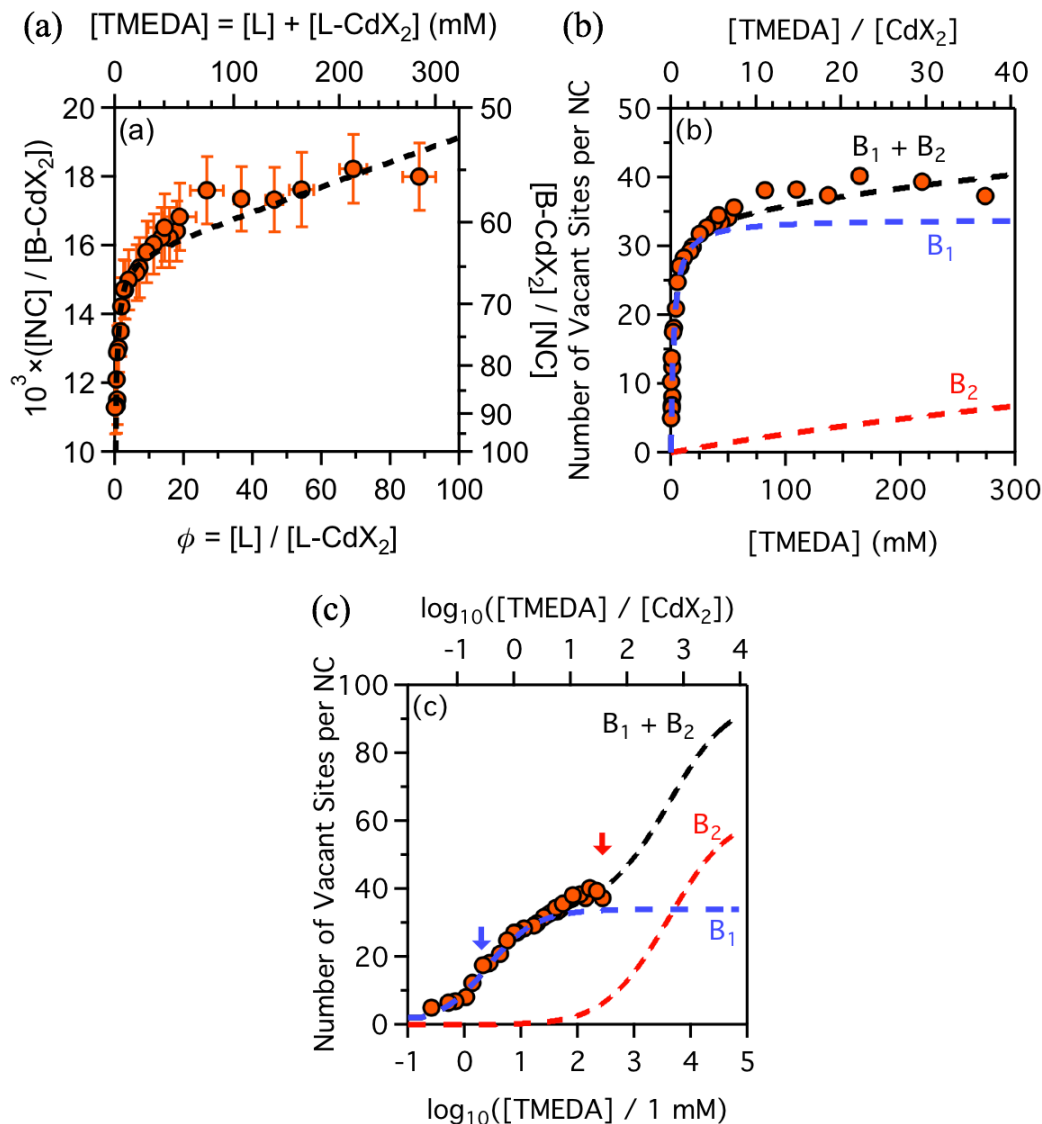


Figure 2.4. a) TMEDA titration of 3.8 nm CdSe NCs (78 μM in *d*-toluene), modeled with eq. 2.11 (black dashed line). The top axis is a transformation of the ratio ϕ reported on the bottom axis (eq. 2.13), and represents the total TMEDA concentration in solution (note the non-linear scale). The right axis is a reciprocal transformation of the left axis, showing the number of bound CdX_2 units per NC. b) Calculated number of vacant sites at the surface of the 3.8 nm CdSe NC sample, for each type of site, B_1 : blue, B_2 : red, all sites: black. The data for the total number of open sites, equivalent to the number of CdX_2 ligands that are removed from each surface site as a function of added TMEDA, is shown by the orange circles. The top axis is linearly scaled to represent the TMEDA concentration in total equivalents of CdX_2 complexes. c) Same data/calculated curves as panel b), but for a wider range of TMEDA concentrations and on a logarithmic scale. The largest magnitudes shown here correspond to unrealistically large concentrations, and are shown here for discussion purposes. The two arrows indicate the TMEDA concentrations where temperature-dependent studies (Figure 2.5) where conducted (blue arrow: 2 mM, red arrow: 274 mM).

$$[B-CdX_2] = [B_1-CdX_2] + [B_2-CdX_2] \quad \text{eq. 2.8}$$

The total number of surface sites, N_{tot} , is given by:

$$N_{tot} = N_1 + N_2 = \frac{[B-CdX_2] + [L-CdX_2]}{[NC]} \quad \text{eq. 2.9}$$

where we assume full coverage of the surface in the absence of TMEDA (*vide infra*). The coupled exchange reactions given by eqs. 2.6a, and 2.6b are fully described by the following equation, which invokes the same two observables as eq. 2.5 above ($[NC]/[B-CdX_2]$ vs. ϕ):

$$\frac{[NC]}{[B-CdX_2]} = \frac{\phi^2 + (K_1 + K_2) \cdot \phi + K_1 \cdot K_2}{(N_1 \cdot K_1 + N_2 \cdot K_2) \cdot \phi + N_{tot} \cdot K_1 \cdot K_2} \quad \text{eq. 2.10}$$

Interestingly, we note that the two limiting linear regimes observed at small and large [TMEDA] in Figure 2.4 can be directly extracted from eq. 2.10 above:

$$\lim_{\phi \rightarrow 0} \left(\frac{[NC]}{[B-CdX_2]} \right) = \frac{1}{N_1 + N_2} + \frac{K_1 + K_2}{(N_1 + N_2) K_1 \cdot K_2} \cdot \phi \quad \text{eq. 2.11a}$$

$$\lim_{\phi \rightarrow \infty} \left(\frac{[NC]}{[B-CdX_2]} \right) = \frac{K_1 + K_2}{N_1 \cdot K_1 + N_2 \cdot K_2} + \frac{1}{N_1 \cdot K_1 + N_2 \cdot K_2} \cdot \phi \quad \text{eq. 2.11b}$$

The data in Figure 2.4 has been fitted to eq. 2.10 using a non-linear regression analysis, yielding values for N_1 , N_2 , K_1 , and K_2 that are listed in Table 2.1.

The good agreement between the model and the observed experimental data validates the assumption that each site on the surface interacts independently from each other, as strongly correlated surface binding would not be well modeled by eq. 2.10 above. Importantly, different CdSe NC sizes are equally well described by the model, and the relevant parameters for each NC

size are listed in Table 2.1. On the other hand, the good agreement between the sum $N_1 + N_2$ obtained from the nonlinear regression analysis and the value N_{tot} extracted from the NMR quantitation analysis should not be regarded as indicative of the validity of the model, as the model is itself designed to yield such a good agreement: the sum $N_1 + N_2$ is related to the y -axis intercept, which is experimentally related to the value N_{tot} obtained from the NMR data, see eq. 2.11 above

Table 2.1. CdSe NC surface-related data, obtained from analysis of TMEDA titration experiments, $T = 293.15$ K.

NC Diameter ^a (nm)	N_1	N_2	K_1	K_2	N_{tot} ^b
3.0 ± 0.2	23 ± 1	34 ± 3	1.0 ± 0.3	$(9 \pm 5) \times 10^2$	57 ± 2
3.8 ± 0.2	34 ± 2	61 ± 4	0.9 ± 0.3	$(7 \pm 4) \times 10^2$	95 ± 2
4.1 ± 0.3	43 ± 4	78 ± 6	0.6 ± 0.3	$(3 \pm 1) \times 10^2$	121 ± 2

NC Diameter ^a (nm)	[NC] ^b (μ M)	[CdX ₂] ^c (mM)	Surface Coverage (CdX ₂ /nm ²)
3.0 ± 0.2	80 ± 2	4.6 ± 0.3	2.1 ± 0.3
3.8 ± 0.2	78 ± 2	7.4 ± 0.7	2.1 ± 0.3
4.1 ± 0.3	78 ± 2	9.4 ± 0.2	2.2 ± 0.2

for $\varphi = 0$. Rather, a subtle point related to this issue is the question of the validity of the assumption that there are no vacant sites prior to displacement of CdX₂ by TMEDA: as vacancies in our study are never probed directly *per se*, it is not strictly possible to verify this assumption, although we can evaluate the possible impact that their presence would have on the exchange dynamics. Given the large difference between K_1 and K_2 , it is clear that under equilibrium, any intrinsic vacant site would have to exist as a B₁ site. As a consequence, neglecting the presence of intrinsic vacant B₁ sites in our model artificially boosts the value of the K_1 equilibrium constants, that is, the mass action of each equivalent of TMEDA in eq. 2.6a is effectively reduced. Consequently, the K_1 values reported in Table 2.1 can be regarded as upper-bound values for the actual equilibrium constants, to the extent that intrinsic B₁ vacancies, present in the as-prepared NC samples, would need to be

taken into account. A more detailed analysis is presented in Section 2.6 below, allowing an estimate of the fraction of vacancies in the as-prepared samples and of the actual equilibrium constant K_1 . It is sufficient for now to regard the values N_1 and K_1 listed in Table 2.1 as effective parameters that describe accurately the equilibria of 2.6a, and 2.6b.

With the values of the equilibrium constants and site densities in hand, a useful analysis of each separate equilibria can be obtained, for instance by relating directly the occupancy of each surface site to the ratio ϕ , or, equivalently, to the total amount of TMEDA added, *cf.* eq. 2.13:

$$\frac{[B_i]}{[NC]} = \frac{N_i \cdot \phi}{\phi + K_i} \quad i = 1, 2 \quad \text{eq. 2.12}$$

$$[L]_0 = \frac{N_{tot}(\phi^3 + \phi^2) + (N_1 K_2 + N_2 K_1)(\phi^2 + \phi)}{\phi^2 + (K_1 + K_2)\phi + K_1 K_2} [NC] \quad \text{eq. 2.13}$$

The displacement of the CdX_2 complexes from the CdSe NC surfaces is plotted separately for each individual site (B_1 and B_2) in Figure 2.4(b), showing clearly that full displacement of CdX_2 from the B_1 surface sites is effectively achieved at around 50 mM of added TMEDA, corresponding to about 650 equivalents per NC. Comparatively, less than 10% of the B_2 sites are vacant under identical conditions; as shown in Figure 2.4(c), there is not any physically realistic scenario under which TMEDA could displace all of the CdX_2 complexes from the B_2 sites, as concentrations higher than the density of pure liquid TMEDA being required.

Close inspection of the data in Table 2.1 reveals a few interesting facts. First, the apportionment of each type of site appears fairly regular across all sizes, with a rough 2:3 ratio between N_1 and N_2 , although we note that this likely depends sensitively on sample preparation conditions, and NCs prepared by different approaches, or those with much smaller superficial coverage than those reported here, might not exhibit the same trend. Second, whereas equilibrium constants for a given

type of sites generally appear to decrease with increasing sizes, the accuracy of the analysis does not allow for firm conclusions to be raised concerning the precise size dependence of these parameters. Furthermore, we note that from a free energy perspective (Section 2.5), there is not a significant difference across the range of values reported for a given site. A much more critical observation stemming from this analysis, and a general feature common to all samples (beyond the existence of two distinct surface sites), is the fact that the equilibrium constants for the binding of CdX_2 on each of the two surface sites differ by about 2-3 orders of magnitude, *i.e.*, $\text{p}K_1 \sim 0$ and $\text{p}K_2 \sim -2$. This points to a significant difference in the free energy of binding CdX_2 between B_1 and B_2 , which we address specifically in the next Section.

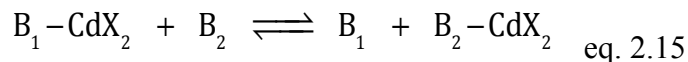
2.5 Thermodynamics of Surface Site Binding

To probe further into the specific nature of the two different types of surface sites, temperature-dependent ^1H NMR studies were conducted as a way to modulate the equilibrium of the CdX_2 exchange reactions and extract the enthalpic contribution to the overall free energy of each exchange process. For each NC sizes, two TMEDA concentrations were selected, each corresponding to a regime where one of the two exchange reactions dominates the overall equilibrium. These two regimes are highlighted with arrows for the 3.8 nm CdSe NC sample in Figure 2.4(c). In each regime, and for all NC sizes investigated here (see Appendix, SI 2.8 and 2.9), NMR studies indicate that the TMEDA-induced displacement of surface-bound CdX_2 becomes more efficient the lower the temperature, indicating that this process is exothermic ($\Delta H < 0$) or, in the framework established above, that eqs. 2.6a, and 2.6b represent endothermic processes ($\Delta H > 0$). A quantitative estimate of the enthalpy of reaction can be obtained from a van 't Hoff analysis of the temperature-dependent equilibria:

$$\frac{d \ln K_{eq}}{d(T^{-1})} = -\frac{\Delta H}{R} \quad \text{eq. 2.14}$$

Figure 2.5 reports the temperature-dependent exchange equilibria data obtained from NMR in the formalism of eq. 2.14. The behavior of $\ln K$ vs. T^{-1} over the whole temperature range investigated (roughly 40 K above and beyond room temperature) is linear, indicating that the enthalpy change is nearly temperature-independent over this range, as expected for the simple ligand exchange processes under consideration. The enthalpy change for each exchange reaction is thus directly related to the gradient of each fitted line in Figure 2.5. The Gibbs free energies for each process are directly obtained from the equilibrium constants in Table 2.1, which then directly yields the corresponding entropic changes; the thermodynamic quantities for eqs. 2.6a, and 2.6b extracted from such van 't Hoff analyses are reported in Table 2.2 for three different CdSe NCs sizes.

Although the thermodynamic data in Table 2.2 is referenced to TMEDA (more precisely, to differences between state functions of the TMEDA-CdX₂ complex and uncoordinated solvated TMEDA), a direct comparison between the binding stability of CdX₂ to B₁ vs. B₂ sites can be obtained by subtracting the two reactions in eqs. 2.6a and 2.6b, yielding the following overall equilibrium:



which is independent of the nature of the Lewis base species used to displace the CdX₂ complexes; the thermodynamic parameters relevant to eq. 2.15 are listed in Table 2.3. The data in Table 2.3 shows directly that the difference in the enthalpic terms associated with the equilibrium of the B₁ and B₂ sites is not only quite small, but also opposite to the thermodynamic stability associated with the B₂-CdX₂ complex. Indeed, as written, eq. 2.15 is a slightly endothermic reaction,

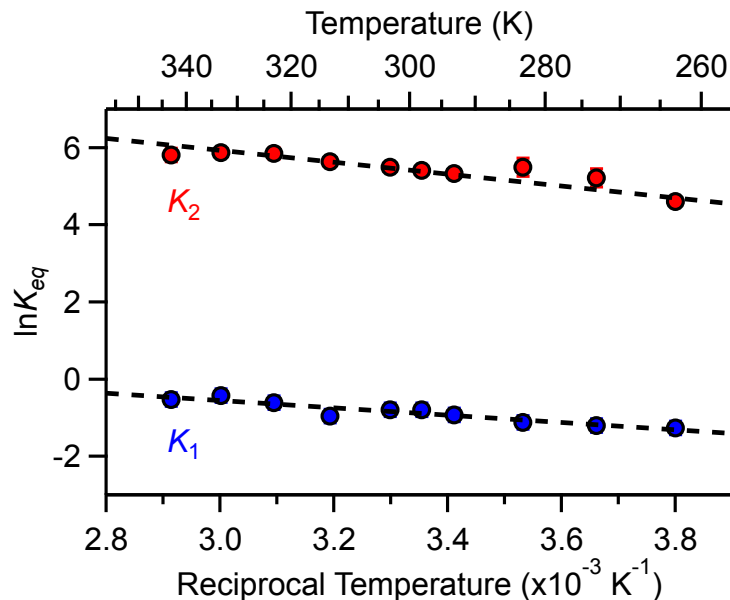


Figure 2.5. Temperature dependence of the equilibrium constants K_1 and K_2 for 3.8 nm CdSe NCs, expressed in the van 't Hoff formalism. Blue circles: [TMEDA] = 2 mM; red circles: [TMEDA] = 273 mM; the error bars are at most as large as the circles shown here. The black dashed lines are linear least squares fitted curves ($R^2 = 0.885$ for K_1 and $R^2 = 0.830$)

demonstrating, somewhat surprisingly, that the large thermodynamic stability of the B_2 -CdX₂ complex relative to the B_1 site analog is intrinsically an entropic effect; further insight into the origin of this effect will be provided in Section 2.6, along with a discussion of the nature of the B_1 and B_2 sites in terms of the specific surfaces of zinc-blende CdSe NCs.

Table 2.2. Thermodynamic parameters for surface-bound CdX₂ exchange with TMEDA of CdSe NCs, $T = 293.15$ K.

NC Diameter (nm)	ΔH_1^a (kJ·mol ⁻¹)	ΔH_2^a (kJ·mol ⁻¹)	ΔS_1^b (J·mol ⁻¹ ·K ⁻¹)	ΔS_2^b (J·mol ⁻¹ ·K ⁻¹)	ΔG_1^c (kJ·mol ⁻¹)	ΔG_2^c (kJ·mol ⁻¹)
3.0 ± 0.2	11 ± 2	14 ± 4	38 ± 10	106 ± 21	0.0 ± 0.7	-17 ± 2
3.8 ± 0.2	8 ± 2	13 ± 1	26 ± 10	99 ± 10	0.3 ± 0.8	-16 ± 2
4.1 ± 0.3	10 ± 5	13 ± 4	30 ± 22	92 ± 17	1.2 ± 1.4	-14 ± 1

^a from the van 't Hoff analysis presented in Figure 2.5; ^b from $\Delta S = (\Delta H - \Delta G) \cdot T^{-1}$, using ΔH and ΔG from this Table; ^c from, $\Delta G_n = -R \cdot T \cdot \ln K_n$, using K_n from Table 2.1.

Table 2.3. Comparison of the thermodynamic binding stability of CdX₂ on the B₂ vs. B₁ surface sites of CdSe NCs.^a

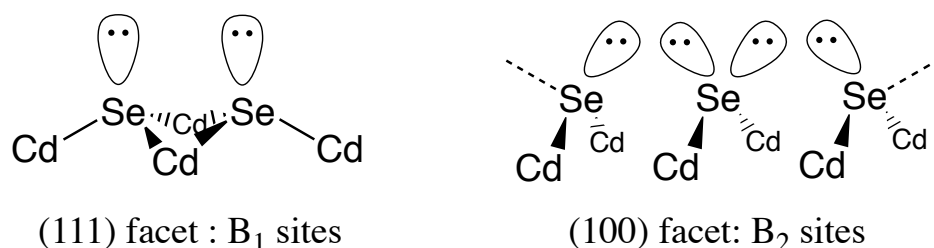
NC Diameter (nm)	ΔH_{2-1} (kJ·mol ⁻¹)	ΔS_{2-1} (J·mol ⁻¹ ·K ⁻¹)	ΔG_{2-1} (kJ·mol ⁻¹)
3.0 ± 0.2	3 ± 4	68 ± 23	-17 ± 2
3.8 ± 0.2	5 ± 2	73 ± 14	-16 ± 2
4.1 ± 0.3	3 ± 5	62 ± 28	-15 ± 2

^a Data referenced to eq. 2.15, $\Delta X_{2-1} = \Delta X_2 - \Delta X_1$; $T = 298.15$ K.

2.6 Microscopic Nature of the Surface Sites of CdSe NCs.

Some insights into the potential microscopic nature of each of the two surface sites, B₁ and B₂ can be obtained from the results presented above. As has been previously recognized,^{1,2,14,35-37} the different crystal facets of semiconductor NCs often exhibit strikingly different behaviors regarding the stability of surface-bound species (ligands or adatoms) and the generation of specific surface defects for excited-state energy-trapping processes. The surface of zinc-blende CdSe NCs is generally described in terms of the two most stable facets, namely the (100) and (111) facets.^{1,37-39} The (100) facet exposes two-coordinated species, either Se or Cd; the idealized “selenium-rich” (100) facet thus presents rows of Se²⁻ ions, each with two lone pairs located in sp³ hybrids. The (111) facets by contrast expose species that are 3-coordinated to the underlying lattice atoms; the

idealized “selenium-rich” (111) facet thus presents arrays of Se^{2-} ions each with a single lone pair pointed perpendicular to the facet plane (Scheme 2.2).



Scheme 2.2. Coordination chemistry of surface atoms at different facets of zinc-blende CdSe NCs.

Although the (100) facet is atomically sparser than the (111) facet:

$$\lambda_{100} = \frac{2}{a_0^2} \cong 5.4 \text{ atoms} \cdot \text{nm}^{-2}$$

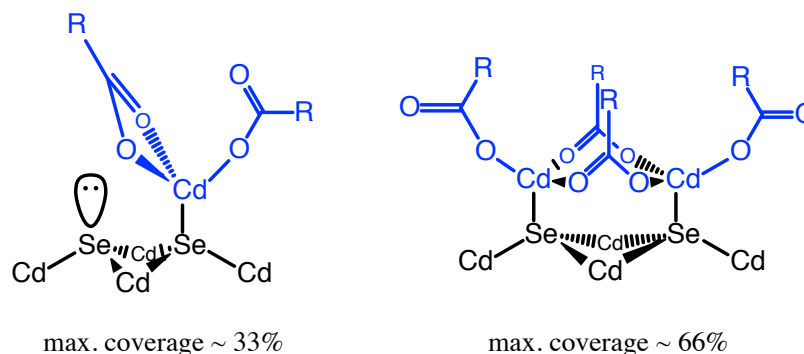
$$\lambda_{111} = \frac{4\sqrt{3}}{3a_0^2} \cong 6.2 \text{ atoms} \cdot \text{nm}^{-2}$$

where a_0 is the lattice constant of zinc blende CdSe (0.608 nm),⁴⁰ the (111) facet has a lower density of “dangling bonds”, and recent studies have suggested that CdX_2 vacancies created on (100) facets of cadmium-rich CdSe NCs lead to the introduction of electronic states in the bandgap that can efficiently trap photo-generated valence-band holes on surface Se^{2-} ions.^{2,41} Following this hypothesis, we assign the B₂ sites (the highly efficient PL quenching sites) to vacancies on (100) facets. Given the large driving force to displace any CdX_2 complexes from B₁ sites onto B₂ vacancies, it is reasonable to assume that, at equilibrium, the (100) facets must be fully covered with CdX_2 complexes, a proposal which is also implied by the Stern-Volmer analysis presented above, where even a single vacancy on the B₂ sites would yield a PL quantum yield

(PLQY) < 1/50, much lower than the observed PLQY of the as-prepared samples studied here (avg. PLQY ~ 13%). The total (100) surface area, S_{100} , is thus simply calculated from:

$$S_{100} = \frac{N_2}{\lambda_{100} / 2} \quad \text{eq. 2.16}$$

where λ_{100} is the atom density of the (100) facet (the factor of 2 arises from the fact that only half of the (100) facets are Se-terminated and able to coordinate CdX_2). The calculated total area for the (100) and (111) facets are listed in Table 2.4; interestingly, the ratio of the (100) vs. (111) areas obtained from this assumption is close to unity, which is consistent with the observed spherical morphology (among the isomorphic Archimedean solids, this specific shape falls in between that of the ideal truncated octahedron and the cuboctahedron).

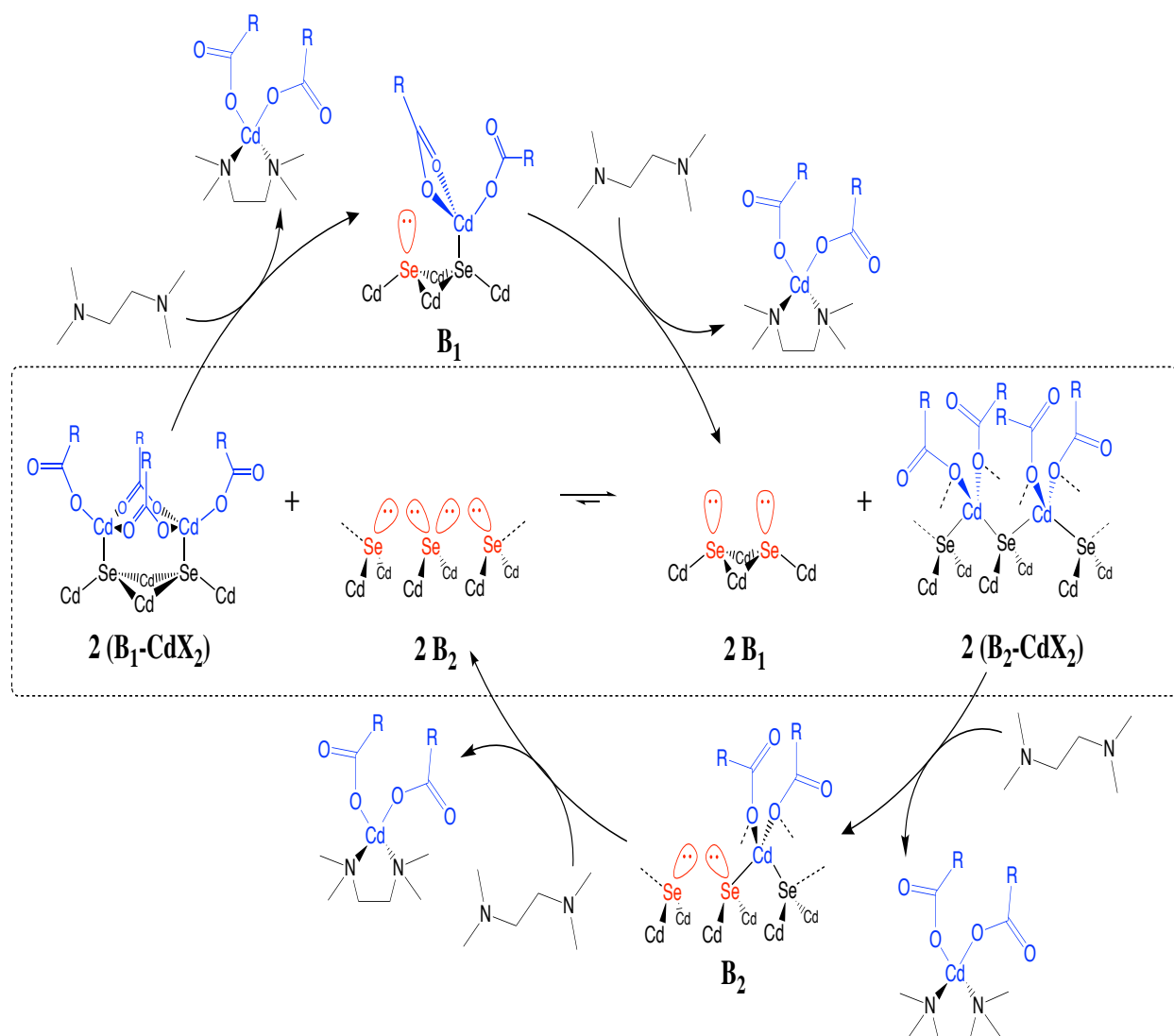


Scheme 2.3. Different possibilities for cadmium carboxylate ligand coverage on the (111) facet

Following on our initial assumption that the B_2 sites correspond to vacancies on the (100) facet, we assign the B_1 sites (initially bound to N_1 CdX_2 complexes) to vacancies on the (111) facet. Since the total surface of each NC sample can be directly estimated from the average diameter, a direct quantification of the surface coverage for the (111) facets can be obtained, as given in Table 2.4. The surface coverage of the (111) facets (measured in CdX_2 units) is lower than the theoretical maximum, $\lambda_{111}/2 \cong 3.1 \text{ nm}^{-2}$, which is expected given the low overall ligand coverage listed in

Table 2.1. The low coverage of the (111) facets is very likely related to the structure of the cadmium carboxylate complex,^{37,4,34} whose cone angle prevents close packing of the CdX₂ complexes, as shown in Scheme 2.3. Whereas CdX₂ monomers would likely require one of the two-carboxylate ligands to adopt a bidentate ligation to avoid a hypovalent cadmium center, it is likely that the κ_2 -carboxylate complex would not be very stable given the strain associated with the 4-members ring. Comparatively, the dimer shown in Scheme 2.3 (di- μ -carboxylato-dicarboxylatodicadmium) is likely more easily formed given the lower strain imposed on the two μ -carboxylato bridging ligands. Furthermore, this cluster arrangement can yield much larger overall coverages, up to 66% of the theoretical maximum for ideally ordered surface coverage (entropic considerations would necessarily lead to lower actual coverages). As shown in Table 2.4, the coverage of the (111) facets estimated here is very close to half the theoretical maximum coverage (taking into account that half of the (111) facets are Se-terminated), which supports the dimer clusters hypothesis.

In spite of the relatively large number of (111) sites that remain unpassivated, it is likely that these sites are actually sterically hindered, suggesting that the CdX₂ coverages reported here are perhaps actually close to the effective maximum that can be achieved for the specific carboxylates and NC shapes under consideration in this study.



Scheme 2.4. Summary of the dual exchange reaction on B₁ and B₂ Surface sites

Importantly, as discussed above, these unpassivated sites – assigned here as B₁ vacancies – do not significantly impact the brightness of the NCs, minimizing the detrimental impact of the low (111) facet coverage. With an estimate of the surface spanned by the (111) facets in hand, the number of B₁ sites that are not initially ligated by CdX₂, which was neglected in the analysis before, can now be evaluated:

$$N_{1,tot} = \frac{\lambda_{111}}{2} \cdot S_{111} \quad (2.17)$$

where, as above, we acknowledge that only half of the surface apportioned to (111) facets is Se-terminated. These values are listed in Table 2.4, showing that there are many B_1 vacancies on these as-prepared NC samples; an estimate of the role that these vacancies might play in the photoluminescence of these “pristine” CdSe NCs is presented in the next Section. As mentioned in Section 2.4 above, neglecting the presence of these B_1 vacancies effectively magnifies the values of K_1 obtained therein; using the values of $N_{1,tot}$ listed in Table 2.4 to analyze the data in Figure 2.2 leads to values of K_1 that are practically identical for all three sizes: $K_{1,corr} = 0.23 \pm 0.03$. This actual value, which is 3-5 times smaller than the effective values listed in Table 2.1, likely provides a better estimate of the actual affinity of the B_1 sites – that is, undercoordinated (111) selenide sites – toward CdX_2 ligation. We note here that although we treat surfaces as uniform distributions, it is possible, and perhaps likely, that specific locales over each surfaces (say edges or corners) play a dominant role in defining the ligand exchange kinetics and/or the efficiency of the recombination processes. Given the likely high mobility of surface ligands over the whole surface of a NC and our inability to distinguish specific surface sites beyond the two types (B_1 and B_2) identified here, we limit our analysis to the attribution of the chemical and photophysical behavior of surface defects as mean values over the two main crystallographic facets.

The conclusion that the (100) facets are fully covered is consistent with the highly organized nature of these facets, which lend themselves well to full packing of the CdX_2 ligands. On the other hand, as each carboxylate is required to bridge two Cd atoms, the (100) faceting can only accommodate half of the carboxylate ligands that are associated with a full Cd coverage; this “enrichment” of Cd^{2+} on the selenide-rich (100) surface balances the net negative charge of these facets, which likely provides a large amount of the driving force favoring the (100) faceting of these zinc-blende nanocrystals (everything else being equal, and prior to reconstruction, (100) facets are always less

stable than (111) facets in diamond-like structures.⁴² Overall charge neutrality can be maintained by the transfer of an equal amount of carboxylates onto the opposite Cd-rich surfaces, which not only provides a mechanism to passivate the 3-coordinated cadmium atoms in the absence of L-type ligands, but also reduces the net positive charge of these facets. Overall, the results presented herein allow to develop a clearer representation of the schematic dual exchange reaction scheme used in the Section 2.3 (Scheme 2.1), where the B₁ and B₂ sites are localized on specific facets as summarized in Scheme 2.4. The overall thermodynamics of the CdX₂ binding favors coverage of the (100) facet vs. the (111) facet, which was shown to arise predominantly from entropic contributions.

Table 2.4. CdSe NCs Surface Areas and Ligand Coverage.

NC Diameter (nm)	S_{tot} ^a (nm ²)	S_{100} ^b (nm ²)	S_{111} ^c (nm ²)	λ_{111}^{eff} ^d (nm ⁻²)	$N_{1,tot}$
3.0 ± 0.2	28 ± 3	13 ± 1	15 ± 4	1.5 ± 0.4	47 ± 2
3.8 ± 0.2	45 ± 3	23 ± 1	22 ± 4	1.5 ± 0.3	69 ± 4
4.1 ± 0.3	53 ± 5	29 ± 2	24 ± 7	1.8 ± 0.5	75 ± 7

^a Surface area of the equivalent sphere; ^b Calculated using eq. 2.16

^c $S_{111} = S_{tot} - S_{100}$

^d $\lambda_{111}^{eff} = N_1 / S_{111}$.

Interestingly, our findings are further confirmed by a similar work by Hens and collaborators.⁴³ In their study, they also reported the existence of two different Se binding sites that are revealed upon addition of TMEDA. They identified these binding sites by analyzing the displacement equilibrium that was monitored by ¹H NMR spectroscopy. They further calculated the binding energies of different surface sites which supported their experimental data.

2.7 Conclusion

Using the general ligand exchange process given here, we demonstrated the existence of at least two types of sites at the surface of zinc-blende CdSe NCs. The model developed here provides for the first-time direct evidence for the specificity of different crystalline facets with regards to the free-energy changes associated with the binding of cadmium carboxylate complexes, allowing for a detailed account of the distribution of these species over the different facets. The thermodynamical analysis of the surface binding allowed a detailed model of the surface composition to be proposed.

APPENDIX

SI 2.1. Optimization of the Relaxation Delay Time in ^1H NMR Measurements

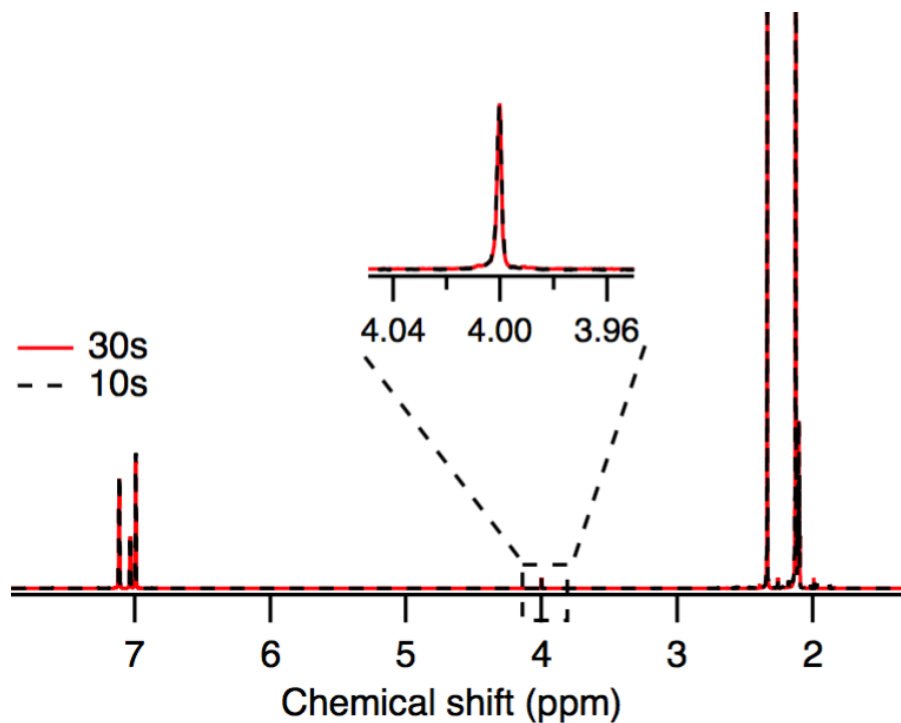


Figure SI 2.1. ^1H NMR spectra of a mixture of ferrocene (0.2 mM) and TMEDA (45 mM) in d-toluene, taken with 45-degree pulse angle and 32 scans but with different relaxation delay time (red solid line and black dashed line are with 30s and 10s relaxation delay respectively). This figure shows the two spectra are identical, indicating with that given pulse angle, 10s relaxation delay is sufficient to allow for a complete relaxation of ferrocene, (TMEDA is used as a reference to check for the concentration of ferrocene, ferrocene has the highest relaxation time about 7s and normally a relaxation delay of 30s should be used if the pulse angle is 90-degree).

SI 2.2. NMR Characterization of CdSe NCs Capping Ligands

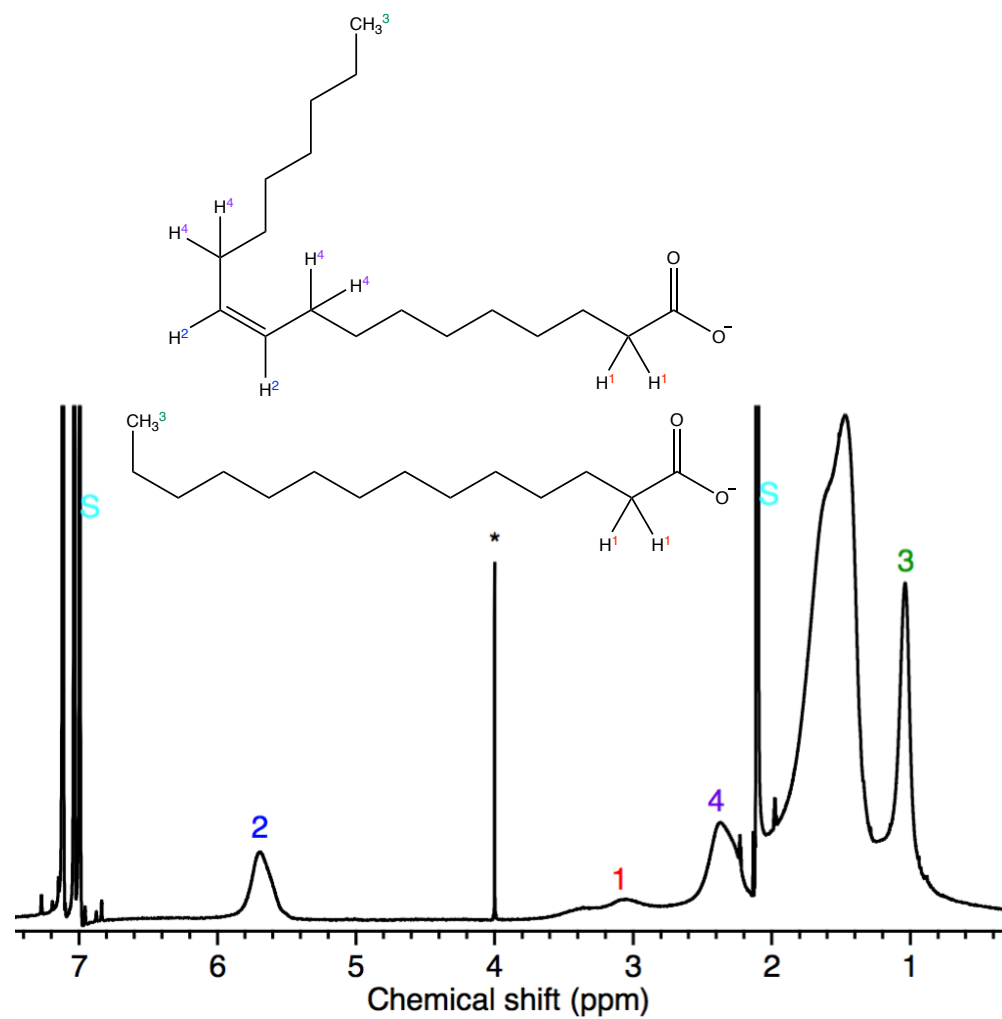


Figure SI 2.2. ¹H NMR spectrum of a clean suspension of oleate/myristate capped CdSe NCs with chemical shift assignments. The protons that are not shown/labeled belong to the big broad peak with chemical shift between 1.2-2.2 ppm. Asterisk sign on the peak at 4 ppm belongs to ferrocene. S sign stands for the solvent, which is d-toluene at 2.1 and 7.1 ppm.

SI 2.3. Calculation of Surface Coverage and Concentration

In a 20 ml vial, 600 μ l of 85 μ M CdSe (3.8 nm) suspension in d-toluene was mixed with 30 μ l of d-toluene and 30 μ l of ferrocene solution in d-toluene (4.2 mM) and then transferred to a NMR tube and NMR was recorded with 32 scans and 30 seconds relaxation delay. Ferrocene is used as internal standard and the integration of methyl peak (which is measured using three Gaussian fits) was referenced to integral of ferrocene, which was set to 10. Below shows the steps to calculate the ligand concentration and ligand coverage per QD.

$$[Methyl](\mu M) = [Ferrocene](\mu M) \cdot \frac{\#H_{ferrocene}}{\#H_{methyl}} \cdot \frac{\int methyl}{\int ferrocene}$$

Therefore, the concentration of all carboxylates ligands is:

$$[Carboxylates] = [methyl] = 14.8mM$$

Assuming each cadmium is attached to two carboxylates, the concentration of cadmium carboxylate (CdX_2) is :

$$[CdX_2] = 7.4mM$$

Assuming the CdSe nanocrystals are spherical, with the diameter of 3.8 nm ($r=1.9$ nm), on average the surface area of each particle is:

$$A = 4\pi r^2$$

$$A = 45.36nm^2$$

and the surface coverage for the solution of 0.078 mM CdSe is:

$$\frac{7.4mM}{0.078mM \times 45.36nm^2} = 2.1nm^{-2}$$

SI 2.4. NMR Fitting Analysis, Deconvolution of Bound and Free Cadmium Carboxylate

With the addition of TMEDA, the NMR peaks corresponding to carboxylates are split into a broad and a sharp peak, which is indicative of bound and free carboxylate, respectively.

They are merged and need to be deconvoluted. For simplicity, vinylic peaks between 5 and 6 ppm are chosen for fitting and calculating the ratio of bound to free ligands. The sum of the ratio of bound and free ligands is normalized to the total number of carboxylate for the analysis (which was calculated in previous section.)

In order to deconvolute the bound and free carboxylate, first the NMR spectra are integrated, then the integrations are fitted with the combination of two sigmoid fits:

$$f(x) = \text{base} + \text{max1} / (1 + \exp((\text{half1} - x)/R1)) + \text{max2} / (1 + \exp((\text{half2} - x)/R2))$$

Here is an example:

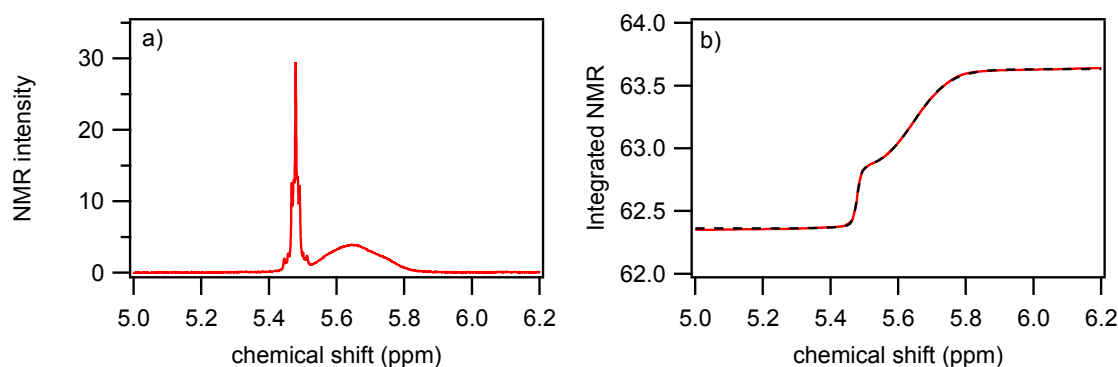


Figure SI 2.4.1. a) ¹H NMR spectrum of 78 μ M CdSe in presence of 37.5 mM TMEDA in the region of interest (5-6 ppm) and b) corresponding integration which is fitted with the bi-sigmoid fit. Fit parameters are given in table S1.

Table S1. Fitting parameters of bisigmoid fits shown in Figure S3-b

Base	max1	max2	half1	half2	R1	R2
62.363	0.44488	0.82419	5.4783	5.6473	0.0064313	0.052491
± 0.000115	± 0.000462	± 0.00051	$\pm 2.56\text{e-}05$	$\pm 8.69\text{e-}05$	$\pm 2.41\text{e-}05$	$\pm 6.08\text{e-}05$

$$\frac{[\text{CdX}_2]^{\text{B}}}{[\text{CdX}_2]^{\text{F}}} = \frac{0.82419}{0.44488} = 1.8526$$

$$[\text{CdX}_2]^{\text{B}} + [\text{CdX}_2]^{\text{F}} = 7.4 \text{ mM}$$

$$[\text{CdX}_2]^{\text{B}} = 4.80 \pm 0.13 \text{ mM}$$

$$[\text{CdX}_2]^{\text{F}} = 2.59 \pm 0.07 \text{ mM}$$

This method is used for all NMR spectra of TMEDA titration of three sizes of CdSe NC. For temperature dependent NMR the combinations of Gaussian and Lorentzian fits were used to find the total integration between 5-6 ppm. In order to find the ratio of bound to free ligands (B/F), total area (the fits) under bound and free peaks were summed and using the method from the previous section, the actual concentrations of free and bound CdX_2 were calculated.

Here are two examples:

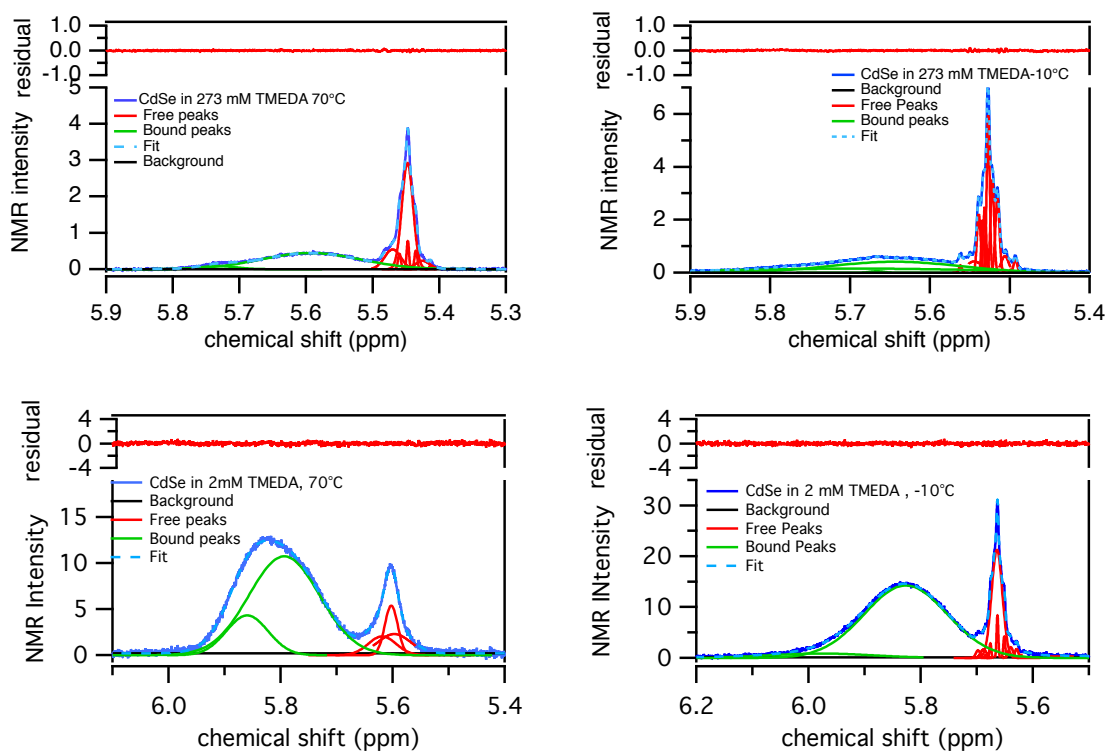


Figure SI 2.4.2 The Top left and right figures show the free and bound CdX_2 peaks in presence of 273 mM TMEDA at 70 °C and -10 °C respectively. The bottom left and right figures show the free and bound CdX_2 peaks in presence of 2 mM TMEDA at 70 °C and -10 °C respectively. At high concentration of TMEDA and in low temperature the sharp peaks from free CdX_2 are more resolved and therefore more fits are needed. Those fits that fall in between the bound and free are used to determine the error on the analysis.

SI 2.5. Change in the Concentration of Bound and Free CdX_2 in Methyl Region vs Vinyl Region

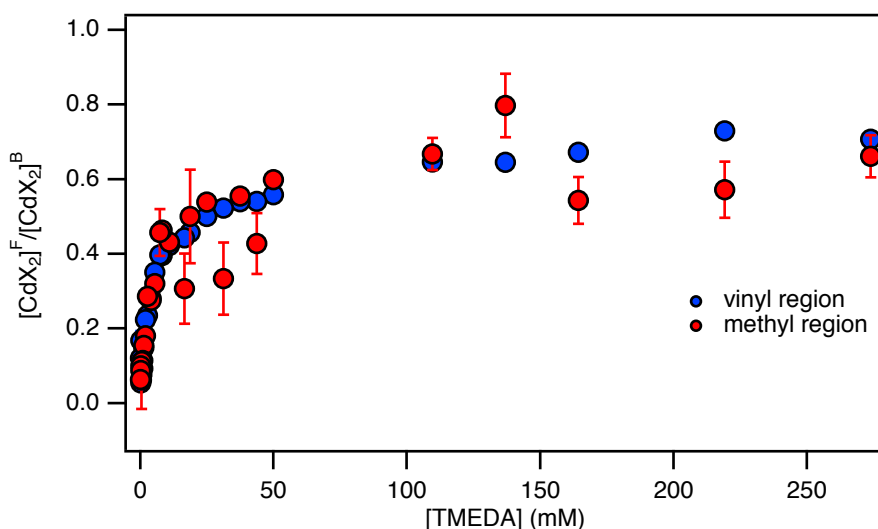


Figure SI 2.5. Ratio of free and bound CdX_2 with the TMEDA addition. Blue circles show the change of the ratio in the vinylic region and red circles show them in the methyl region of the NMR spectra. This figure indicates that the binding affinity of oleate and myristate are similar and for simplicity we can use the ratio from the oleate region instead of methyl region. Also the error bars are smaller when the ratio at vinyl region and this is due to the more flat baseline of that region (since the chemical shift is between 5 and 6 and these peaks are isolated from the rest of the spectrum).

SI 2.6. ^1H NMR Spectra of the Addition of TMEDA to CdSe NCs

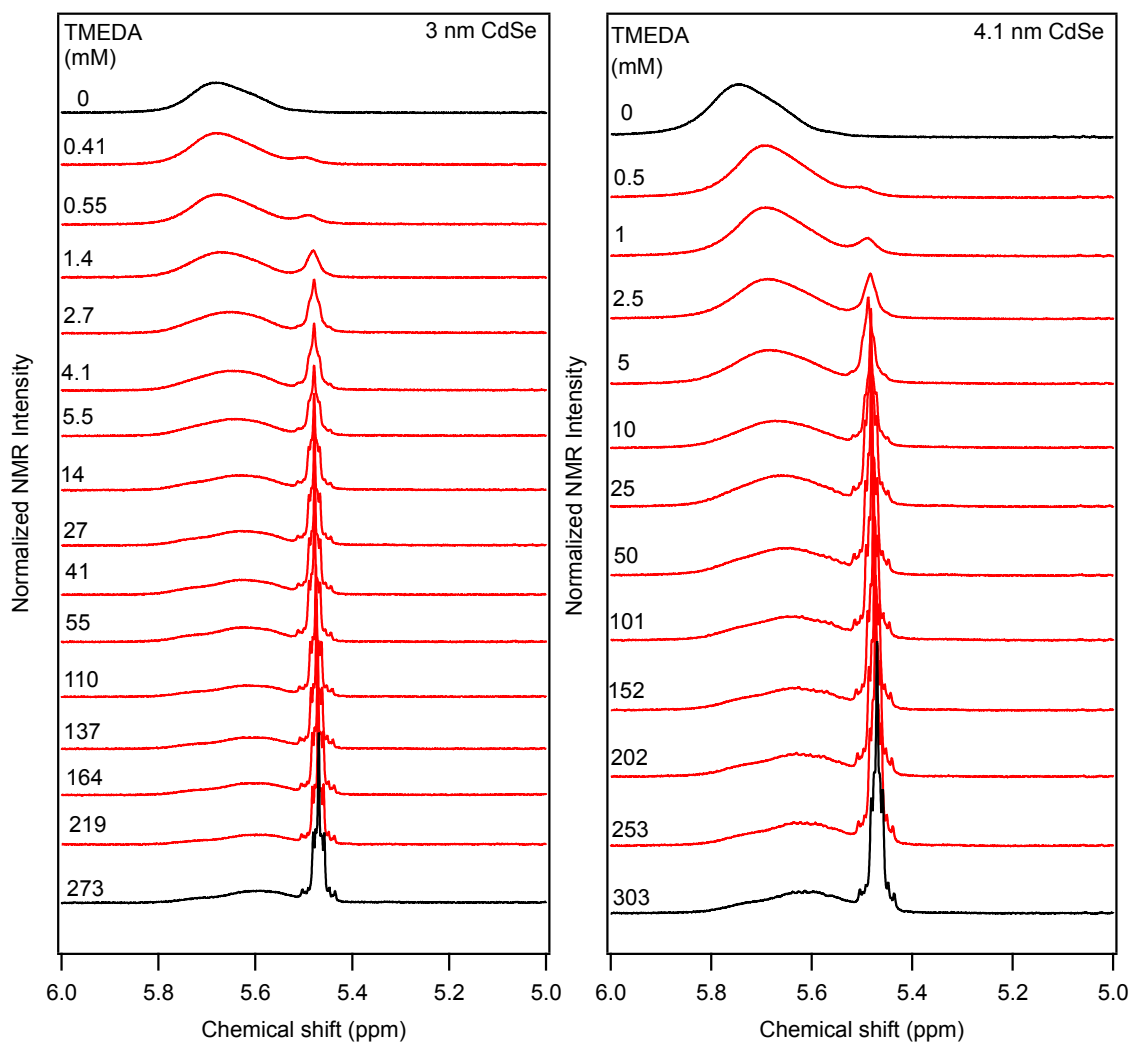


Figure SI 2.6.1 ^1H NMR Spectra (5-6 ppm) of a) 3 nm CdSe (80 μM) and b) 4.1 nm CdSe (78 μM) in presence of different concentration of TMEDA.

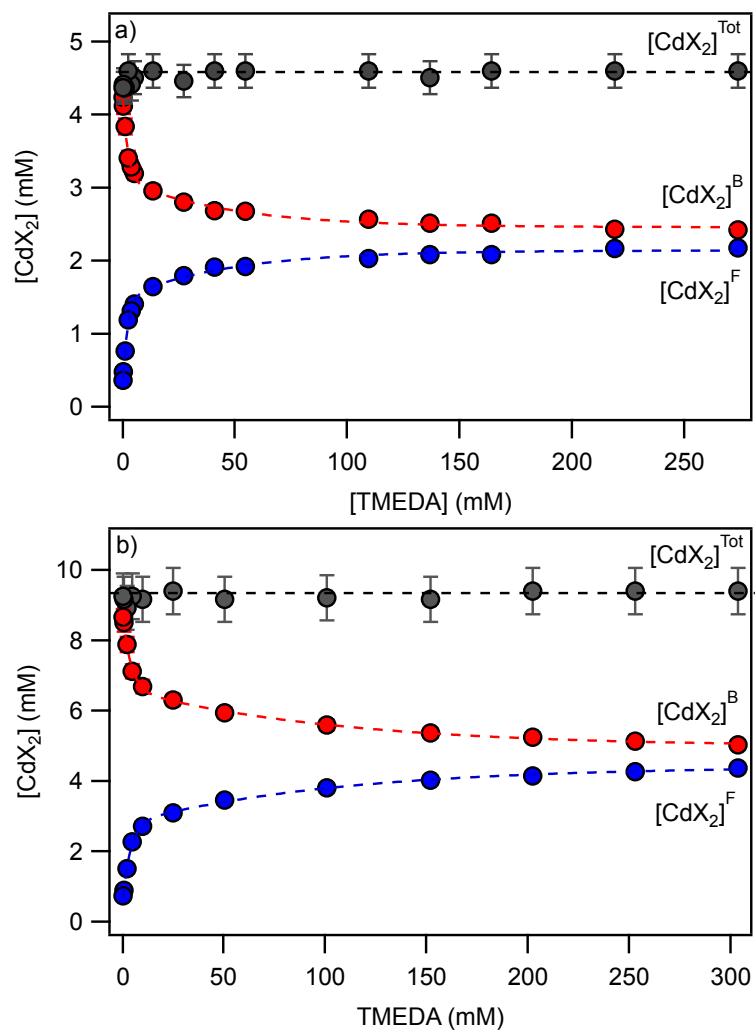


Figure SI 2.6.2. Concentration of CdX_2 in a) 80 μM of 3 nm CdSe and b) 78 μM of 4.1 nm CdSe with different concentration of TMEDA, gray, red and blue circles show the total concentration of CdX_2 , concentration of bound CdX_2 and concentration of free CdX_2 respectively. In all data points there is an equilibrium where the total number of CdX_2 is preserved.

SI 2.7. Analysis of TMEDA Addition to CdSe NCs

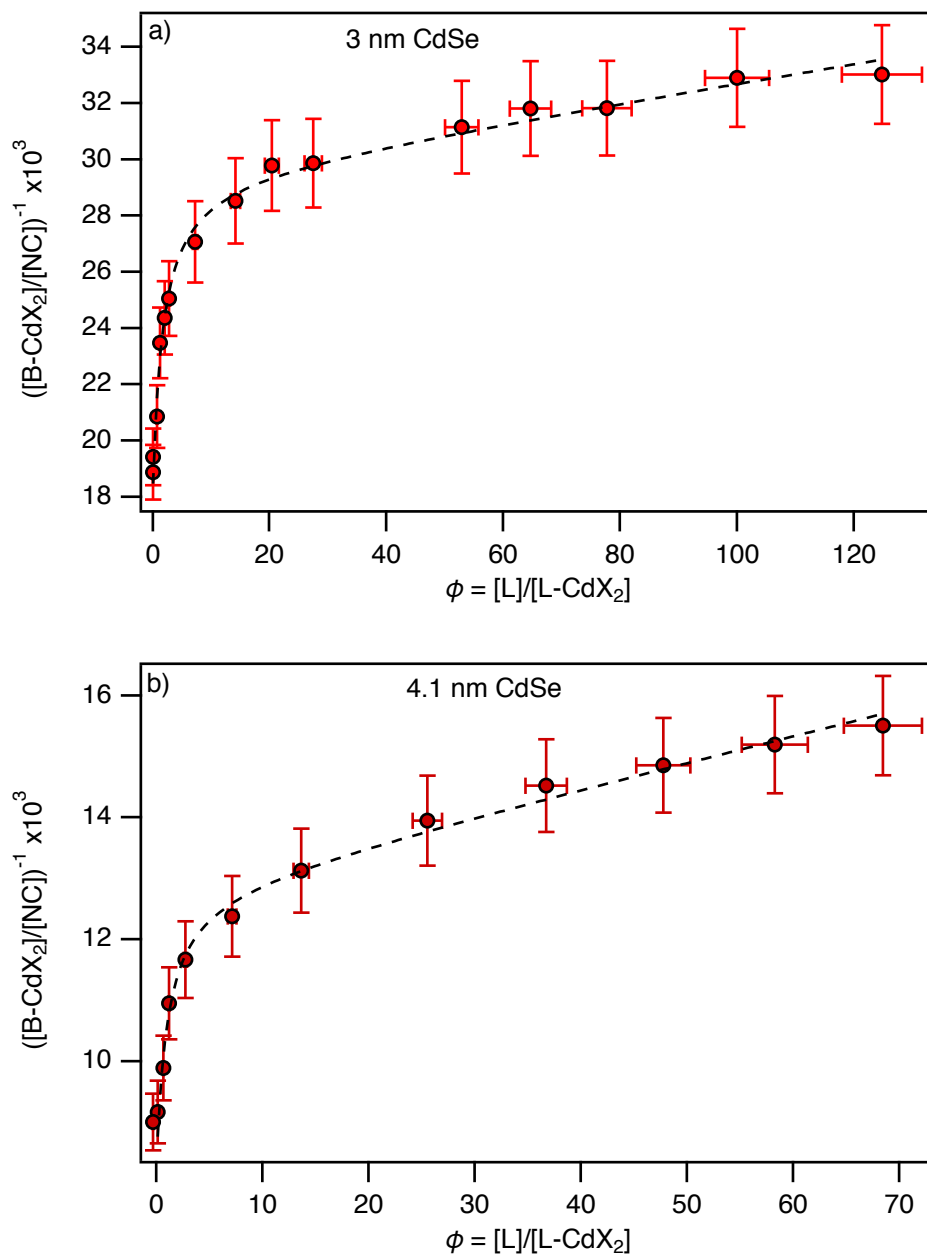


Figure SI 2.7. TMEDA titration of a) 3 nm CdSe NCs and b) 4.1 nm CdSe NCs, modeled with eq. (11) (black dashed lines).

SI 2.8. Temperature Dependent ^1H NMR Spectra of CdSe with TMEDA

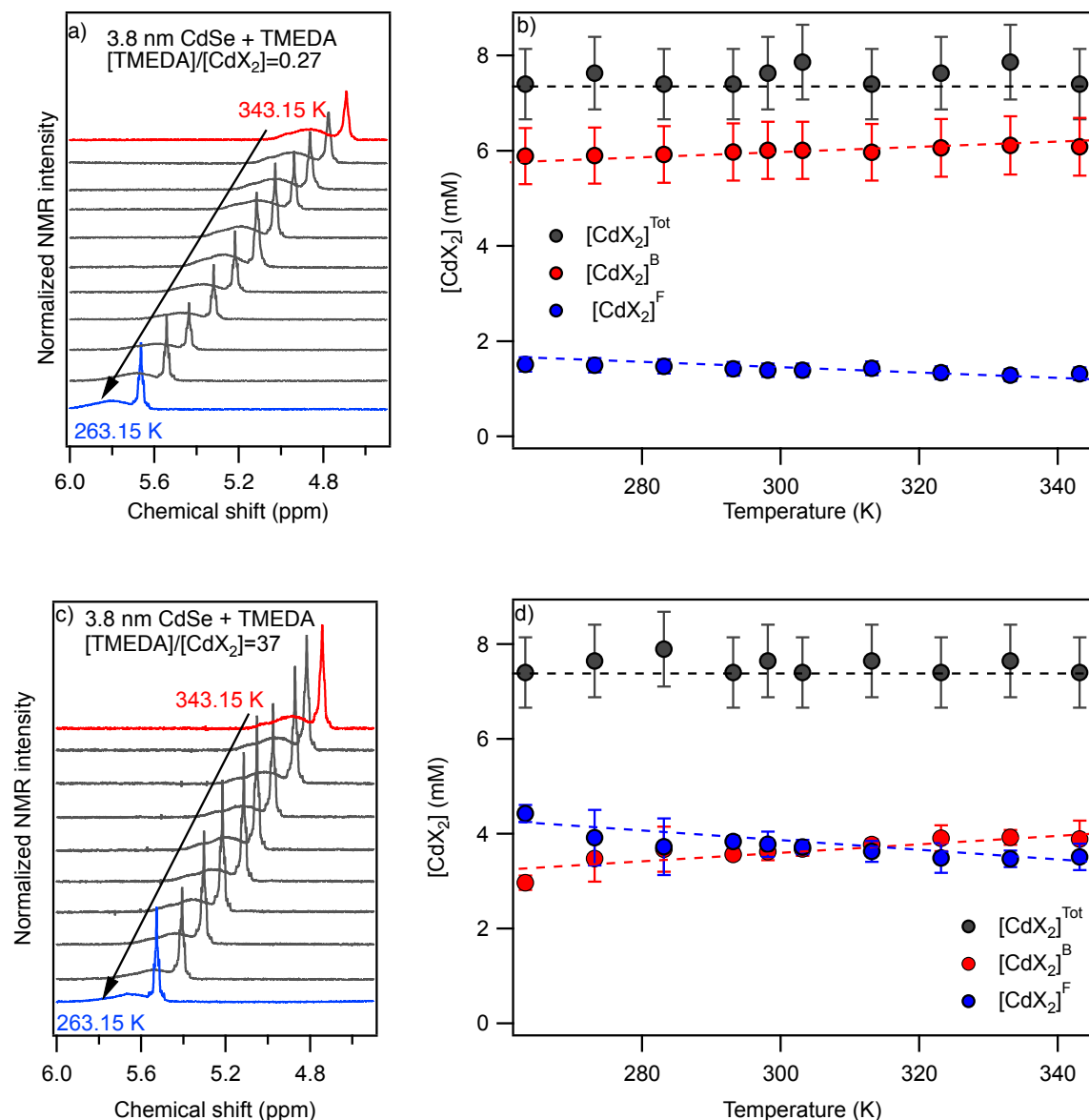


Figure SI 2.8.1 Temperature dependent ^1H NMR of 3.8 CdSe (78 μM) with a) 2 mM TMEDA and c) 273 mM TMEDA. Chemical shifts in part a and c don't change. The shifts towards right are due to visual purposes. Figures b and d show the change in concentration of free and bound CdX₂ with temperature from figures a and c, respectively. In both cases the total concentration of CdX₂ is preserved. Total concentrations are achieved from the direct integration of the NMR spectra (5.4-6 ppm) and are referenced to ferrocene. The concentrations of free and bound CdX₂ are achieved using the fitting parameters described in SI 2.4. Dashed lines are guides to the eye.

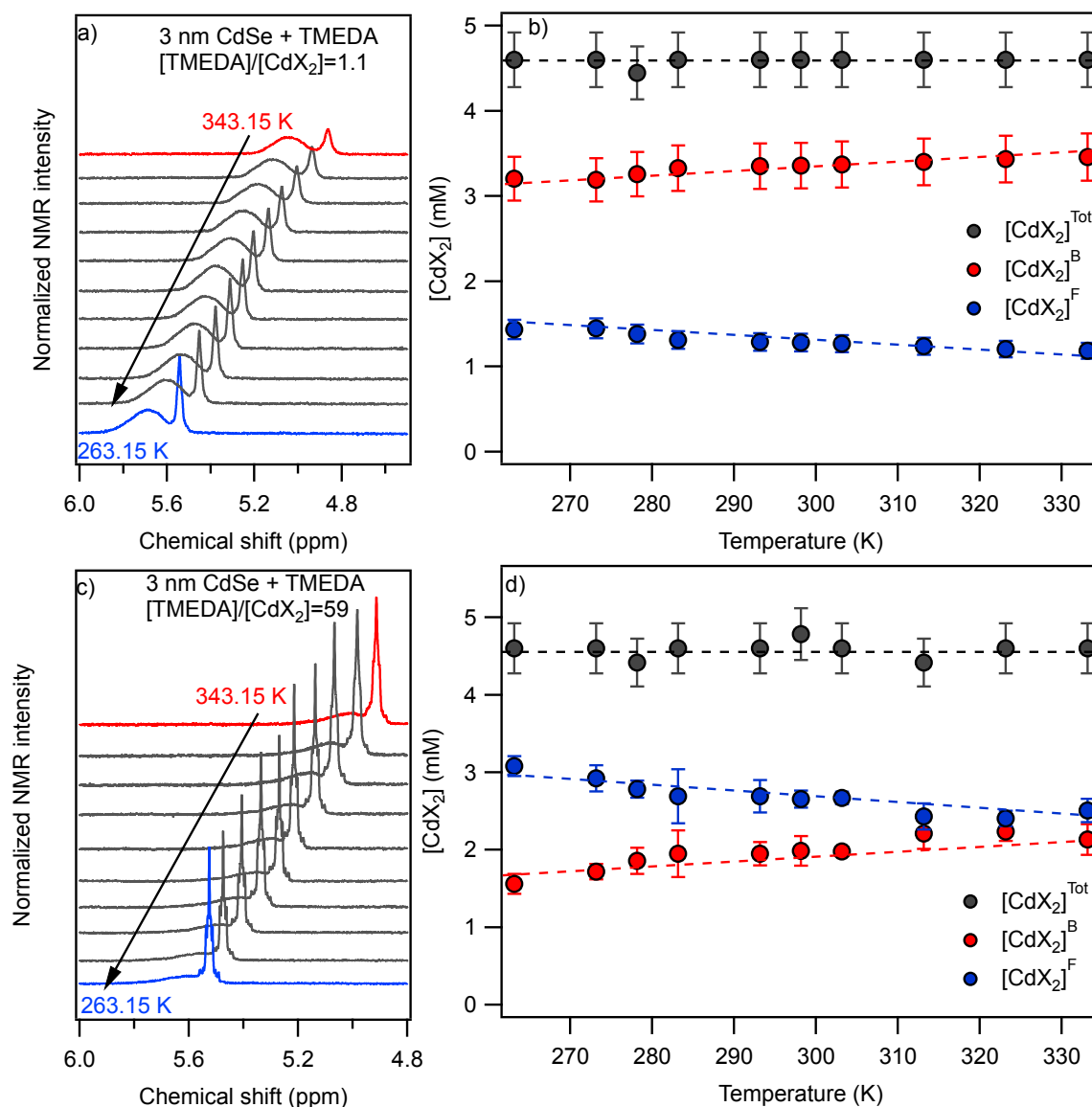


Figure SI 2.8.2. Temperature dependent ^1H NMR of 3 nm CdSe ($80\ \mu\text{M}$) with a) 5 mM TMEDA and c) 273 mM TMEDA. Chemical shifts in part a and c don't change. The shifts towards right are due to visual purposes. Figures b and d show the change in concentration of free and bound CdX_2 with temperature from figures a and c, respectively. In both cases the total concentration of CdX_2 is preserved. Total concentrations are achieved from the direct integration of the NMR spectra (5.4-6 ppm) and are referenced to ferrocene. The concentrations of free and bound CdX_2 are achieved using the fitting parameters described in SI 2.4. Dashed lines are guides to the eye.

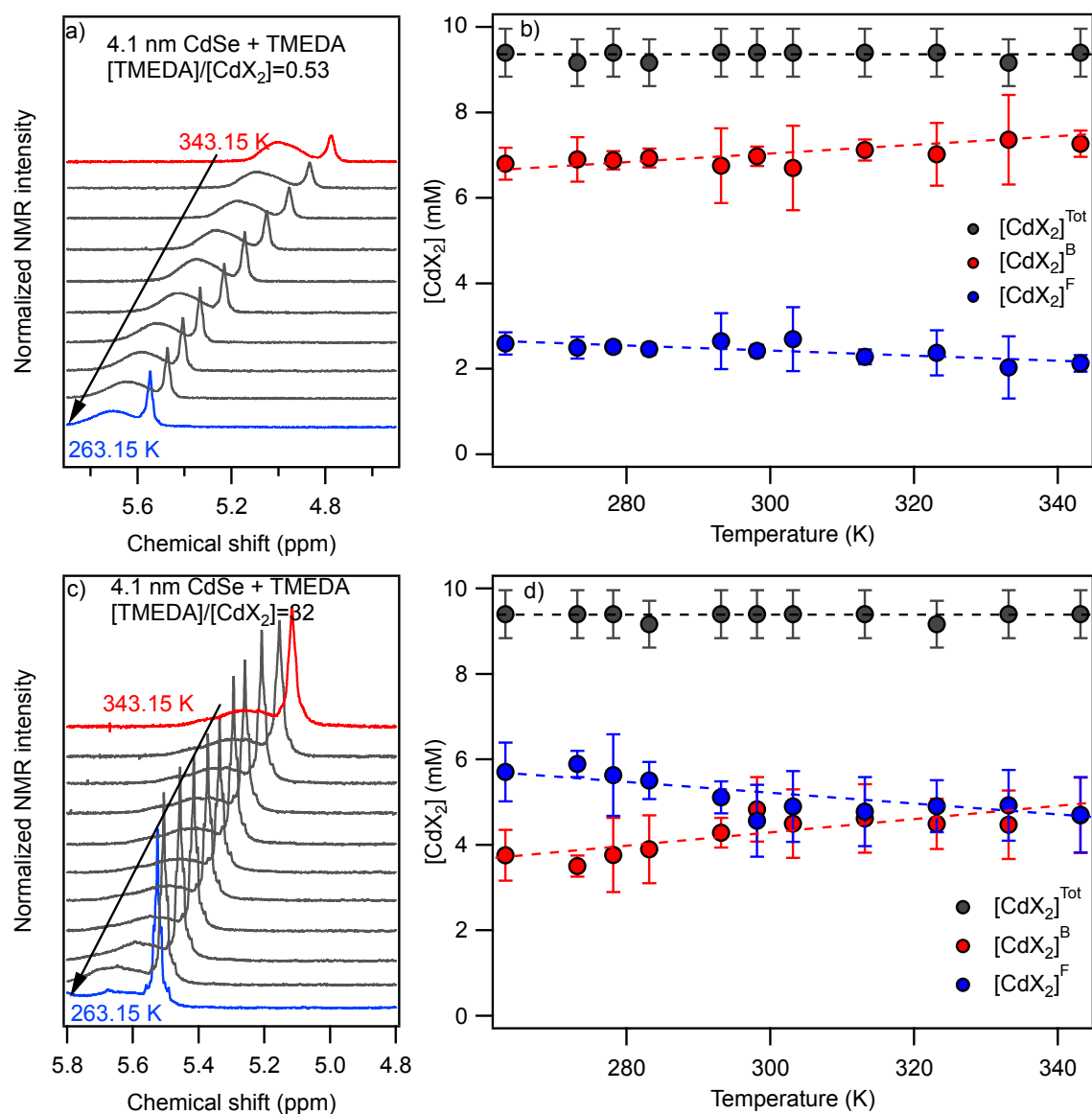


Figure SI 2.8.3. Temperature dependent ^1H NMR of 4.1 nm CdSe (78 μM) with a) 5 mM TMEDA and c) 303 mM TMEDA. Chemical shifts in part a and c don't change. The shifts towards right are due to visual purposes. Figures b and d show the change in concentration of free and bound CdX₂ with temperature from figures a and c, respectively. In both cases the total concentration of CdX₂ is preserved. Total concentrations are achieved from the direct integration of the NMR spectra (5.4-6 ppm) and are referenced to ferrocene. The concentrations of free and bound CdX₂ are achieved using the fitting parameters described in SI 2.4. Dashed lines are guides to the eye.

SI 2.9. Van 't Hoff Analysis on the temperature dependent ^1H NMR

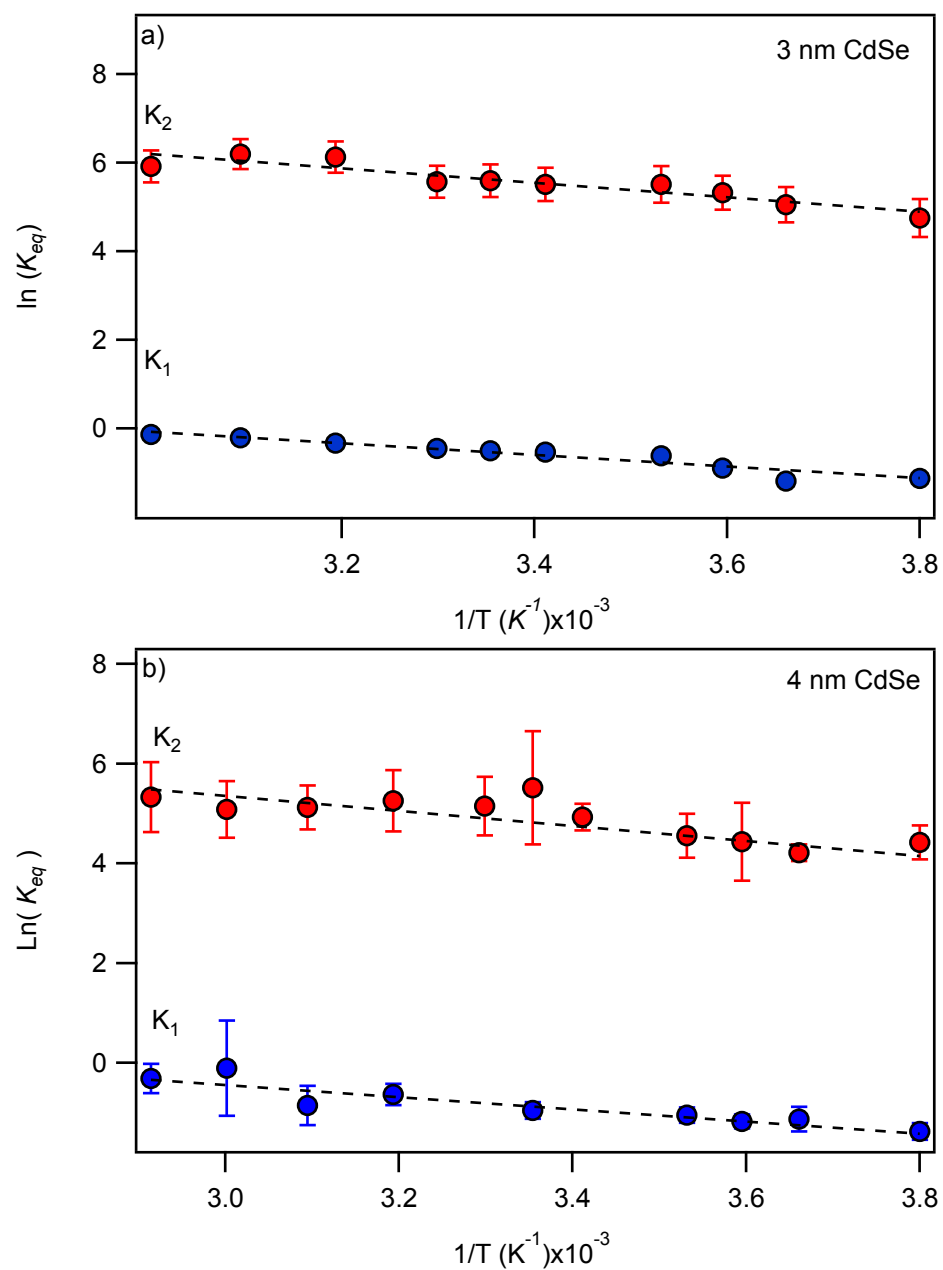


Figure SI 2.9. Temperature dependence of the equilibrium constants K_1 and K_2 for a) 3 nm CdSe NCs and b) 4.1 nm CdSe NCs. Blue circles: a,b) [TMEDA]= 5 mM. Red circles: a) [TMEDA]= 273 mM and b) [TMEDA]=303 mM.

SI 2.10. Transmission Electron Microscopy (TEM)

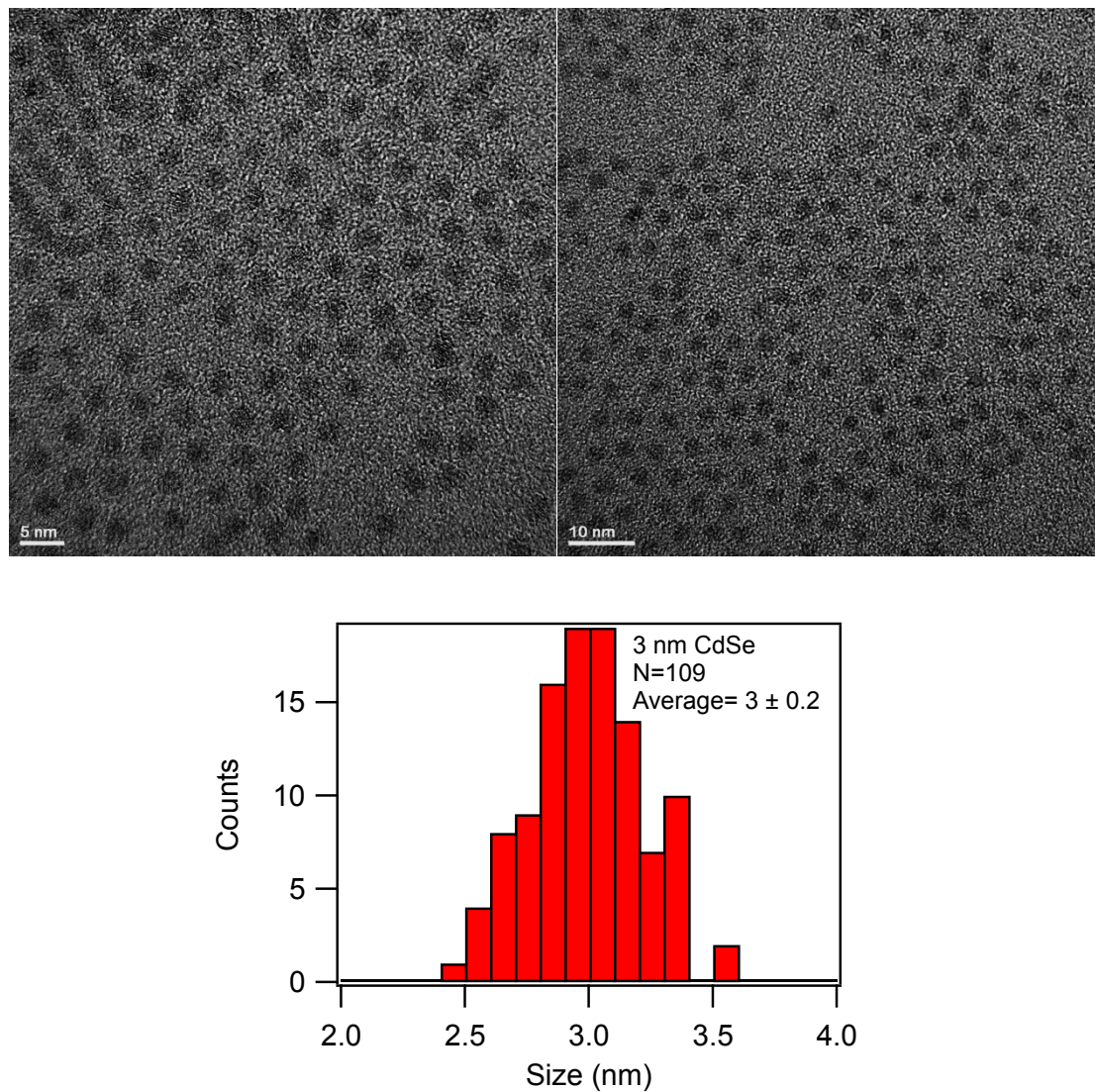


Figure SI 2.10.1. TEM images and histograms of 3 nm CdSe NCs.

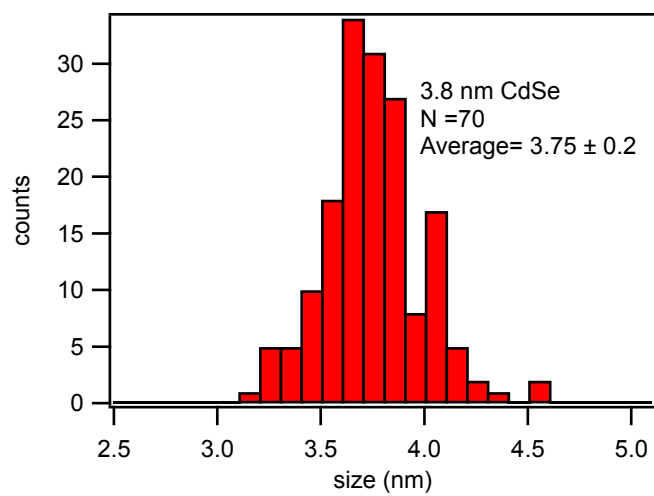
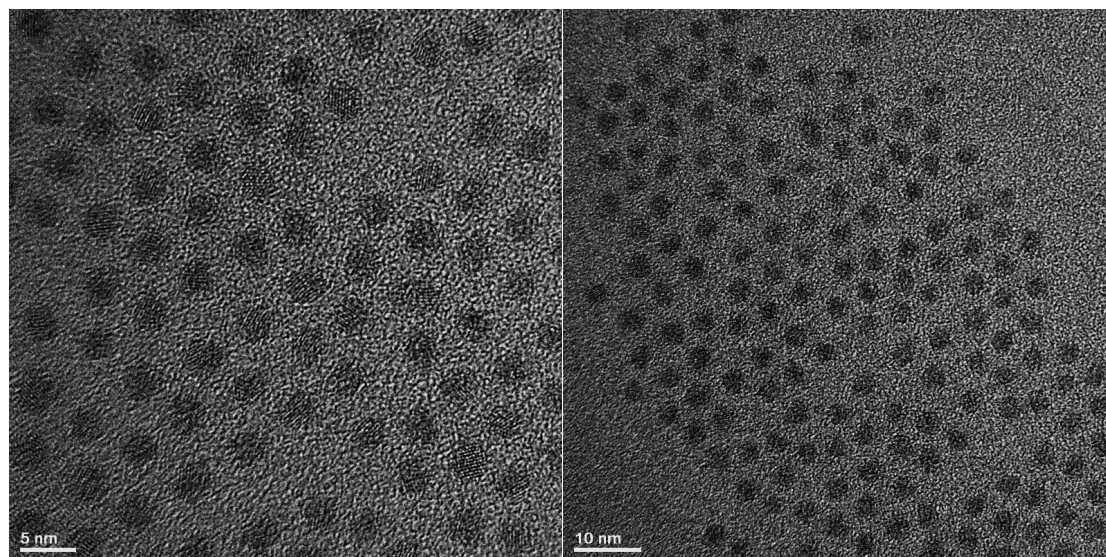


Figure SI. 2.10.2. TEM images and histograms of 3.8 nm CdSe NCs.

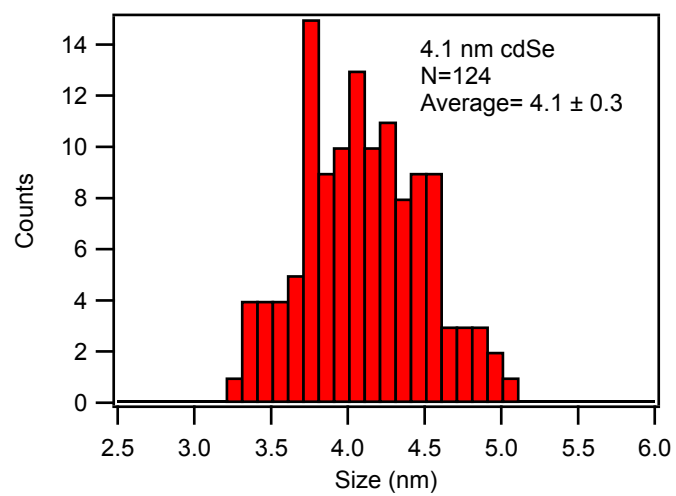
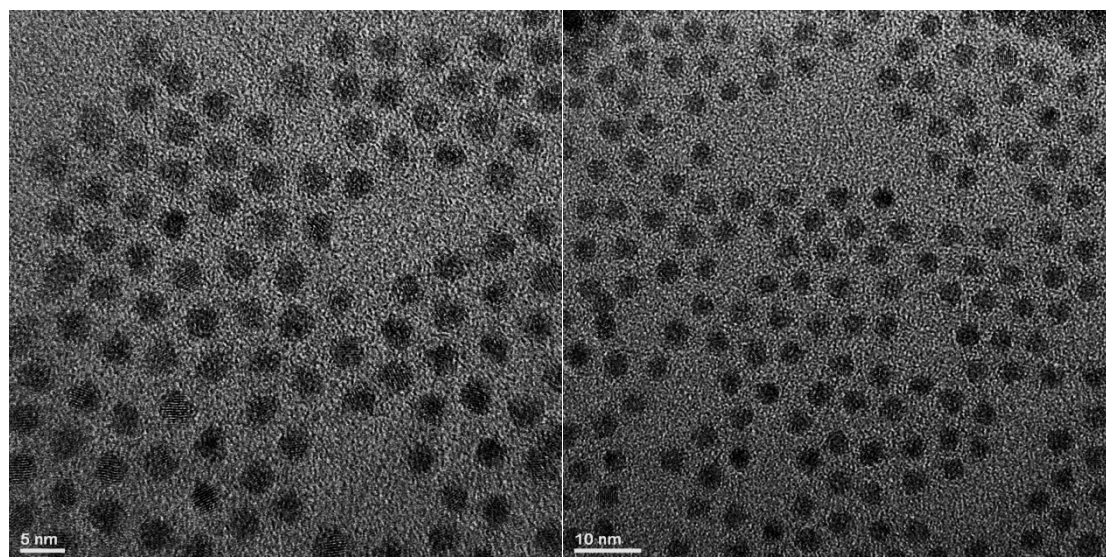


Figure 2.10.3. TEM images and histograms of 4.1 nm CdSe NCs.

SI. 2.11. Powder X-ray Diffraction

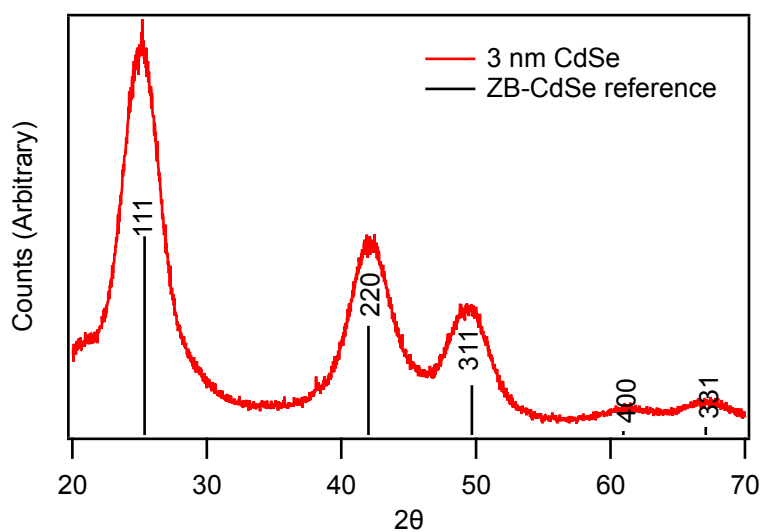


Figure 2.11.1. XRD of 3 nm CdSe . Reference diffraction angles for bulk zinc blende CdSe are given as black bars.

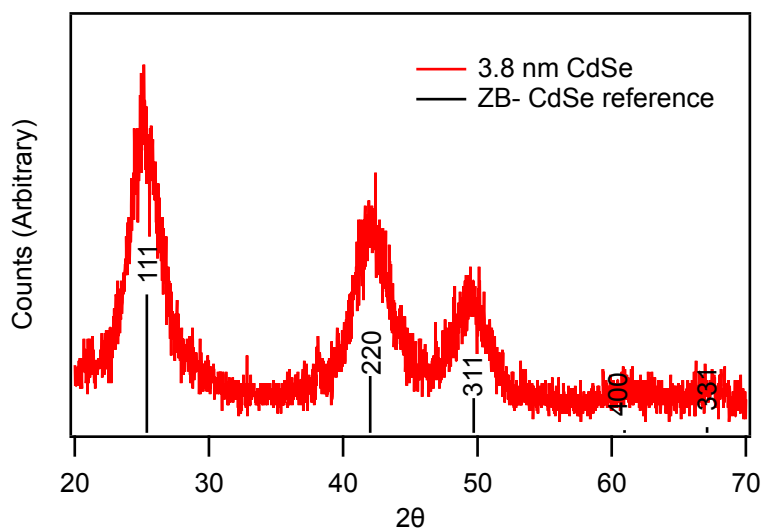


Figure SI 2.11.2. XRD of 3.8 nm CdSe. Reference diffraction angles for bulk zinc blende CdSe are given as black bars.

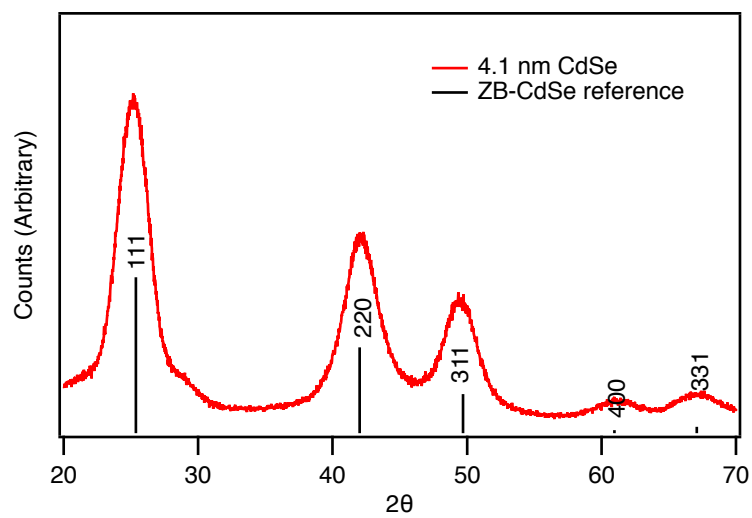


Figure SI 2.11.3. XRD of 4 nm CdSe. Reference diffraction angles for bulk zinc blende CdSe are given as black bars.

SI 2.12. Temperature Calibration Curve

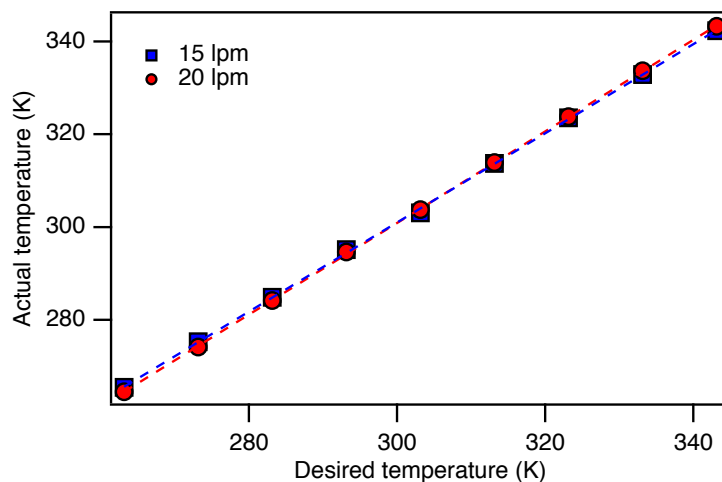


Figure SI 2.12. Temperature calibration curve with two different cooling nitrogen flow rates (blue, 15 lpm, and red, 20 lpm). This figure indicates that 20 lpm flow has least deviation from the desired temperature and the variations in temperature are negligible.

SI 2.13. Kinetics of ^1H NMR CdSe and TMEDA at -10°C

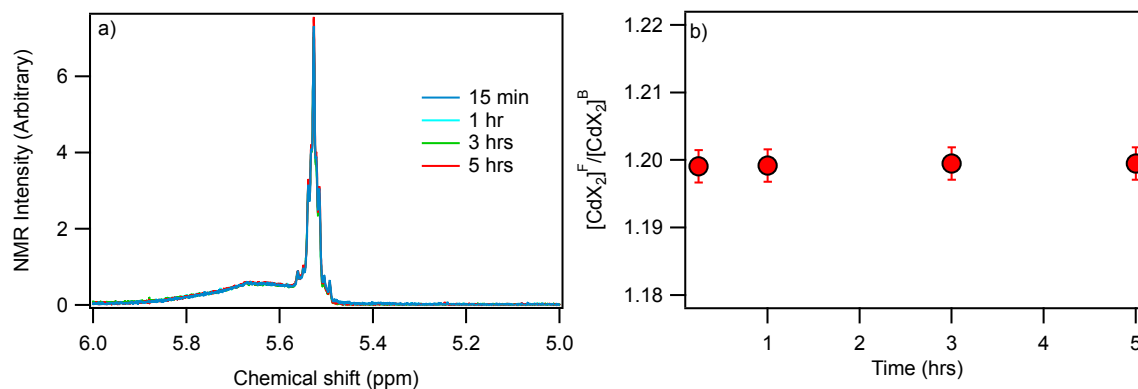


Figure SI 2.13. a) ^1H NMR spectra of 3.8 nm CdSe (78 μM) in the presence of 273 mM TMEDA at -10°C in different delay time b) kinetics of the ratio of free to bound CdX_2 indicating that 15 min delay is sufficient for the sample to equilibrate at lowest temperature in which it has the highest viscosity. Therefore 15 min delay is sufficient for samples to equilibrate in all other temperatures

SI 2.14. Fourier Transform Infrared (FTIR) Spectroscopy.

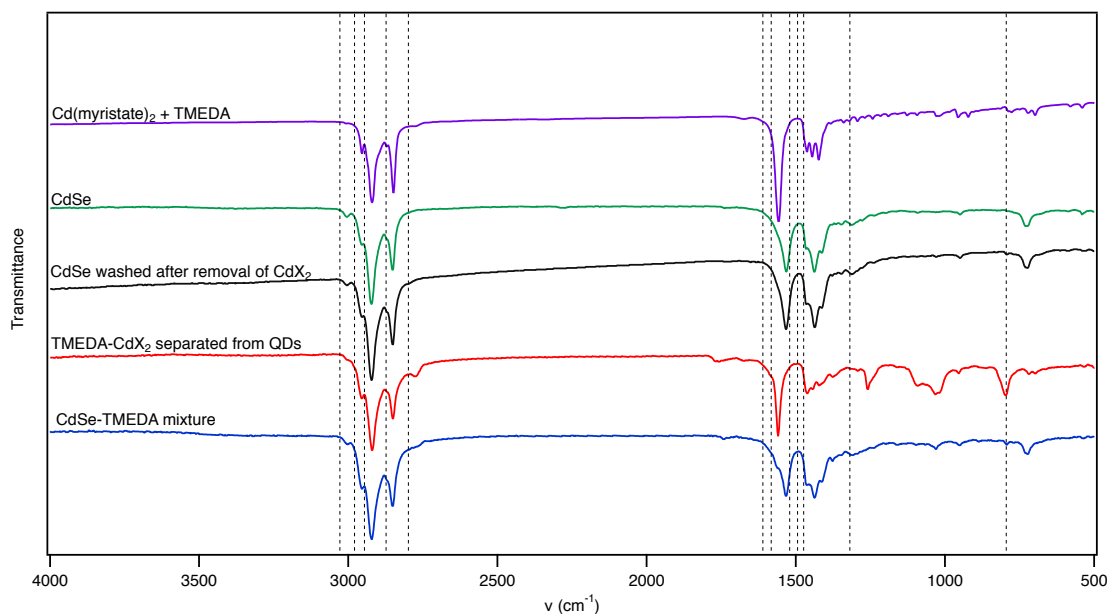


Figure SI 2.14. FTIR spectra of a separately made $\text{Cd}(\text{myristate})_2 + \text{TMEDA}$ mixtures (purple), CdSe NCs (green), washed CdSe after adding TMEDA and removal of CdX_2 ligands (black), separated TMEDA-CdX_2 complex (red) and the mixture of CdSe and TMEDA (blue). The asymmetric stretching band in the purple and red spectra is matched (both at $\nu=1560$ cm^{-1}) and they are shifted to higher wavenumber than the corresponding band in the CdSe only spectrum ($\nu=1533$ cm^{-1}), indicating the formation of free CdX_2 carboxylate species (as a form of TMEDA-CdX_2 complex).

SI 2.15. Reaction of CdSe NCs with Diethylzinc

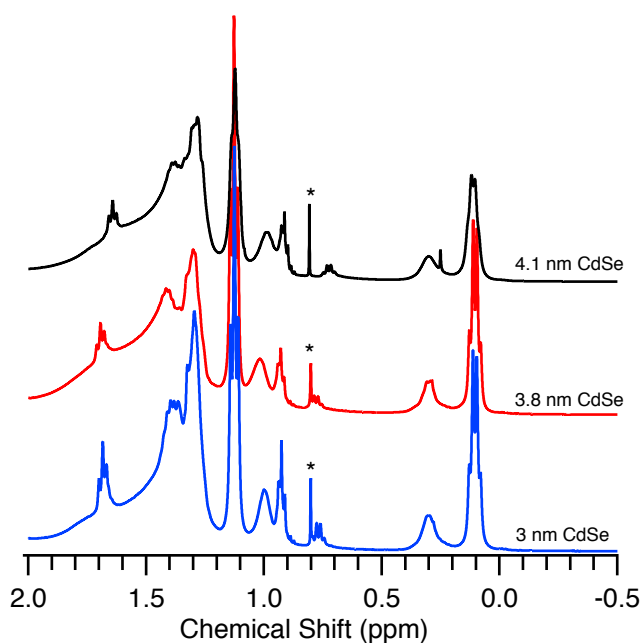


Figure SI 2.15. ^1H NMR spectra of NCs in presence of extra diethylzinc. (*) at $\delta=0.8$ is indicative of ethane gas that is released from the reaction of carboxylic acid and diethyl zinc. 3 nm CdSe (blue), 3.8 nm CdSe (red) and 4.1 nm CdSe (black).

Table SI 2.15. Final concentration of the species present for diethylzinc test

NC Diameter	[NC]	[RCOO ⁻]	[Et ₂ Zn]	[Fc]	[C ₂ H ₆]	% Carboxylic acid in NC sample
3 ± 0.2	1 ± 0.05	114 ± 9	235 ± 11	0.9 ± 0.05	5 ± 1	3-5
3.8 ± 0.2	0.36 ± 0.02	69 ± 7	142 ± 7	1.3 ± 0.05	3 ± 1	3-6
4.1 ± 0.3	1 ± 0.05	246 ± 20	460 ± 20	0.8 ± 0.1	16 ± 3	6-8

SI 2.16. Diffusion Ordered Spectroscopy (DOSY) on the mixture of CdSe NCs and TMEDA

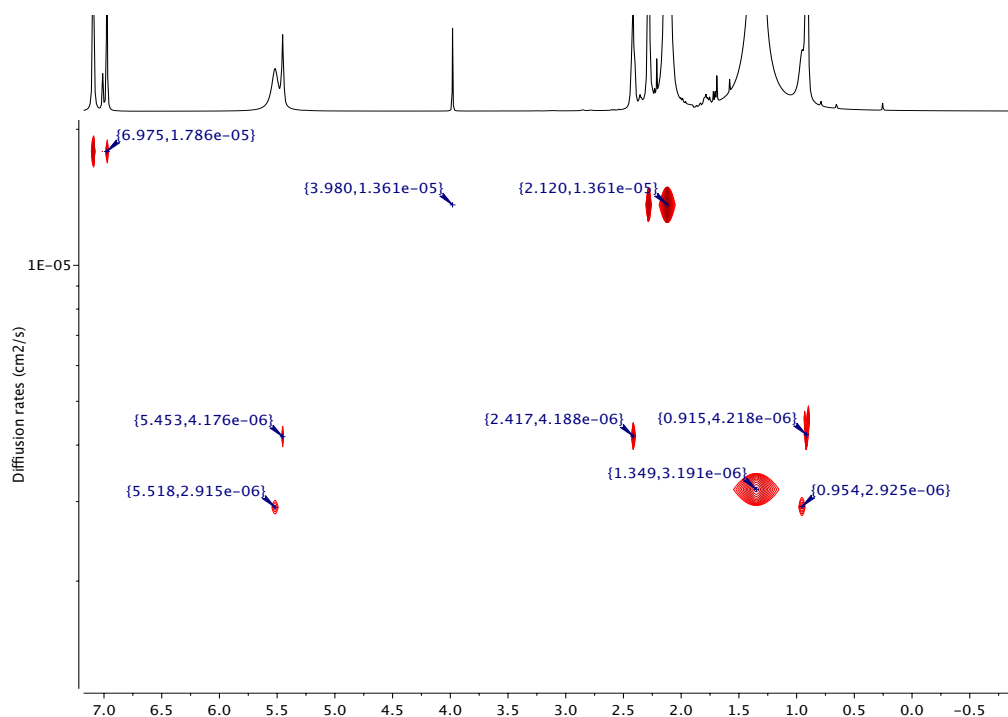


Figure SI 2.16. DOSY NMR spectrum of a d-toluene solution of 3.7 nm CdSe NCs with TMEDA ([TMEDA]/[QD]=~50) diffusion rates at 5.518 ppm and 5.453 ppm show the bound and free CdX₂ ligands.

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REFERENCES

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Chapter 3: Correlating the Efficiency of Nonradiative Excited State Processes to Specific Defects

3.1 Introduction

The surface chemistry of semiconductor NCs plays a critical role in our ability to tune their optoelectronic properties for variety of applications, for instance for electroluminescent-based devices.¹⁻³ This perspective has resulted in a re-evaluation of long-standing ideas in the surface science of semiconductor NCs and therefore has demanded new comprehensive research studies.⁴⁻⁸ The most common and informative approach to understanding the impact of surface of NCs on their excited state processes is PL spectroscopy.^{7,9} Many research groups have utilized PL spectroscopy to investigate the impact of different ligands on the optical properties of NCs.^{4,6,10-13} However, most of these studies, have neglected the impact of surface structure, surface defects and/or surface chemistry phenomena which affect the PL of NCs, for lack of detailed information about them. Previously, it has been realized that Z-type ligands above all other ligand types, have significant impact on the PL of NCs.¹⁴⁻¹⁶ In Chapter 2, we distinguished two different surface defects on CdSe NCs. We also correlated each defect to a specific surface type and modeled the creation of individual defects with the addition of TMEDA. In this Chapter, we began by discussing the impact of TMEDA on the PL of CdSe NCs. We show that TMEDA is not the actual PL quencher, but rather creates surface defects by exposing the Se surfaces, which can then directly be correlated to the PL quenching of CdSe.

3.2 Experimental Section

3.2.1 Chemicals

For list of all chemicals, please see Chapter 2, Section 2.2.3.

3.2.2 Synthesis of Cadmium Myristate

The synthesis of cadmium myristate was described in Chapter 2, Section 2.2.4.

3.2.3 Synthesis and Purification of CdSe NCs

The synthesis and purification of CdSe NCs were described in Chapter 2, Section 2.2.5.

3.2.4 Optical Spectroscopy

Optical spectroscopy instrumentation and measurements were described in detail in Chapter 2, Section 2.2.6.

3.2.5 Sample Preparation for Photoluminescence Spectroscopy

Samples for photoluminescence (PL) spectra measurements were prepared by diluting 30 μ L aliquots from each NMR sample (described in Chapter 2, Section 2.2.12) to 2 mL with toluene. Equilibrated samples of CdSe NCs with various amounts of TMEDA exhibit surprisingly sustained stability for colloidal materials. The same samples were used for different spectroscopy measurements after 8 months of storage in a glovebox, and they exhibited similar surface coverage as measured by ^1H NMR, PLQY, and absorption spectra, confirming no change in the average size, surface composition, or concentration of suspended NCs during the storage time.

3.2.6 Isolation of CdSe NCs Samples After Their Treatment with TMEDA

To investigate the impact of isolating NCs from the TMEDA/free CdX_2 species, each CdSe NC sample was treated with two different values of TMEDA and analyzed by PL and ^1H NMR to

quantify the surface coverage and PLQY before and after isolation of NCs from TMEDA. The two separate TMEDA treatments were selected as follows:

(1) 5 mM TMEDA to 0.078 μM CdSe NCs, keeping the displacement of CdX_2 in the first displacement regime.

(2) 303 mM TMEDA to 0.078 μM CdSe NCs, driving the equilibrium into the second regime.

(each regime is identified with an arrow in Figure 2.4(c)). The parameters for each ^1H NMR measurements and for different sizes of CdSe NCs are given in Appendix, SI 3.1. Ferrocene was used as internal standard (final concentration was 0.23 mM for all measurements). For PLQY measurements, samples were diluted to 1.0-1.5 μM concentration, and measured using an integrating sphere.

Isolation of NCs: The mixtures of TMEDA and NCs were cleaned by first removing the solvent under vacuum and following by addition of ethyl acetate to crash out the particles and centrifugation. Two more cycles of washing with pentane and ethyl acetate were repeated and then samples were allowed to dry under nitrogen for 48 hours, and then resuspended in 600 μL of *d*-toluene. 30 μL of each NMR sample was taken and diluted for absorption (to calculate the new concentrations) and PL measurements. Ferrocene was then added for quantitative NMR analyses. From the combined NMR and UV-Vis data, new surface coverages (post-isolation) were measured. The PL spectra were collected for all samples and normalized to their concentration for comparison purposes. The whole procedure of NMR, PL and absorption measurements were repeated three times (every time starting with a fresh sample) for statistical purposes. At the end, for more accurate measurements, similar isolated samples from each trial were combined together and dried under nitrogen and vacuum, then dissolved in *d*-toluene and then all previous measurements (^1H NMR, PL, UV-Vis) were repeated. PLQY of these combined samples were also

measured independently using an integrating sphere (I_0/I values measured from both methods were in great agreement). Surface coverages reported here are the average values from the analysis of NMR (same as surface coverage section).

3.3 Impact of Specific Surface Vacancies on PL Efficiency

With the knowledge of the energetics of CdX_2 surface binding in hands from Chapter 2, we proceed to analyze the impact that the displacement of this group from the NC surfaces has on the excitonic photoluminescence (PL). As shown in Figure 3.1, the addition of TMEDA to CdSe NC suspensions dramatically impacts the PL intensity, an indication that efficient non-radiative recombination processes are becoming operative in the presence of TMEDA.^{14,17} The normalized PL ratios from these PL spectra are plotted in Figure 3.2(a).

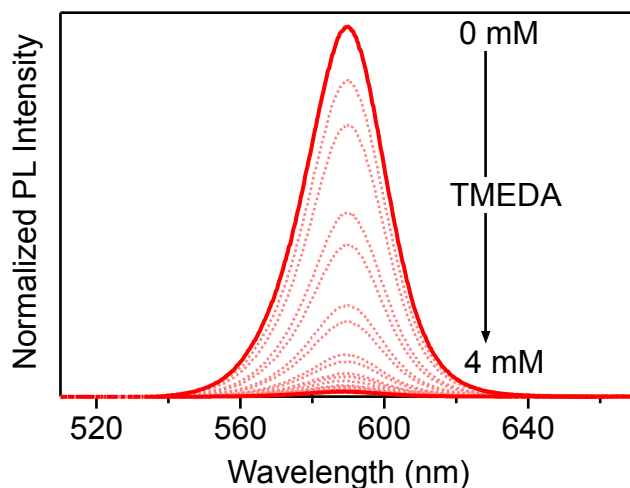


Figure 3.1. PL spectra of 3.8 nm CdSe NCs ($\sim 1.0 \pm 0.1 \mu\text{M}$ in toluene), with varying amounts of TMEDA (0–4 mM).

Quantitatively, the PL quenching efficiency is better characterized through the Stern-Volmer formalism, whereby the reciprocal of the PL intensities, normalized to the PL intensity in the absence of the quencher (I_0), as reported in Figure 3.2(b):

$$\frac{I_0}{I} = 1 + K_{SV}[Q] \quad \text{eq.3.1}$$

where $[Q]$ is the quencher species concentration and K_{SV} is a constant characterizing the efficiency of the PL quenching process; from the onset of the Stern-Volmer data for TMEDA presented in Figure 3.2(b), $K_{SV} = (57,000 \pm 1,000) \text{ M}^{-1}$. Of course TMEDA is not itself the direct PL quenching species, but rather acts indirectly by creating CdX_2 vacancies on the NC surfaces that are active trap centers, presumably as efficient hole trapping species.^{15,16} As the impact of TMEDA on the displacement of CdX_2 has been fully characterized above, a direct connection between the PL efficiency (which is indirectly reporting on the presence of trap centers) and the precise composition of the NC surface can be made, as presented in Figure 3.2(c). This figure clearly indicates a strong correlation between the overall PL quenching and the creation of B_2 sites vacancies: comparatively, the removal of CdX_2 species from B_1 sites does not appreciably quench the NC PL (the rise of the Stern-Volmer ratio at large B_1 displacement values is actually due to the concomitant creation of B_2 vacancies).

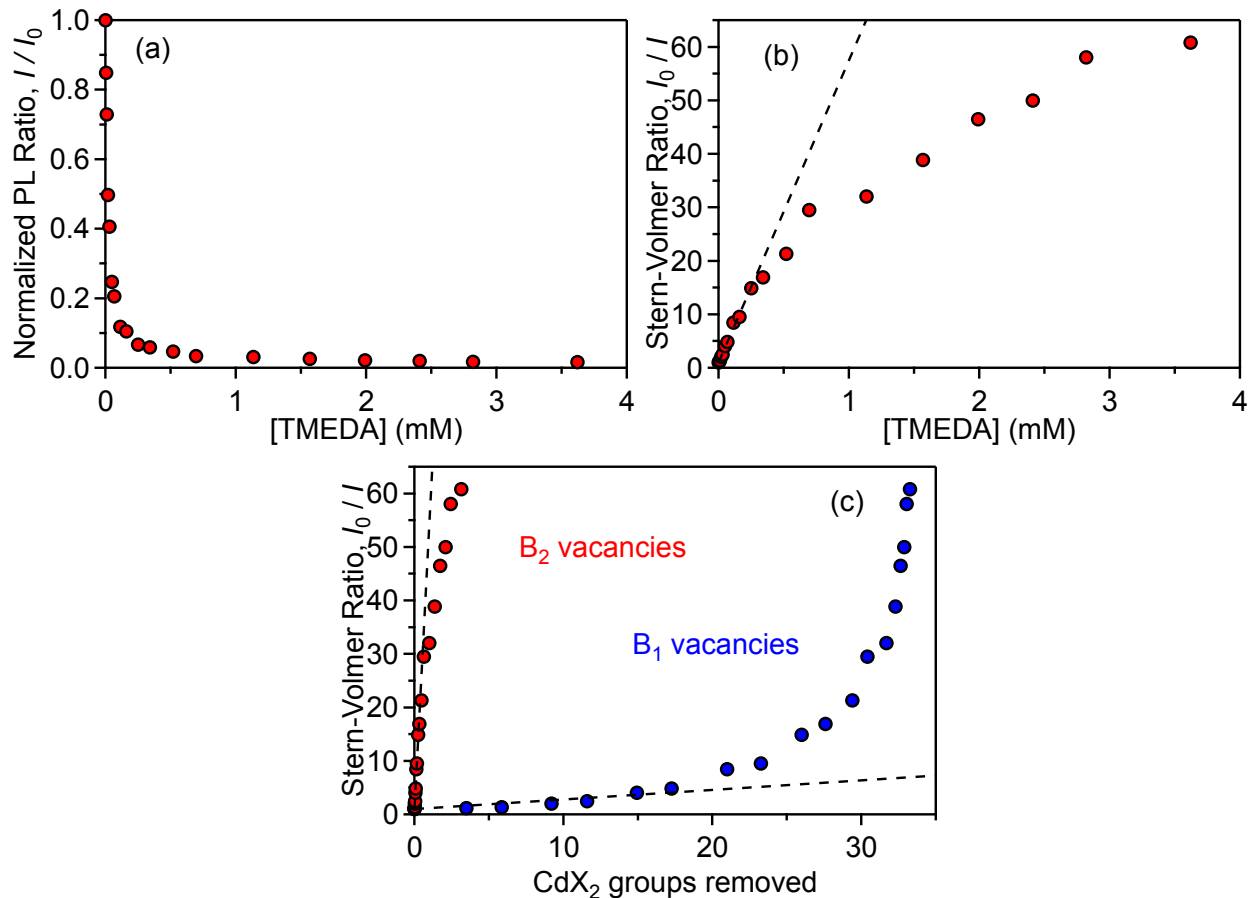


Figure 3.2. a) PL intensity of 3.8 nm CdSe NCs ($\sim 1.0 \pm 0.1 \mu\text{M}$), with varying amounts of TMEDA (0 -3.6 mM). Intensities have been normalized to the integrated PL intensity of the CdSe NCs-only sample (I_0), after baseline subtraction. b) Quantification of the TMEDA-induced CdSe NC PL quenching, reported as the Stern-Volmer ratio, I_0/I . the dashed line is the linear fit on the onset of the data, giving the slope (K_{SV}) of $57,000 \pm 1,000 \text{ M}^{-1}$ (c) CdSe NC PL quenching efficiencies of each type of vacancies, as induced by displacement of CdX₂ by TMEDA. The dashed lines are linear least squares fitted curves, constrained to the initial quenching region. The PL quenching correlates well with the creation of vacancies on the B₂ sites. Data for 3 and 4.1 nm CdSe NCs are given in Appendix, SI 3.2.

From the values of the Stern-Volmer constants extracted from the onset of each regime, the efficiency of a B₂ vacancy is estimated to be nearly 300 times larger than that of a B₁ vacancy: $K_{SV} = 0.18/\text{CdX}_2$ for B₁ vs. $53/\text{CdX}_2$ for B₂ (Table 3.1). This stark contrast between the two types of vacancies underlines that not all surface defects are necessarily equivalent, even for such defects that are in appearance quite similar (here, CdX₂ vacancies). Furthermore, although the overall stability of the B₂-CdX₂ complex overwhelmingly surpasses that of the B₁-CdX₂ (making B₂ vacancies much rarer species under equilibrium conditions), the creation of even a single B₂

vacancy leads to a greater impact on the PL quenching (by over one order of magnitude) than would occur from the removal of every CdX_2 group bound to B_1 sites. Ultimately, the brightness of CdSe NCs is exceedingly sensitive to B_2 vacancies, and without the strong thermodynamic stability of CdX_2 complexes bound to these sites, the use of Cd-based Z-type ligands to passivate under-coordinated Se sites would unlikely be a successful strategy to mitigate non-radiative recombination processes.

Interestingly, a systematic trend between the quenching efficiency of single vacancies and the average NC diameter is observed, whereby smaller NCs are most efficiently quenched by each surface defects (Table 3.1); the same trend is also observed in the ratios between the Stern-Volmer constants for the two sites. The magnitude of the effect, which does not scale directly with the surface-to-volume ratio, might possibly indicate enhanced coupling to the surface states in more strongly quantum confined systems; a quantitative evaluation of this complicated effect is complicated and was not attempted.

3.4 The Photoluminescence and Surface Coverage of the Isolated CdSe NCs Sample After Their Treatment with TMEDA

We note that the PLQY of isolated NC samples (following repeated ethyl acetate/pentane crashing/resuspension cycles) are always markedly higher than for the same samples in the TMEDA/free CdX_2 mixtures (data for 3.8 nm CdSe NCs is shown in Figure 3.3, data for 3 nm and 4.1 nm are given in the Appendix, SI 3.1). Interestingly, an analysis of the surface coverage after isolation shows a concomitant increase in the surface coverage which follows precisely the trend observed for the NC/TMEDA/free CdX_2 mixtures (see Appendix, SI 3.1) suggesting that NCs before and after isolation are behaving identically, provided proper correction for the change in the

surface coverage. This also suggests that TMEDA does not impact the PLQY of CdSe NCs, as there are not significant differences observed between samples with very high concentrations of TMEDA and those after isolation. The increase in the surface coverage for isolated NCs is likely attributable to a reduction of the solubility of the TMEDA-CdX₂ complex in the non-polar/polar solvent mix, which drives the rebinding of the cadmium complex onto the surface.

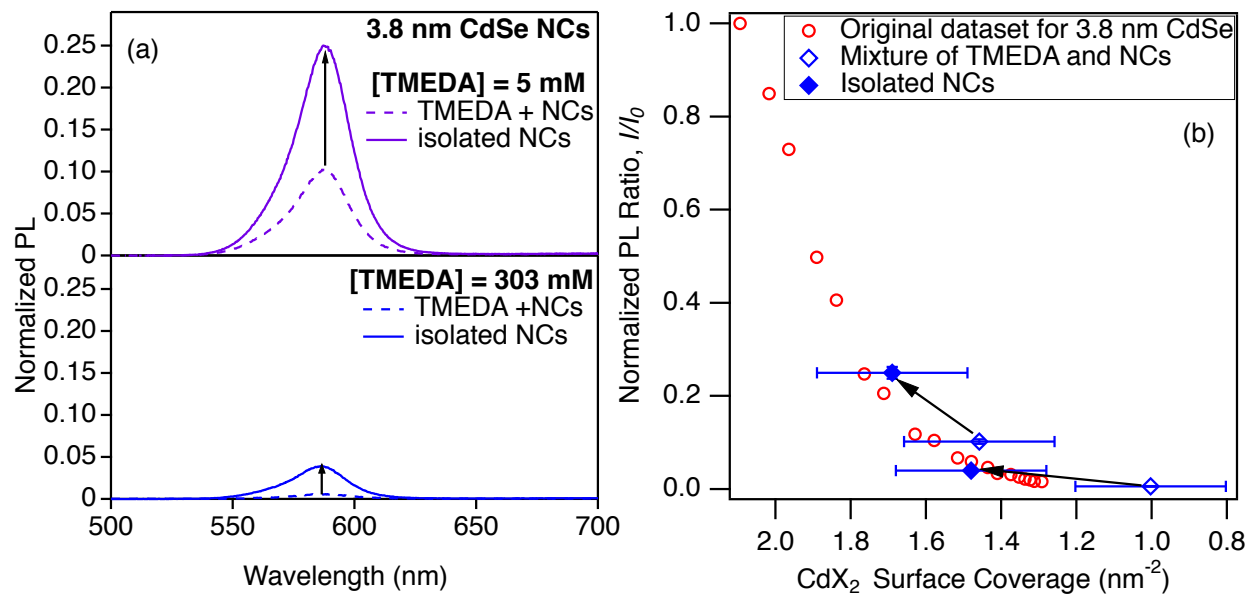


Figure 3.3. a) Photoluminescence of CdSe NCs in presence of TMEDA (purple, 5 mM, and blue, 303 mM) and isolated after the TMEDA treatment. b) Correlation of the relative PLQY and the surface coverage for mixture of TMEDA and NCs (blue open diamonds) and isolated NCs (blue filled diamonds) are shown and compared with the original dataset of TMEDA titration to CdSe NCs. This figure illustrates the correlation of PL and surface coverage of before and after TMEDA treatment (black arrow showing the change from prior to after isolation). Same data for other sizes of NCs is shown in the Appendix, SI 3.1.

Table 3.1. CdSe NCs PL and Stern-Volmer analysis data.

NC Diameter (nm)	$K_{SV}^{B_1}$ (M^{-1})	$K_{SV}^{B_2}$ (M^{-1})	$\frac{K_{SV}^{B_2}}{K_{SV}^{B_1}}$
3.0 ± 0.2	0.22 ± 0.04	170 ± 20	800 ± 200
3.8 ± 0.2	0.18 ± 0.02	53 ± 4	290 ± 40
4.1 ± 0.3	0.11 ± 0.03	12 ± 1	150 ± 60

NC Diameter (nm)	PLQY _{bright} ^a (%)	PLQY _{dark} ^b (%)	P_{dark} ^c (%)	Observed PLQY (%)	Predicted PLQY ^d (%)
3.0 ± 0.2	17 ± 2	0.1 ± 0.1	0.4	16 ± 3	16 ± 2
3.8 ± 0.2	14 ± 2	0.3 ± 0.3	1.0	10 ± 2	13 ± 2
4.1 ± 0.3	22 ± 5	2 ± 1	2.0	12 ± 2	22 ± 5

^a Calculated PLQY of a NC without a B₂ vacancy, eq.3.1; ^b Calculated PLQY of a NC with a single B₂ vacancy, eq. (20); ^c Probability that a NC has a single B₂ vacancy; ^d Overall calculated PLQY = $(1 - P_{dark}) \times \text{PLQY}_{bright} + P_{dark} \times \text{PLQY}_{dark}$

3.5 Correlating Specific Facet Vacancies with Photoluminescence Quantum Yields: Dark vs Bright NCs.

In Section 3.3, we correlated how vacancies generated on each of the two specific sites, B₁ and B₂, affected the photoluminescence efficiency. Having now in hand a better microscopic description of the nature of each of these sites (Chapter 2, Section 2.6), we complete this study by correlating the proposed surface composition of zinc-blende CdSe NCs with their observed photoluminescence behavior. Although we found in Section 3.3 that B₁/(111) vacancies are not as effective as B₂/(100) vacancies in quenching the PL of CdSe NCs, we were also led in Chapter 2 (Section 2.6) to postulate the existence of a rather large number of B₁/(111) vacancies that are present in the as-prepared samples (that is, before the deliberate displacement of CdX₂ complexes

by TMEDA). As a consequence, assuming that each of these vacancies provides the same types of non-radiative relaxation pathways than those we found for B₁/(111) vacancies generated by the action of TMEDA, we can readily estimate the starting PLQY of such as-prepared NCs (which we label here as “bright” NCs, to distinguish with “dark” NCs we will soon discuss):

$$\text{PLQY}_{\text{bright}} = \frac{1}{1 + K_{SV}^{B_1} (N_{1,tot} - N_1)} \quad \text{eq.3.1}$$

where the difference between $N_{1,tot}$ (Table 2.5) and N_1 (Table 2.3) corresponds to the number of B₁/(111) vacancies per NC, and we assume that a NC without any vacancies would possess unity PLQY. The estimated $\text{PLQY}_{\text{bright}}$ obtained from eq.3.1 are listed in Table 3.1, and qualitatively compare well with the observed PLQY of each sample, although being systematically larger. One additional contribution to the PLQY of CdSe NCs might arise from the presence of B₂/(100) vacancies. Although such vacancies cannot be predominant given the free energy cost, any NC with even a single of these vacancies would have a significantly lower PLQY than NCs with only B₁/(111) vacancies, and would properly be described as a “dark” NC compared to the ensemble. The probability that a B₂/(100) vacancy is found, P_{dark} can be calculated from the equilibrium of eq. (2.15), using the number of B₁/(111) vacancies and the revised equilibrium constant K_1 (~ 0.2) obtained in Chapter 2 (Section 2.6); the calculated values for P_{dark} are listed in Table 3.1, and are all found to be on the order of 1% for the different NC sizes sampled here (calculations of P_{dark} are given in the Appendix, SI 3.3). The photoluminescence of these “dark” NCs can be obtained from the Stern-Volmer analysis data of Section 3.1:

$$\text{PLQY}_{\text{dark}} = \frac{1}{1 + K_{SV}^{B_1} (N_{1,tot} - N_1 + 1) + K_{SV}^{B_2}} \quad \text{eq.3.2}$$

where for simplicity only the case of single $B_2/(100)$ vacancy per NC is treated (the probability that a NC is found with more than one vacancy is lower than 0.1% in all cases). The values listed in Table 3.1 show that photoexcited “dark” CdSe NCs are at least ten times less likely to radiatively recombine than their “bright” counterparts, with smaller NCs presenting the most striking dark/bright contrasts. It is important to point out here that the distinction made here between “dark” and “bright” NCs is likely not linked to the ubiquitous “blinking”, or PL intermittency, phenomenon exhibited by most NC materials,^{18,19} as the “dark” PLQY values calculated here are still too large to sufficiently explain that phenomenon. Recent studies have suggested that PL blinking is probably linked to electron trapping processes that lead to delayed PL on long timescale;²⁰⁻²³ such electron trapping processes, the microscopic origin of which is still under debate, are not taken into account here, but perhaps explain partly the remaining discrepancy between the PLQY values we simulate and the observed ones. At any rate, we emphasize emphatically here that the proposed model of the overall PLQY discussed in this Section should not be taken too literally given the complexity of the actual problem. Rather, these results should be taken as representing part of the puzzle: inasmuch as the specific surface sites we uncovered here do exist on CdSe NCs, there will be unavoidable non-radiative losses associated with these; using an objective assessment of the actual prevalence of each site vacancy leads to qualitative agreement with the observed PLQY, suggesting that our estimate of the non-radiative recombination efficiencies of each type of site and of the surface composition are reasonably accurate. In this case, whereas full coverage of the Se-rich (100) facets appears absolutely critical to limit efficient non-radiative recombination in zinc blende CdSe NCs, for carboxylate-capped species the (100) facets rarely exhibit vacancies, and it is the low coverage of the (111) facets that effectively dictates the relatively low PLQY of the as-prepared materials.

3.6 Conclusions

we have demonstrated a direct correlation between specific surface defects and nonradiative recombination processes occurring at the surface of cadmium-rich zinc-blende CdSe NCs. We show that the two types of site not only differ strikingly in their binding affinity to CdX_2 complexes, but also lead to very different nonradiative excited-state relaxation mechanisms. Our results directly support the proposal that Cd vacancies on (100) facets are efficient trapping centers, but also provide a wider context by allowing a direct quantitative estimate of the overall (ensemble) PLQY of CdSe NCs from the knowledge obtained in this study about the thermodynamic stability and prevalence of specific surface defects. These results provide insights into the complexity of the surface of CdSe NCs, which are expected to impact the development of targeted designs of efficient NC systems for energy-conversion applications.

APPENDIX

SI 3.1. Correlation of photoluminescence and surface coverage of the isolated CdSe NCs sample after their treatment with TMEDA

Table SI 3.1. concentrations of NCs and the relative ratios of TMEDA to NCs in NMR measurements

NC Diameter	[NC] (mM)	[TMEDA]/[NC] first regime
3.0 ± 0.2	0.086 ± 0.002	58 ± 1
3.8 ± 0.2	0.066 ± 0.002	76 ± 1
4.1 ± 0.3	0.053 ± 0.002	95 ± 1

NC Diameter	[TMEDA]/[NC] second regime	[TMEDA]/[CdX ₂] first regime	[TMEDA]/[CdX ₂] second regime
3.0 ± 0.2	3523 ± 1	1 ± 0.1	62 ± 2
3.8 ± 0.2	4591 ± 1	0.8 ± 0.1	48 ± 2
4.1 ± 0.3	5717 ± 1	0.8 ± 0.1	49 ± 2

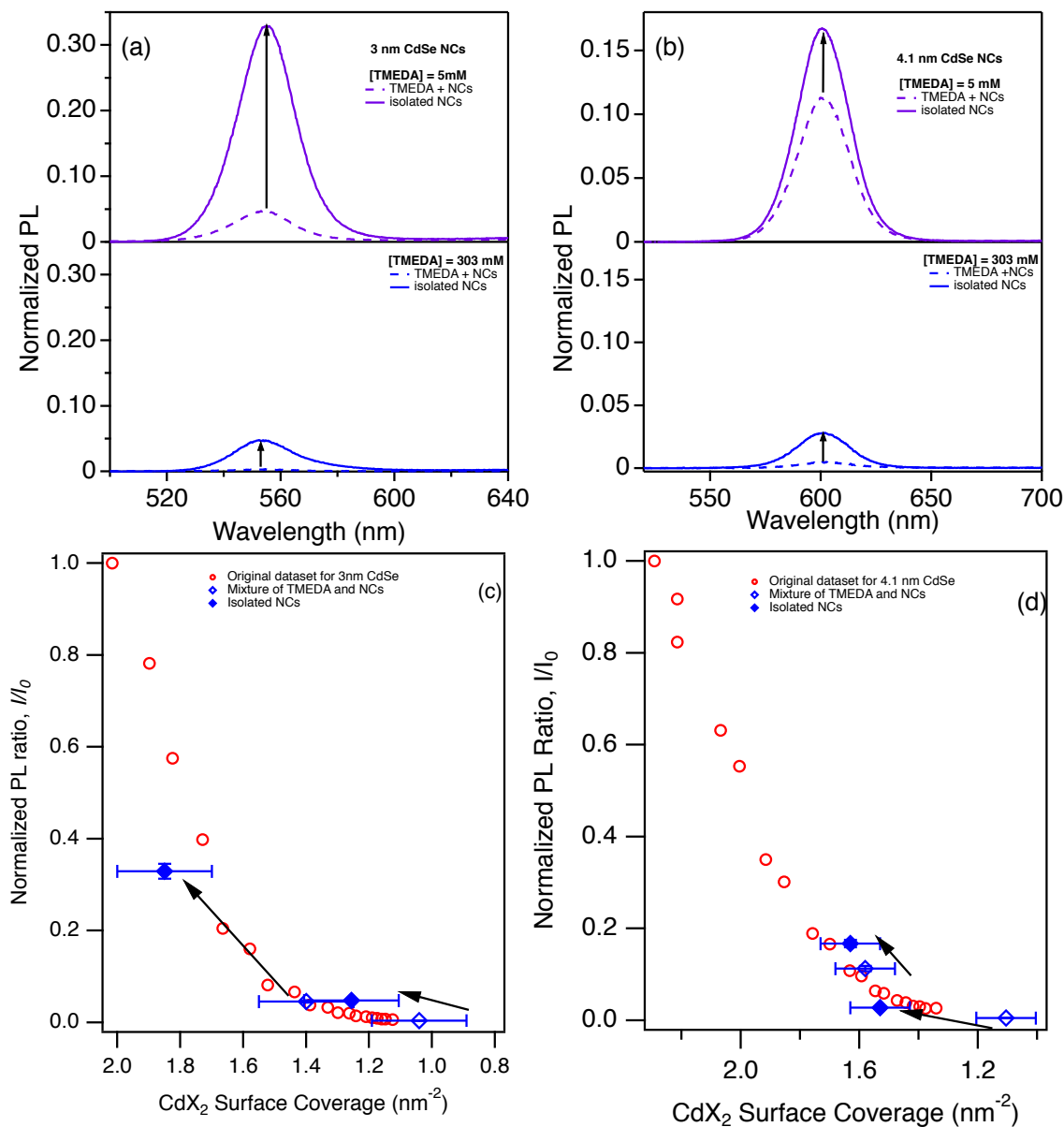


Figure SI 3.1. Photoluminescence of CdSe NCs (a,b are 3 nm and 4.1 nm respectively) in presence of TMEDA (purple, 5 mM, and blue, 303 mM) and isolated after the TMEDA treatment. Correlation of the relative PLQY and the surface coverage for mixture of TMEDA and NCs (blue open diamonds) and isolated NCs (blue filled diamonds) are shown and compared with the original dataset of TMEDA titration to CdSe NCs. (c and d are these correlation for 3 nm and 4.1 nm respectively)

SI 3.2. Correlation of Surface Vacancies to the Optical Properties of CdSe NCs

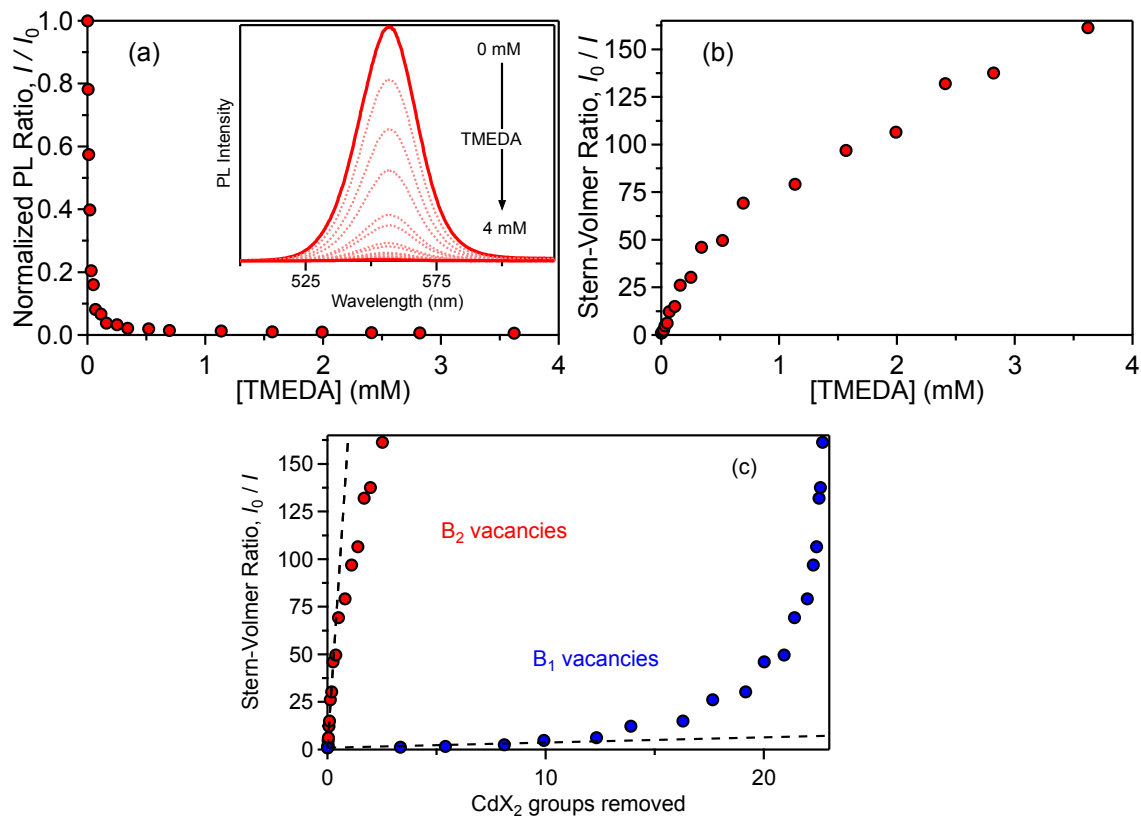


Figure SI 3.2.1 a) PL intensity of 3 nm CdSe NCs ($\sim 1.0 \pm 0.1 \mu\text{M}$), with varying amounts of TMEDA (0-4 mM). Inset: PL spectra of the same samples. Intensities have been normalized to the integrated PL intensity of the CdSe NC-only sample (I_0), after baseline subtraction and correction for dilution effects. b) Quantification of the TMEDA-induced CdSe NC PL quenching, reported as Stern-Volmer ratio, I_0/I . c) CdSe NC PL quenching efficiencies of each type of vacancies, as induced by displacement of CdX₂ by TMEDA. The dashed lines are linear least square fitted curves, constrained to the initial quenching region. The PL quenching correlates well with the creation of vacancies on the B₂ sites.

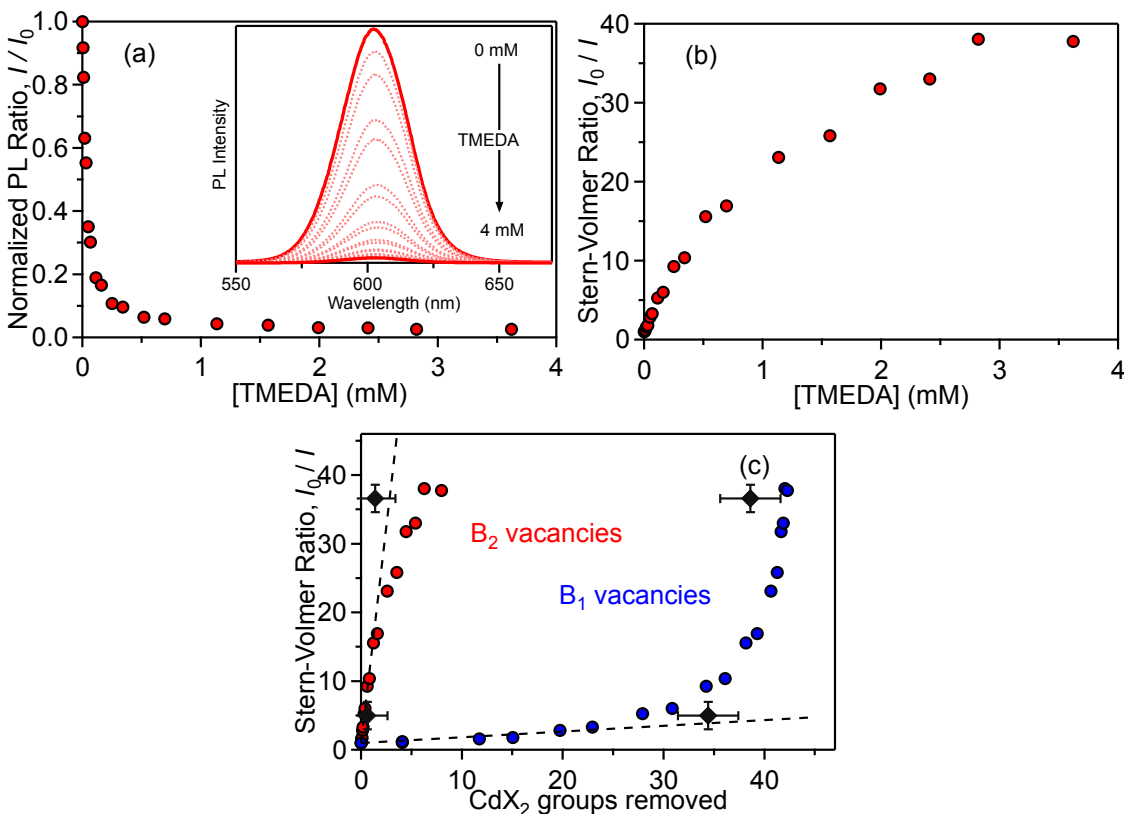


Figure SI 3.2.2. a) PL intensity of 4.1 nm CdSe NCs ($\sim 1.0 \pm 0.1 \mu\text{M}$), with varying amounts of TMEDA (0-4 mM). Inset: PL spectra of the same samples. Intensities have been normalized to the integrated PL intensity of the CdSe NC-only sample (I_0), after baseline subtraction and correction for dilution effects. b) Quantification of the TMEDA-induced CdSe NC PL quenching, reported as Stern-Volmer ratio, I_0/I . c) CdSe NC PL quenching efficiencies of each type of vacancies, as induced by displacement of CdX₂ by TMEDA. The dashed lines are linear least square fitted curves, constrained to the initial quenching region. The PL quenching correlates well with the creation of vacancies on the B₂ sites.

SI 3.3. Calculation of P_{dark}

The probability that a NC is found with a single B2 vacancy is calculated assuming a Poisson distribution:

$$P_{dark} = \lambda e^{-\lambda}$$

where λ is the ensemble average number of B2 vacancy per NC; this quantity is obtained from the equilibrium between the two sites, recognizing that there are $N_{1, tot}$ B1 sites and N_2 B2 sites, and $(N_1 + N_2)$ total sites that are occupied. As described in the text, given the large differences in the equilibrium constants K_1 and K_2 , most B2 sites will be occupied, and almost all vacancies will be found on the B1 sites. λ is thus obtained by solving the following quadratic equation:

$$\frac{K_2}{K_1} = \frac{[B_2 - CdX_2][B_1]}{[B_1 - CdX_2][B_2]} = \frac{(N_2 - \lambda)(N_{1, tot} - N_1 - \lambda)}{(N_1 + \lambda)\lambda}$$

where N_1 , N_2 , K_2 are given in Table 1, $N_{1, tot}$ is given in Table 5, and $K_1 = 0.23$ for all sizes (i.e. the revised value taking into account the vacant B1 sites; see Section 3.5 of the main text).

The values of λ and P_{dark} for each NC size studied in the text are given in Table S4 below.

Table SI 3.3. Calculation of P_{dark}

NC Diameter	λ	P_{dark}
3.0 ± 0.2	0.009	0.009
3.8 ± 0.2	0.021	0.02
4.1 ± 0.3	0.044	0.042

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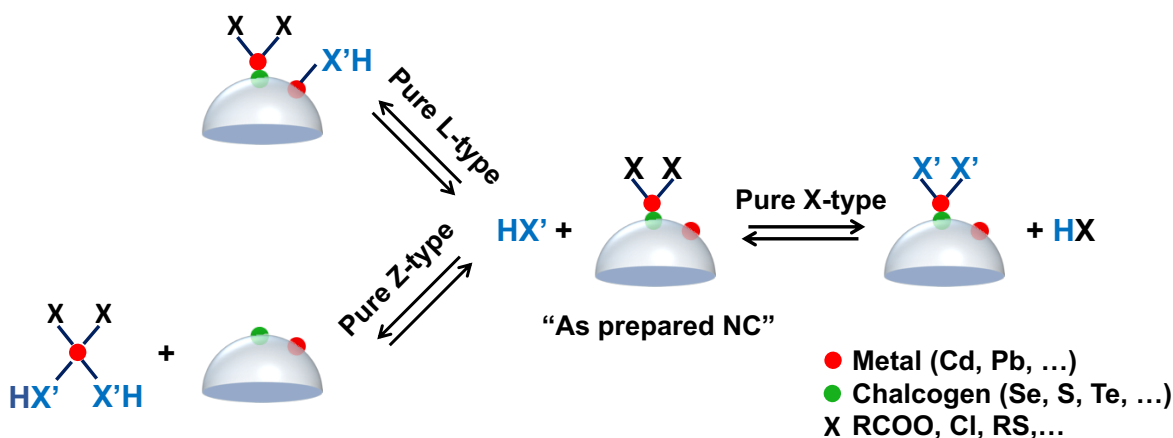
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Chapter 4: Ligand Exchange and Role of Various Ligands in Surface Chemistry and Physical Properties of CdSe NCs

4.1 Introduction

The surface chemistry of CdSe NCs capped with carboxylate ligands was studied in Chapter 2 and 3. Although these ligands lead to enhanced NC stability and narrow size distributions,¹ they are not necessarily suitable for all NCs applications, (e.g. for solar cell applications, short ligands are needed to minimize the space between NCs for efficient charge transport)², and often need to be exchanged with other ligands. Depending on the end application, one might choose long or branched aliphatic chains, aromatic groups or ligands containing different functional groups (such as thiolate, phosphonate, carbamate, etc.). Due to the difference in nature and chemistry of these ligands, the surface coverage and optical properties of NCs can be expected to be different. Even when the ligand exchange process seems straightforward, there are often complications that yield results that differ significantly from the desired outcome. For instance, a common way to perform a X-type exchange at the surface of NCs is by protonating the native X-type ligand, and exchanging it for the conjugated base of the acid used.^{3,4} However, as shown in Scheme 4.1, there are two other pathways that may occur which might be more favorable depending on the nature of the ligand involved in exchange process. For instance, it is known that long chain carboxylic acids favor the X-type reaction and are quite inefficient at displacing Z-type ligands from the surface.^{5,6} By contrast, amines either promote the Z-type displacement of ligands from the surface of NCs or bind directly to the surface as L-type ligands.⁵⁻¹² So far, there has been many experimental and theoretical studies on the ligand exchange process at the surface of NCs, where the effect of ligand exchange on the optical properties of II-IV NCs have been discussed.^{6,13-24} These studies mainly focused on the effects of various ligands on the optical properties of NCs without considering the nature of the different NCs surface sites involved in the ligand exchange.^{7,25} Recently, studies have focused on Z-type displacements of native carboxylate ligands and of their impact on the optical

properties and surface structure of the NCs.^{12,26,27} However, these studies all addressed the binding affinity of Se surface sites for the Z-type cadmium carboxylates. It is not well known yet how this binding affinity changes if the carboxylates are replaced with other X-type ligands. The first step to address this question is to prepare Cd-rich NCs where the extra cadmiums are charge- balanced with different X-type ligands. Therefore, it is important to develop X-type exchange reactions without perturbing the NC surface coverage (pure X-type exchange). To achieve this goal, the origin of undesired ligand exchange pathways must be identified and subsequently blocked by certain strategies.



Scheme 4.1. X, Z, and L-type ligand exchanges that can occur at the surface of metal chalcogenide NCs.

In this Chapter, the X-type exchange process of different ligands (oleic acid, benzoic acid, oleylthiol, and benzenethiol) and the subsequent effect on the surface coverage and optical properties of CdSe NCs were studied. First, the exchange of myristate by oleate and oleylthiolate was studied. Then, the exchange of myristate/oleate by benzoate and benzenethiolate ligand was studied to investigate the X-type reaction and other undesired pathways during these exchanges. Long chain thiolate and carboxylate ligands are commonly used for the synthesis and maintaining colloidal stability of NCs. Short aromatic ligands are also interesting to study as they are known

to enhance the absorption of NCs.²⁸ Finally, Z-type displacement of these different ligands with TMEDA was explored. The problems and challenges regarding these Z-type exchanges are also discussed.

4.2 Experimental Section

4.2.1 Chemicals

Cadmium nitrate tetrahydrate ($\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, 98%), oleic acid (90%), octadecene (ODE, 90%), oleyl alcohol (technical grade, 85%), carbon tetrabromide (*reagentplus*, 99%), potassium thioacetate (98%), myristic acid (>99%), Selenium dioxide (SeO_2 , 99.9%) ferrocene (Fc, 98%), sodium sulfate (ACS grade, >99%), diethylether (anhydrous, >99.7%), triphenylphosphine (*reagentplus*, 99%), benzoic acid (ACS reagent, >99.5%), benzenethiol (ACS grade, >98%) were purchased from Sigma Aldrich. Ethyl acetate (HPLC grade), toluene (ACS grade), hydrochloric acid (ACS grade, 36.5-38%), sodium hydroxide (>98%), anhydrous methanol (HPLC grade), ethanol (ACS grade), dichloromethane (ACS grade), hexane (ACS grade) were purchased from Macron Fine Chemicals. Pentane was purchased from Fisher Chemical. *d*-toluene *d*-benzene and *d*-chloroform was purchased from Cambridge Isotope Laboratories (CIL). Ethyl acetate was degassed by bubbling nitrogen for 2 h and dried over molecular sieves for at least two days prior to use. Oleic acid was degassed through 3 cycles of vacuum/purge with nitrogen and kept under nitrogen atmosphere just prior to use. Ferrocene was recrystallized from methanol solutions. Toluene and pentane were dried using an alumina distill columns.

4.2.2 Synthesis and Preparation of CdSe NCs for ^1H NMR Studies

The protocol for synthesis of oleate/myristate capped CdSe NCs is described in Chapter 2 section 2.2.5. Suspensions of these oleate/myristate capped NCs were used for X-type ligand exchange with benzoic acid and benzenethiol. For the ligand exchange with oleic acid and oleylthiol, myristate capped CdSe NC solutions were used. To prepare myristate capped CdSe NCs, 2 ml of oleate/myristate capped CdSe NCs (0.135 mM) suspension was mixed with 115 mg of myristic acid (ratio of myristic acid to native oleate was about 10:1) and the mixture was allowed to stir for 24 hours at room temperature. Then sample was washed with 3 cycles of crashing and dispersing with ethyl acetate and pentane (10:1 ratio of ethyl acetate to pentane). The washed myristate capped sample was dispersed in d-toluene to make a stock solution of 0.116 mM CdSe NCs for further use.

4.2.3 Synthesis of Oleyl Bromide

Oleyl bromide was synthesized using a protocol adapted from Smith *et. al.*²⁹ Oleyl alcohol (2.405 g, 8.96 mmol) and CBr_4 (3.451 g, 10.41 mmol) and 50 ml dichloromethane were mixed in a 100 ml round bottom flask and transferred to a 100 ml additional funnel. In a 250 ml round bottom flask, PPh_3 (3.453g, 13.16 mmol) was dissolved in 50 ml dichloromethane. A magnetic stir bar was added, and the round bottom flask was placed in an ice bath. After 30 minutes, the additional funnel was mounted, and the alcohol solution was added slowly to the chilled phosphine solution while stirring. After the addition, the reaction flask was capped and allowed to warm up to room temperature and was stirred for 6 hours to complete the reaction. During this time, the flask was wrapped in aluminum foil and kept in the dark. After reaction completion, the solvent was evaporated and the impure oleyl bromide was purified using silica gel column chromatography

with gradient of hexane: AcOEt = 10:1 eluent. Pure oleyl bromide was characterized using ^1H NMR and reaction yield was 80%. ^1H -NMR (500 MHz, CDCl_3): δ =5.35 (2H, m), 3.41 (2H, t, J =6.88 Hz), 2.01 (4H, m), 1.85 (2H, m), 1.31 -1.42 (22H, m), 0.88 (3H, t, J =6.82 Hz)

4.2.4 Synthesis of Oleyl Thioacetate

Oleyl thioacetate was synthesized using literature procedures with slight modification.³⁰ Oleyl bromide (2.375 g, 7.16 mmol) and 15 ml ethanol were degassed and mixed in a 50 ml Schleck flask. A solution of potassium thioacetate (1.226 g, 10.74 mmol) in 15 mL of ethanol was made and degassed for 20 minutes and was added to the oleyl bromide solution in the Schleck flask. The mixture was heated for 20 hours until the reaction was completed. The reaction mixture was diluted with 20 mL of water and extracted with 3 portions of 20 mL pentane using a separatory funnel. The organic portions were combined, and solvent was evaporated using a rotary evaporation. The impure oleyl thioacetate was purified using silica gel column chromatography with gradient of hexane: AcOEt 95:5 eluent. Pure oleyl thioacetate was characterized using ^1H NMR and reaction yield was 70%. ^1H -NMR (500 MHz, CDCl_3): δ =5.35 (2H, m), 2.86 (2H, t, J =6.88 Hz), 2.32 (3H, s), 2.01 (4H, m), 1.55 (2H, m), 1.21-1.38 (22H, m), 0.88 (3H, t, J =6.82 Hz)

4.2.5 Synthesis of Oleylthiol

Oleylthiol was synthesized using literature procedures with slight modification.³⁰ Under nitrogen, oleyl thioacetate (1.6 gr, 4.67 mmol) was placed in a three-necked round bottom flask with a magnetic stir bar. A condenser was mounted and 12 ml of degassed ethanol was added to the flask dissolved in. Degassed NaOH solution (350 mg, 9 mmol in 2.5 ml of degassed H_2O) was added dropwise to thioacetate solution. Reaction then was allowed to reflux for 3 hours and then was

cooled down to room temperature. The mixture was neutralized with degassed solution of 2 M HCl and in a glove bag solution was transferred to a separatory funnel. Then 20 ml of degassed diethyl and 10 mL of degassed water were added to the separatory funnel. Organic layer was washed with 10 mL of degassed water and dried over sodium sulfate. Then it was filtered, and the solvent was evaporated using a rotavapory evaporation. The impure Oleylthiol was purified using a column chromatography over silica gel using a gradient hexane: AcOEt 90:10 eluent. Pure Oleylthiol was characterized using $^1\text{H-NMR}$ and reaction yield was 70%. $^1\text{H-NMR}$ (500 MHz, CDCl_3) δ 5.38 (2H, m), 2.51 (2H, q, $J = 6.87$ Hz), 1.98 (4H, m), 1.59 (2H, q, $J = 6.79$ Hz), 1.44–1.16 (22H, m), 0.88 (3H, t, $J = 6.81$ Hz).

4.2.6 ^1H NMR Sample Preparation for X-type Ligand Exchange Titration

For each ligand exchange, various concentration of ligands (benzoic acid, oleic acid, Oleylthiol and benzenethiol) were titrated to a known concentration of CdSe NCs (0.062-0.115 mM) where the ratio of ligand to NC varied two orders of magnitude (tens to thousands). 30 μl of 5.7 mM ferrocene was added to the solutions as internal standard. For absorption and photoluminescence studies, 2 ml of 1-2 μM CdSe solutions were added to cuvettes in which the ligands were titrated with ratios of ligands (benzoic acid, oleic acid, oleylthiol, benzenethiol) to NCs similar to their corresponding NMR samples.

4.2.7 X-type Ligand Exchange Reaction and Isolation of CdSe NCs

Excess amount of oleic acid (0.1 ml), Oleylthiol (0.35 ml), benzenethiol (3 μl) and benzoic acid (45 mg) were added separately to 2 ml of 0.086 mM oleate/myristate CdSe NCs suspension. These amounts were estimated based on the ^1H NMR spectra of different titrations in Figures 4.1., 4.6,

4.11, and 4.16. For example, based on Figure 4.1(a), 1670 equivalent of oleic acid (~ 40 μ l) is needed to displace most of the myristate.

In each case, the mixture was allowed to stir for 24 hours at room temperature. Then solvent was removed under nitrogen flow and 5 ml ethyl acetate was added to the mixture. Mixture was sonicated for 30 seconds, centrifuged and supernatant was discarded. This process (ethyl acetate addition, sonication and centrifugation) was repeated 5 times. Then, the clean ligand exchanged CdSe NCs were dried under vacuum for 2 hours following by addition of 2 ml of d-toluene to make a stock solution for further use. In every case, first, 30 μ l of stock CdSe was diluted with 2 ml of toluene for absorption measurements and calculation of concentration. Then 600 μ l of stock suspension (with known concentration) was mixed with 30 μ l of 5.7 mM ferrocene and placed in NMR tube. Using combination of ^1H NMR and absorption spectroscopies, ligand coverages were measured. Also, an absolute PL quantum yield spectrometer (using integrating sphere) is used for calculating the absolute PLQY of each sample.

4.3 Ligand Exchange of Oleic Acid with Native Myristates.

Figure 4.1 shows the ^1H NMR spectra of myristate capped NCs change upon addition of different amount of oleic acid. The top spectrum in Figure 4.1 shows myristate-capped CdSe NCs (93% myristate and 7% oleate). The signals associated with bound myristates fall in the 0.9-2 ppm region (aliphatic region) of the spectrum; a small signal at 5.7 ppm from bound oleate (from the ligand exchange) is hardly noticeable. Upon addition of oleic acid, a clear signal associated with bound oleate and free oleic acid were observed at 5.7 ppm and 5.4 ppm respectively (the calculation of the concentration of ligand and number of ligand per nanocrystal was performed as described in Chapter 2, section 2.2.13). The methyl region around 0.9 and 1 ppm shows the total free and bound

carboxylate (mixture of oleate and myristate) respectively. Since the broad methyl peak between 0.9-1 ppm represents all myristate and the broad vinyl peak at 5.7 only accounts for oleate ligands, the number of bound myristates can be assessed by calculating the differences between the bound methyl and bound vinyl groups. Similarly, the difference between the free carboxylates (myristate and oleate) at 0.9 ppm and free oleic acid at 5.4, presents the number of free myristate.

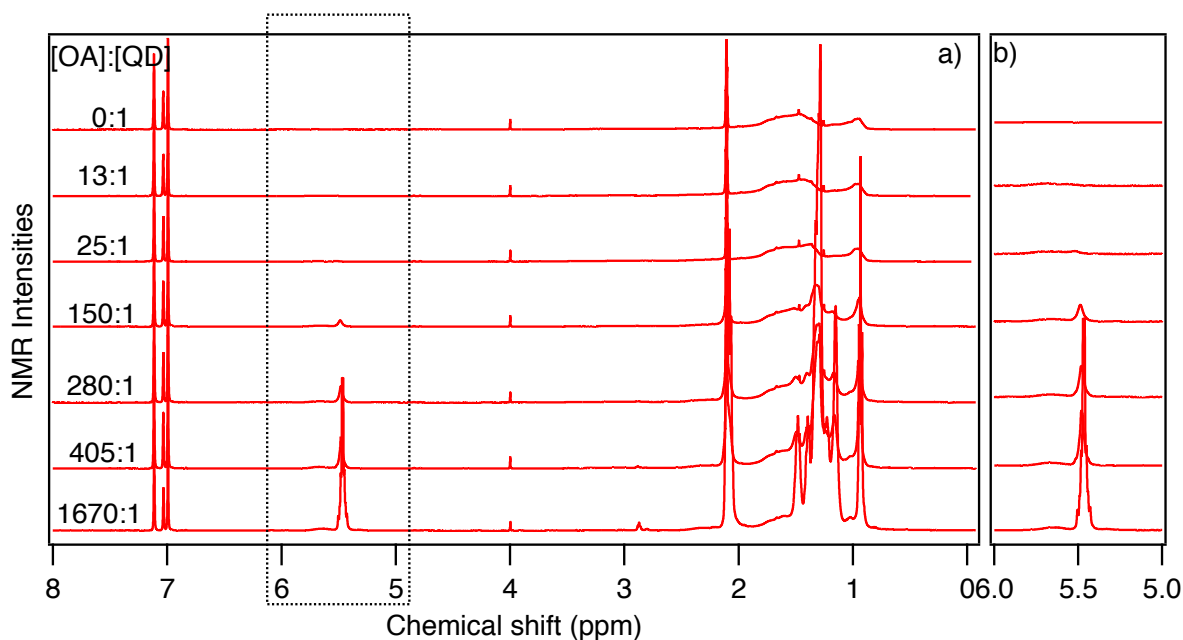


Figure 4.1. a) ^1H NMR spectra of 110 μM (starting concentration, before addition of oleic acid) myristate capped CdSe NC (3.8 nm) suspensions in d-toluene in presence of different concentrations of oleic acid, measured at room temperature. b) Zoomed-in spectra (from part a) between 5 and 6 ppm that shows the bound and free oleic acids.

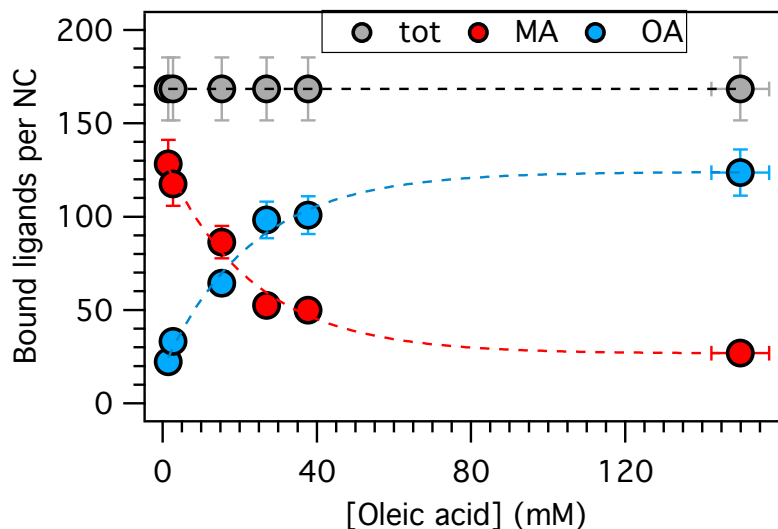
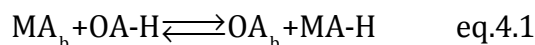


Figure 4.2. Number of bound ligands per CdSe NC, total oleate and myristate ligands (gray circles), oleate ligands (blue circles), and myristate ligands (red circles). Dashed lines are guide to the eye.

The analysis of these NMR spectra is given in Figure 4.2 showing that the total number of bound ligands remains constant in the range investigated here, showing that for each oleate bound to the NCs, an equal amount of myristate ligands are released in solution (presumably as myristic acid). Therefore, we conclude that there is an equilibrium between the carboxylate species (eq.4.1), defined by the equilibrium constant of eq.4.2:



$$K_{eq} = \frac{[\text{MA-H}][\text{OA}_b]}{[\text{MA}_b][\text{OA-H}]} \quad \text{eq.4.2}$$

In this equation, MA_b is bound myristate, OA-H is free oleic acid, OA_b is the bound oleate and MA-H is free myristic acid. As expected from the analysis given in Figure 4.2, there are two linear regimes in which the exchange takes place. In the first regime, the ratio of oleic acid to NC ranges from 13 to 280 (the first four blue circles in Figure 4.2, $[\text{OA}] = 2\text{-}30$ mM). In this range and for each spectrum, concentrations of bound and free oleate and myristate (which was already calculated) were plugged in eq. 4.2 (Table 4.1) and the average of four calculated K_{eq} value was 0.85 ± 0.15 . In the second region where the ratio of oleic acid ranges from 405 to 1670 (the last

two blue circles in Figure 4.2, [OA]= 40-150 mM) the average of two calculated K_{eq} decreases to 0.5 ± 0.1 . This is somewhat expected because at high concentrations of oleic acid, the K_{eq} will be mainly proportional to the reciprocal of the oleic acid concentration. Overall, these NMR data suggest a 1:1 replacement of oleate for myristate; this result agrees with previous ligand exchange studies.^{4,5}

Table 4.1. K_{eq} values at different ratios of oleic acid to NCs

[OA]/[QD]	K_{eq}^*
13	0.6 ± 0.1
25	0.9 ± 0.2
150	0.8 ± 0.2
280	1.1 ± 0.2
405	0.5 ± 0.1
1670	0.5 ± 0.1

* K_{eq} values are calculated using eq.4.2

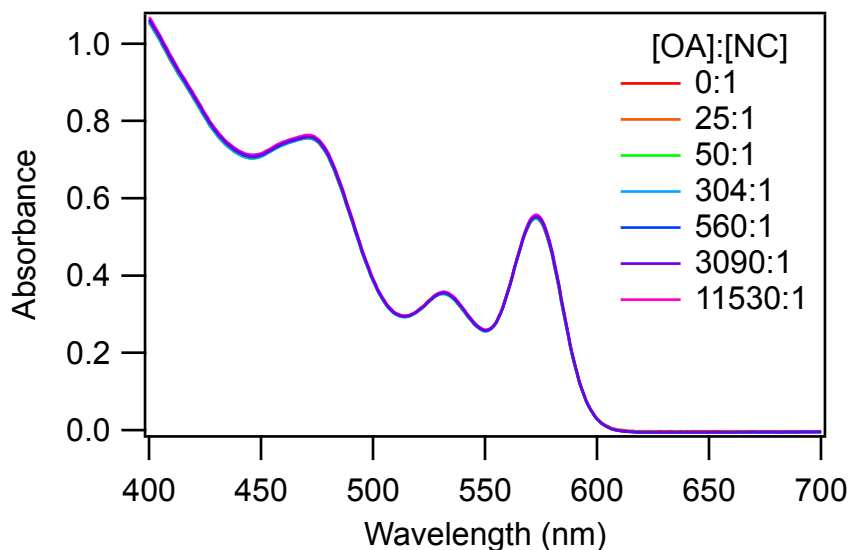


Figure 4.3. Absorption spectra of 1.8 μM CdSe NCs (3.8 nm) in presence of different concentration of oleic acid in toluene. (surface coverage of starting CdSe suspension: 3.5 ± 0.2 MA and 0.3 ± 0.1 OA)

To further elucidate the X-type exchange of myristate for oleate ligands, absorbance and photoluminescence spectra were recorded after each addition of oleic acid to myristate-capped CdSe NCs (Figure 4.3 and 4.4). After correction for the dilution effect of the titration, no change in the absorption spectra of CdSe NCs could be detected. However, upon addition of oleic acid, the photoluminescence data showed an instantaneous increase ($\sim 5\%$) followed by gradual increase up to 25% PLQY (Figure 4.4) of the original myristate capped CdSe NCs. Although this could suggest that L-type binding of oleic acid may have happened in addition to X-type exchange, the NMR data presented above does not agree with this hypothesis because the total number of bound ligands per NCs does not change. Hence, this suggests that the increase in PLQY arises from the reorganization of the surface of NCs associated with the exchange of myristate for oleate ligands.

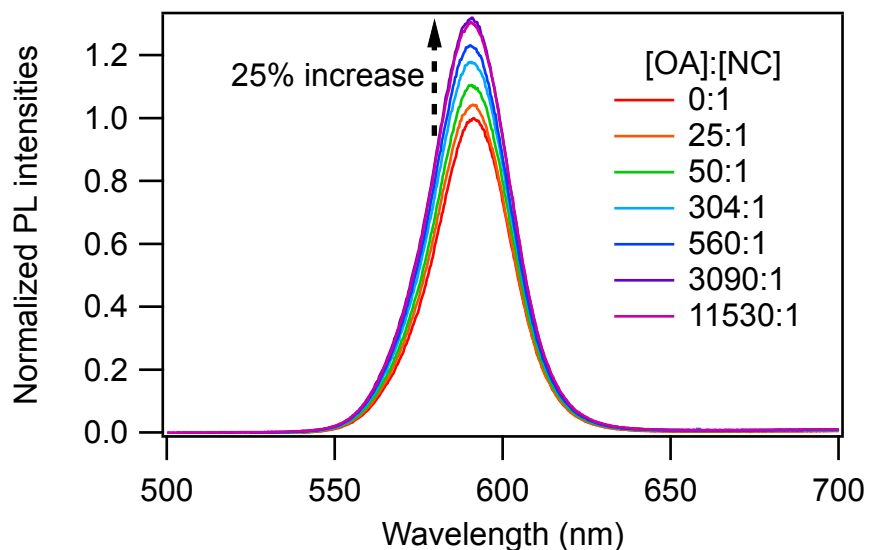


Figure 4.4. Photoluminescence spectra of 1.8 μM CdSe NCs (3.8 nm) in the presence of different concentration of oleic acid in toluene. (starting surface coverage of CdSe NCs: 3.5 ± 0.2 MA and 0.3 ± 0.1 OA, starting PLQY = 11%)

Although during the titration of myristate capped CdSe NCs with oleic acid, PLQY was increased by 25%, cleaned oleate capped CdSe NCs (after the ligand exchange of myristate capped CdSe NCs with oleic acid) showed a similar PLQY ($\sim 10\%$, obtained from absolute PLQY spectrometer) to the original myristate capped CdSe NCs. This could suggest that ligands fell off the surface during the washing steps. FTIR spectrum of cleaned oleate capped CdSe NCs (Figure 4.5) did not show the acidic form of oleic acid but the sensitivity of FTIR did not allow for accurate measurements. Addition of diethyl zinc to NCs (as described in Chapter 1, section 2.2.11) provides more information about the L-type binding of oleic acid.³¹ However, given the similar PLQY and surface coverage of NC by oleate ligands, the L-type binding is ruled out, meaning this exchange is almost a pure X-type exchange.

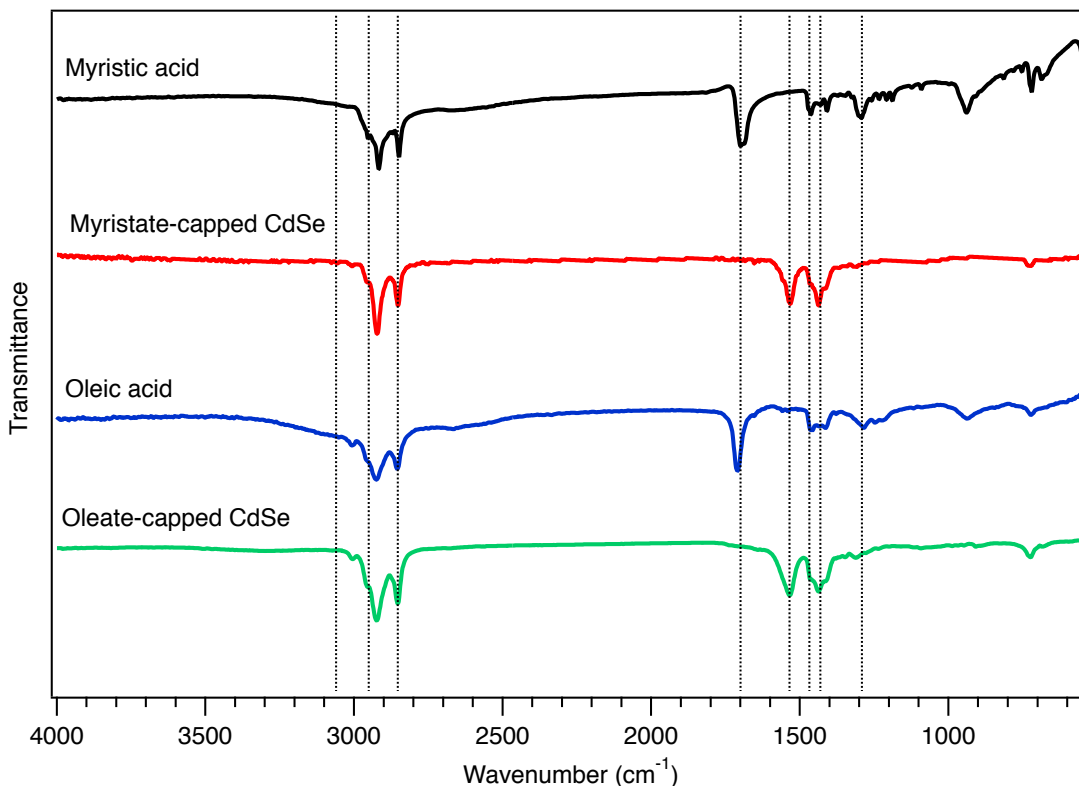


Figure 4.5. FTIR spectra of myristic acid (black), myristate-capped CdSe NCs (red), oleic acid (blue) and oleate-capped CdSe NCs (green). Disappearance of the peak at 1700 cm^{-1} in both oleate and myristate capped CdSe NCs, and comparison to myristic acid and oleic acid, indicates the binding of oleate and myristate to the surface of NCs. FTIR of both carboxylate capped NCs are almost identical.

4.4 Ligand Exchange of Oleylthiol with Myristate

Similar to section 4.3, solutions of Oleylthiol with different concentrations were added to myristate capped CdSe NCs suspension and ^1H NMR spectra were recorded after each addition. As shown in Figure 4.6, upon addition of oleylthiol, free (sharp peak) and bound (broad peak) ligands are appeared between 5 and 6 ppm. Analysis of the vinyl and methyl regions is given in Figure 4.7. Unlike the case of oleic acid titration, the integration of total bound species did not remain the same. The integration of methyl peak at 1 ppm, which is broad and associated with all the bound carboxylate ligands (myristate and oleylthiolate) decreases upon addition of oleylthiol.

Furthermore, the growth of the broad vinyl peak at 5.7 implies the X-type binding of oleylthiolate (or oleylthiol, as L-type) to the surface of CdSe NCs.

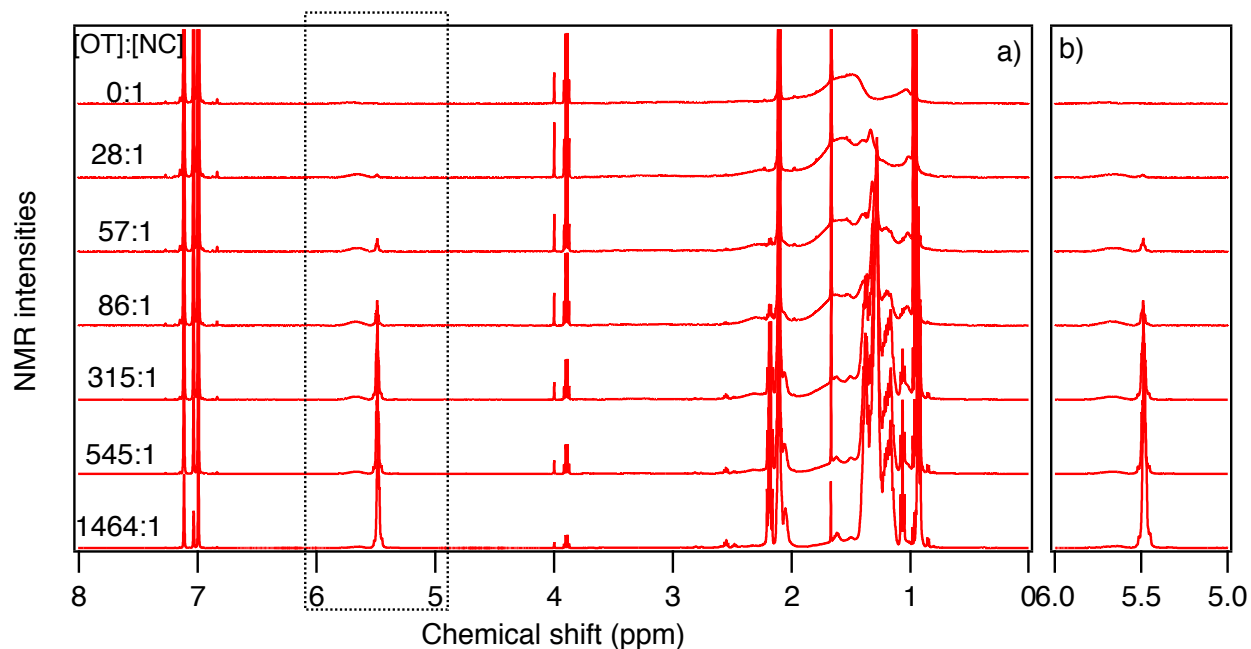


Figure 4.6. a) ¹H NMR spectra of 62 μ M (starting concentration, before addition of oleylthiol) myristate capped CdSe (3.8 nm) suspensions in d-toluene in presence of different concentrations of Oleylthiol, measured at room temperature. b) Zoomed-in spectra (from part a) between 5 and 6 ppm that shows the bound Oleylthiolate and free oleic acid. (Note: the sharp peaks at 3.9, 1.7 and 0.96 ppm are peaks associated with ethyl acetate impurities, from washing process)

Overall, these data show that X-type exchange of oleylthiolate with myristate ligands was accompanied by Z-type displacement of cadmium myristate from the surface. The free peak around 5.4 ppm is a mixture of free oleylthiol and a form of cadmium myristate complex, most likely a tetrahedral complex of cadmium with two myristates and two oleylthiol ligands.⁶ The number of bound myristates converges to zero at the highest concentration of Oleylthiol added to NCs (Figure 4.7, red circles), which perhaps is due to the dual role (X-type and Z-type) of oleylthiol ligands. However, the FTIR Spectrum of cleaned oleylthiolate capped CdSe, shows a residue of bound myristate ligands (Figure 4.10). This can be due to the error in calculating the methyl peak at 1 ppm (which is highly dominated by the free thiol) or rebinding of myristate after the washing

cycles. This means that a small portion of thiol ligands stayed as ion-pairs at the surface and temporary separated the myristate ligands from the surface.

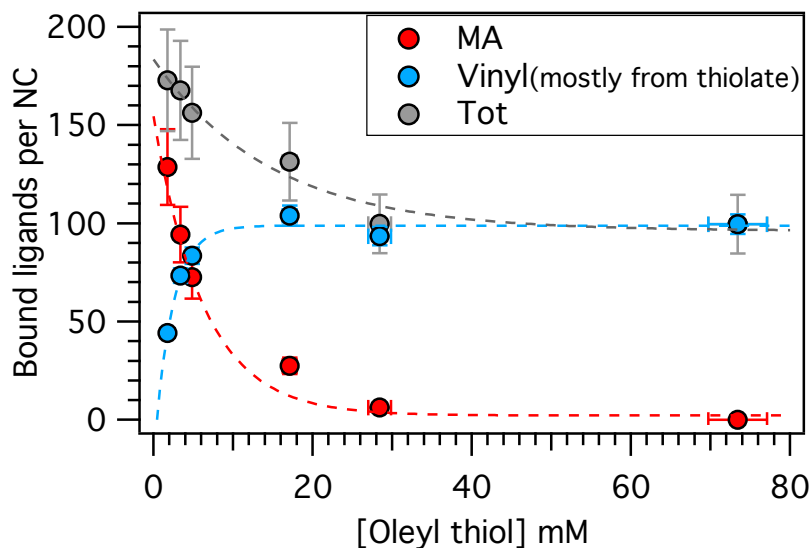


Figure 4.7. Number of bound ligands per CdSe NC, total oleylthiolate and myristate (gray circles), Oleylthiolate (blue circles), and myristate (red circles).

Absorption and photoluminescence of myristate capped CdSe during titration with oleylthiol show different result compared to titration of oleic acid. As shown in Figure 4.8 a and b, absorption of the NCs changed upon addition of oleylthiol. However, this change is not constant for all the excitonic peaks ($\lambda = 574, 530,$ and 475 nm) of NCs. While signal increase was observed for the first ($\lambda = 574$ nm) and third ($\lambda = 475$ nm) excitonic absorption peaks, the second excitonic peak ($\lambda = 530$ nm) initially increased and then decreased. It is known that some ligands can increase the absorption of NCs,²⁸ which is attributed to the ground state mixing of NC/ligand orbital mixing. By contrast, to increase the absorption, removal of Z-type ligands from the surface is known to affect the second excitonic peak of NCs.¹⁹

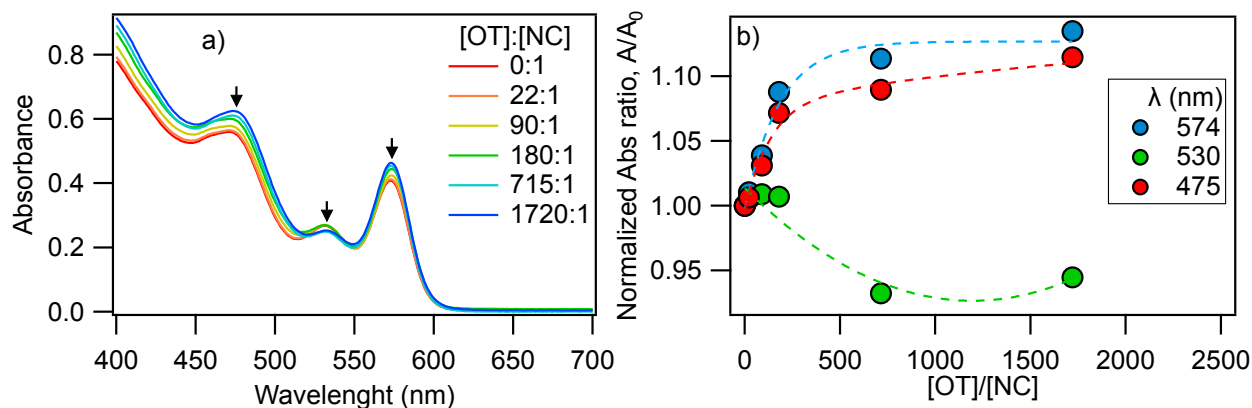


Figure 4.8. a) Absorption spectra of 1.5 μ M CdSe NCs (3.8 nm) in presence of different concentration of Oleylthiol in toluene. (starting surface coverage of CdSe NCs: 3.5 ± 0.2 MA and 0.3 ± 0.1 OA, starting PLQY= 11%). b) Normalized absorbance ratios (from part a, shown with arrows) at 574 nm (blue circles), 530 nm (green circles), 475 nm (red circles) against the ratio of the concentration oleylthiol added to NCs. For example, at 574 nm (blue circles), the absorbance of each spectrum at 574 nm is divided by the absorbance of the NCs at 574 nm before addition of oleylthiol (red spectrum in part a). Dashed lines are guide to the eye.

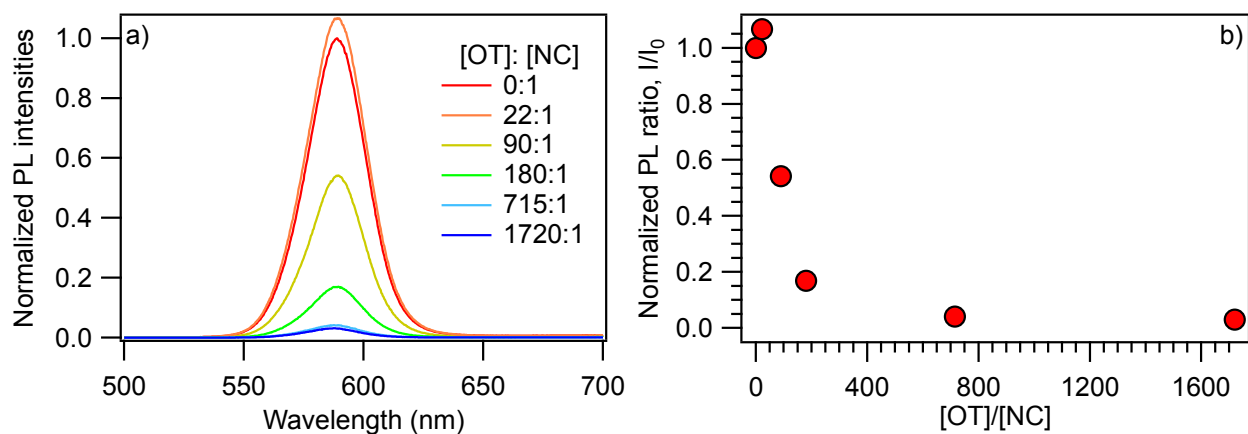


Figure 4.9. a) Photoluminescence spectra of 1.5 μ M CdSe (3.8 nm) NCs in presence of different concentration of oleylthiol in toluene. (starting surface coverage of CdSe NCs: 3.5 ± 0.2 MA and 0.3 ± 0.1 OA, starting PLQY= 11%). b) Normalized PL intensity (from part a) of CdSe NCs against the ratio of concentrations of oleylthiol added to NCs.

It seems the evolution of the absorption spectra in Figure 4.8 shows the mixing of both X-type exchange and Z-type displacement. Moreover, in PL spectra of titration of oleylthiol to CdSe NCs, there is an initial increase followed by decrease in PLQY of NCs until almost 98% of PL got quenched (Figure 4.9 b). The small increase is most likely attributed to the L-type binding of

oleylthiol and the subsequent decrease in PLQY is due to the Z-type displacements of cadmium myristate ligands.

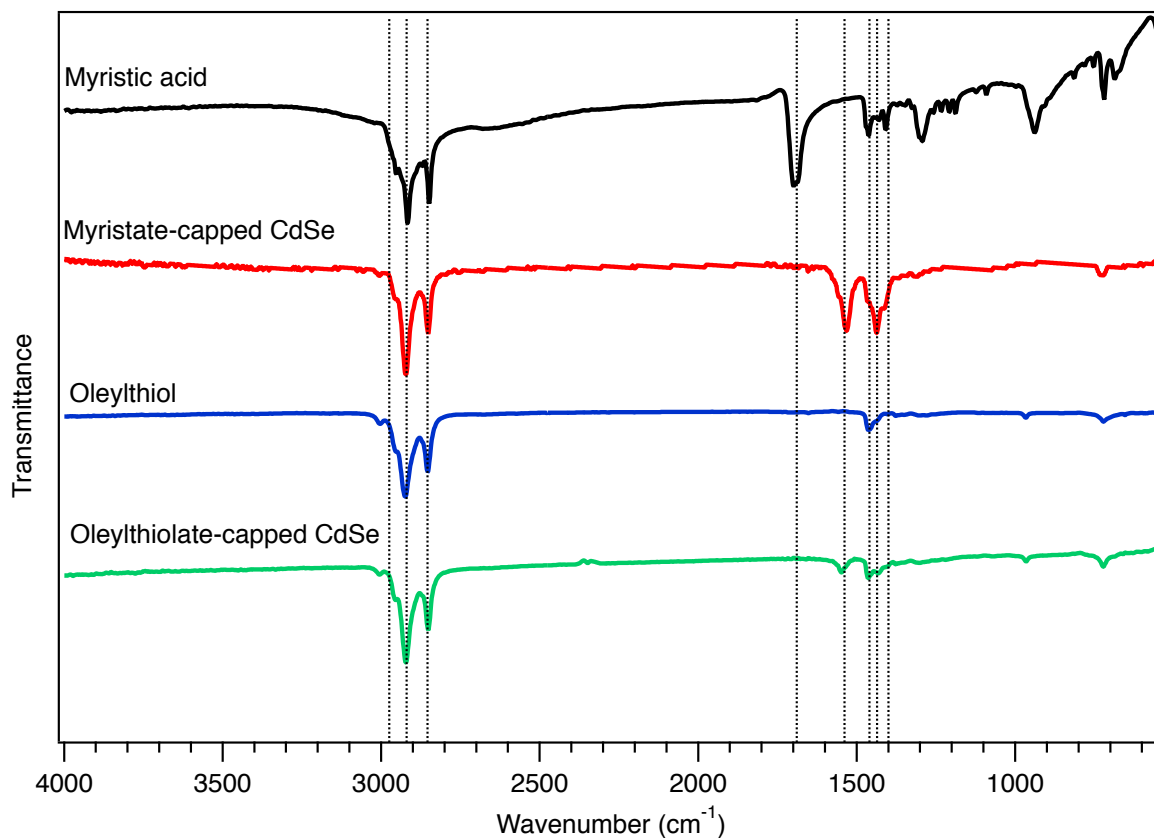


Figure 4.10. FTIR spectra of myristic acid (black), myristate-capped CdSe NCs (red), Oleylthiol (blue) and oleylthiolate-capped CdSe NCs (green). The ratio of peaks at 2800-2900 cm^{-1} to peaks around 1500 cm^{-1} are increased and the peak at 1500 cm^{-1} is identical to that of oleylthiol. There are residues of myristate at 1550 cm^{-1} , though they are mostly replaced or displaced by oleylthiol.

4.5 Ligand Exchange of Benzoic Acid with Native Carboxylates

In order to monitor the X-type exchange between benzoic acid and native carboxylates, myristate/oleate capped CdSe NCs was titrated with benzoic acid at different concentrations and ^1H NMR spectra of the suspension were recorded for each concentration of benzoic acid. From the ^1H NMR spectra, both vinyl and methyl peaks can be used to assess the amount of bound and free carboxylates; however, changes in the vinyl region between 5 and 6 ppm is more apparent for this

purpose as shown in Figure 4.11. The difference between free benzoic acid (sharp peak at 8 ppm) and the added benzoic acid to the NCs suspension, yields the number of benzoates that exist

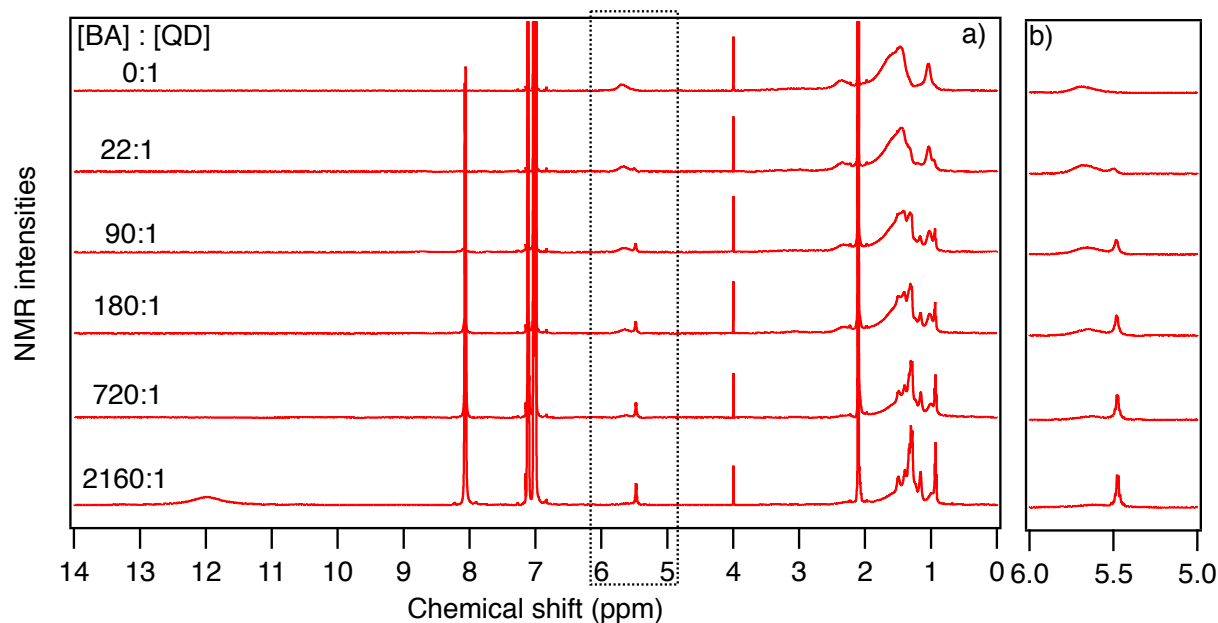


Figure 4.11. a) ^1H NMR spectra of 67 μM (starting concentration, before addition of benzoic acid) oleate/myristate capped CdSe (3.8 nm) suspensions in d-toluene in presence of different concentrations of benzoic acid, measured at room temperature. b) Zoomed-in spectra (from part a) between 5 and 6 ppm that shows the bound and free oleate (or oleic acid)

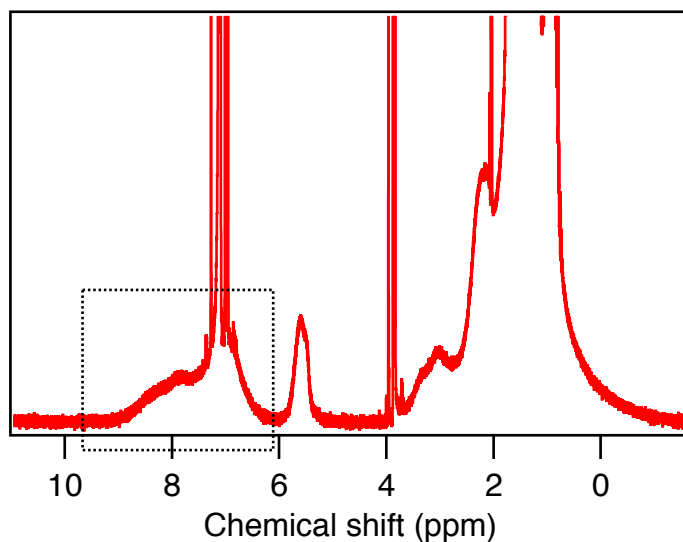


Figure 4.12. ^1H NMR spectrum of 125 μM suspension of partially benzoate capped CdSe (3.8 nm) in d-benzene. The spectrum is zoomed-in to better show the broad benzoate peak (bound) between 6.2-9 ppm (squared with dashed line).

partially at the surface of NCs (as X-type or L-type ligands) and partially as ligands to the Z-type Cd released to the solution. The free component with peaks at 5.5 ppm or 0.9 ppm is a mixture of oleic acid and free Z-type Cd complexes, (perhaps in the form of $\text{Cd}(\text{carboxylate})_2(\text{benzoic acid})_2$) hence not easily distinguishable due to overlapping peaks. On the other hand, bound benzoates are seen as a very broad peak in the aromatic region which is obscured by the solvent peak and free benzoic acid (7-8 ppm), and cannot be measured accurately. However, bound benzoate in the ^1H NMR spectrum of clean CdSe NC sample after ligand exchange with benzoic acid is observable (Figure 4.12, the broad peak between 6.2-9 ppm is indicative of bound benzoate). As shown in Figure 4.13, it seems that at the onset of the ligand exchange, there is no Z-type displacement as the number of benzoates are almost equal to the number of free carboxylates (Figure 4.13, compare the blue with green circles at $[\text{BA}] < 10 \text{ mM}$). Then, the increasing number of benzoates (Figure 4.13, compare the blue with green circles at $[\text{BA}] > 10 \text{ mM}$) is speculated to be due to some competing L-type binding to the surface. This was also observed in the PL data in Figure 4.14 a and b, PLQY increases at first up to 5%. The 35% decrease in PLQY at high concentrations of benzoic acid shows a small amount of Z-type displacement.

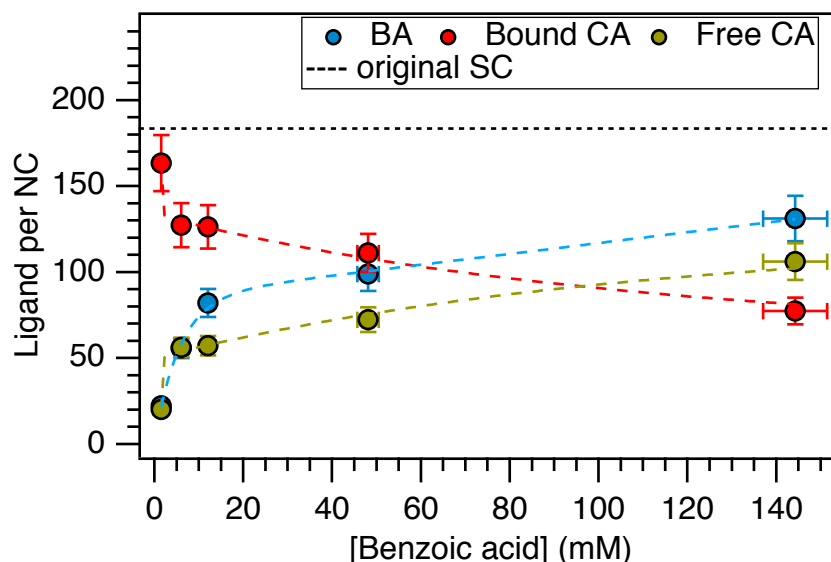


Figure 4.13. Number of ligands per CdSe NC, mixture of benzoate ligands, X-type, L-type or a component for Z-type (blue circles), bound carboxylate (red circles), free carboxylate (green circles). Dashed line shows the original surface coverage with carboxylate native ligands.

In Chapter 3, we showed the correlation between removal of Z-type ligands and PLQY (Figure 3.2) of 3.8 nm CdSe NCs (PLQY=12%, SC= 4.4 nm²). Since the samples used here are similar in size, PLQY, and SC (3.8 nm, PLQY=10%, SC=4.1 nm²), by using Figure 3.2 (part a and c,) and comparing with Figure 4.15 (b), we can conclude that the 35% of quenching in PLQY is attributed to removal of about 10 Z-type ligands per NC. If we assume the 35% decrease is only due to the Z-type displacement, 20 benzoic acid and 20 Carboxylates per NCs are needed for the Z-type displacement to happen (each Z-type ligand counts for two oleate/myristate ligands to compensate the charge of Cd, and two benzoic acid to remove the Z-type ligands). Additionally, it seems that there are about 25 extra benzoic acids (Figure 4.13, compare the green and blue circles at [BA]= 145 mM), suggesting that they do not participate in X-type or Z-type reactions, and therefore are likely attached as L-type ligands. A diethyl zinc test (as described in Chapter 2, Section 2.2.11) can confirm this hypothesis.

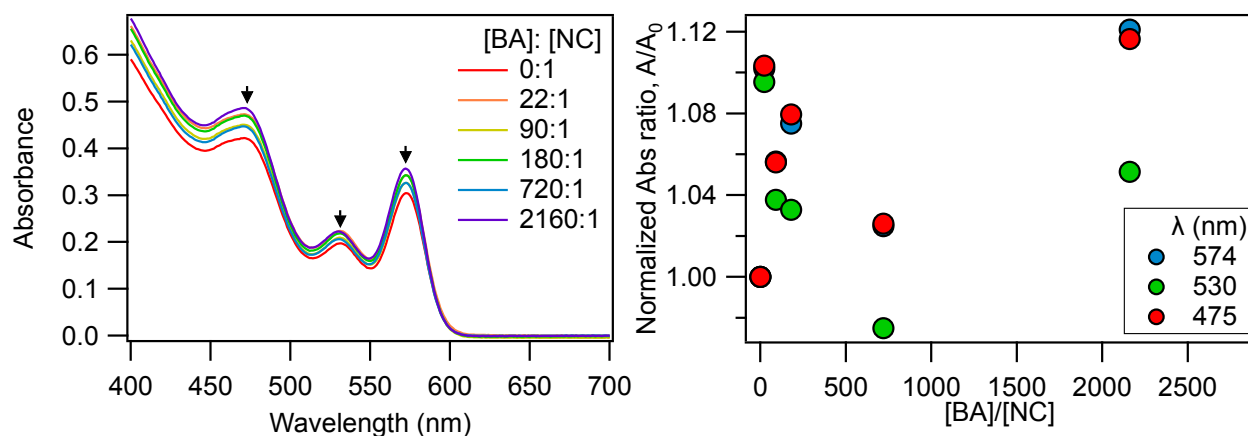


Figure 4.14. a) Absorption spectra of 1 μ M CdSe NCs (3.8 nm) in presence of different concentration of benzoic acid in toluene. (starting surface coverage of CdSe NCs: 4.1 ± 0.2

MA and OA, starting PLQY= 13%) b) Normalized absorbance ratios (from part a, shown with arrows) at 574 nm (blue circles), 530 nm (green circles), 475 nm (red circles) against the ratio of the concentration benzoic acid added to NCs. For example, at 574 nm (blue circles), the absorbance of each spectrum at 574 nm is divided by the absorbance of the NCs at 574 nm before addition of benzoic acid (red spectrum in part a).

The absorption spectra of CdSe NCs show a nonlinear change relative to the NCs without any benzoic acid and moreover, the signal changes are inconsistent within the three excitonic peaks of individual spectrum (Figure 4.14 b). This is perhaps due the complexity of the ligand exchange process and the fact that a significant amount of each type of ligand exchange pathways occur in the case of benzoic acid addition.

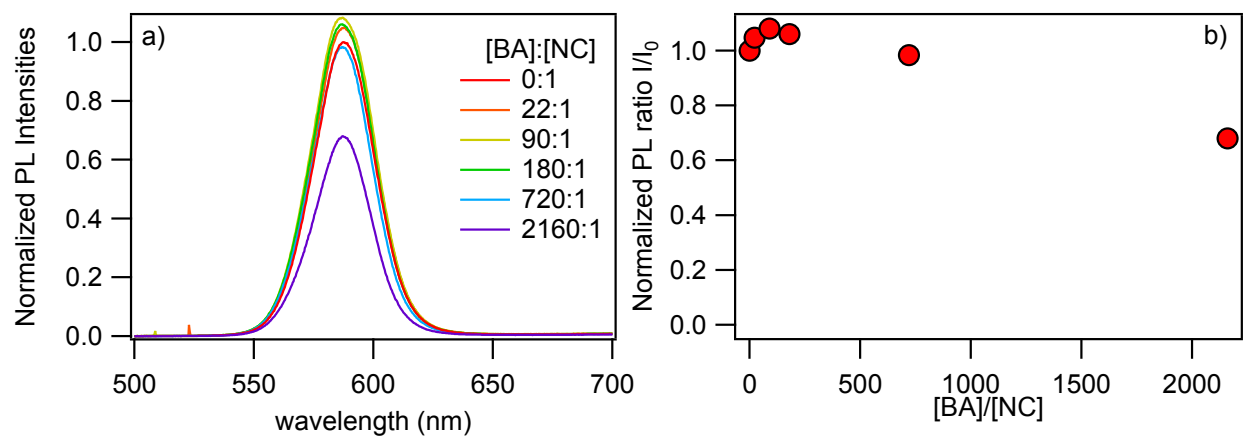


Figure 4.15. Photoluminescence spectra of 1 μM CdSe NCs (3.8 nm) in presence of different concentration of benzoic acid in toluene (starting surface coverage of CdSe NCs: 4.1 ± 0.2 MA and OA, starting PLQY= 13%). b) Normalized PL intensity (from part a) of CdSe NCs against the ratio of concentrations of benzoic acid added to NCs.

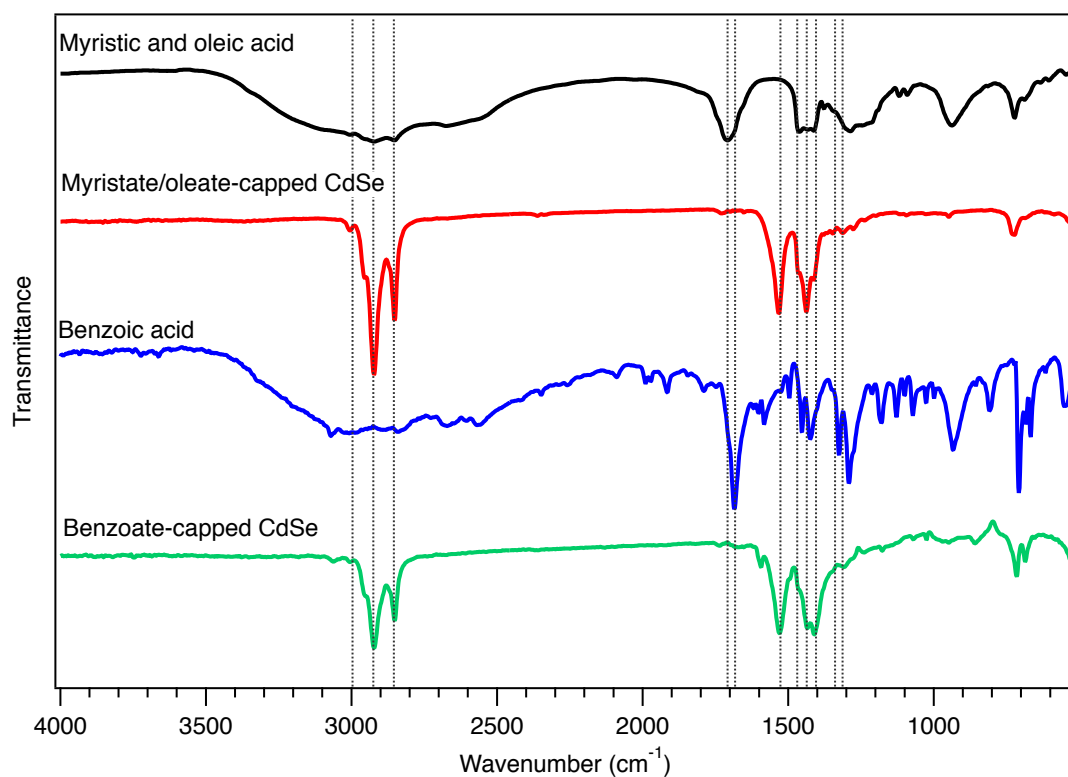


Figure 4.16. FTIR spectra of a mixture of myristic acid and oleic acid (black), myristate/oleate capped CdSe NCs (red), benzoic acid (blue), and benzoate capped CdSe NCs (green). Change in the ratio of peaks at 3000 and 1500 cm^{-1} show a mixture of ligand binding

4.6 Ligand Exchange of Benzyl Thiol with Native Carboxylates

Similar to previous sections, various concentrations of benzenethiol was added to myristate/oleate capped CdSe NCs. Note that the highest ratio of benzenethiol to NCs is only 180:1 because higher concentrations of benzenethiol make the NCs crash out of the solution. Similar to the previous section, from the difference between the free (Figure 4.17 c) and initial amount of benzenethiol, we can calculate the number of benzenethiolate that are not free in the solution.

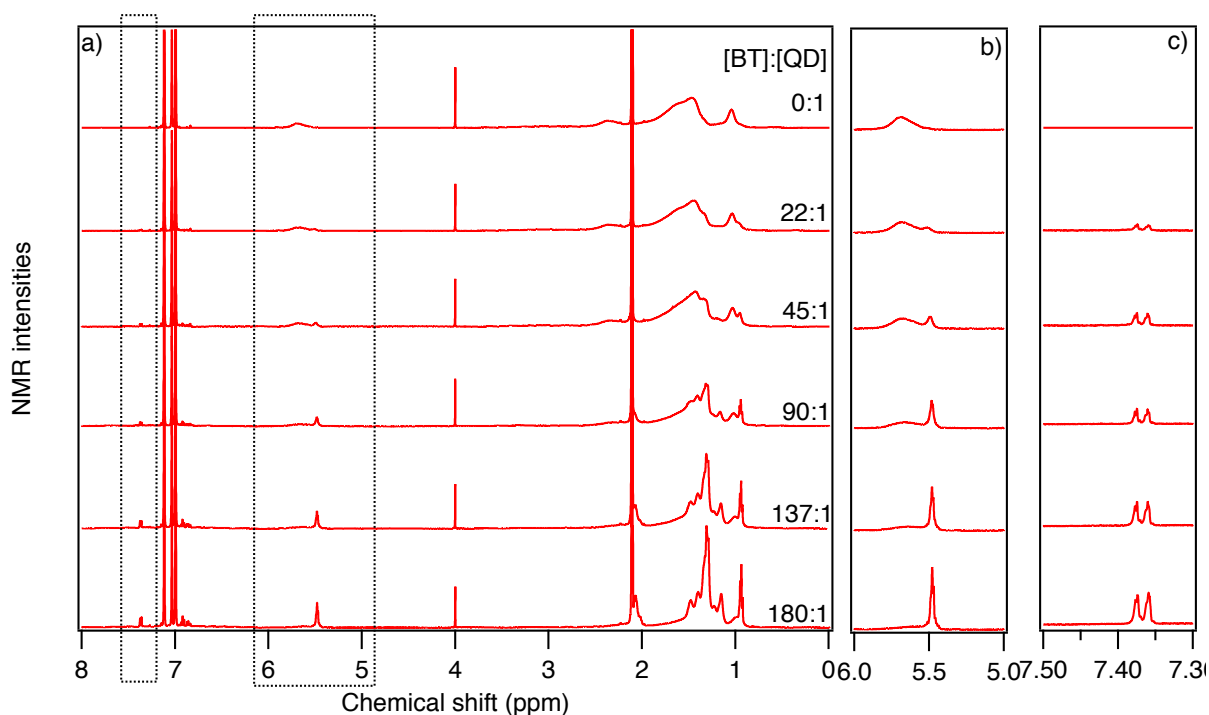


Figure 4.17. a) ^1H NMR spectra of 75 μM (starting concentration, before addition of benzenethiol) oleate/myristate capped CdSe (3.8 nm) suspensions in d-toluene in presence of different concentrations of benzenethiol, measured at room temperature. b) Zoomed-in spectra (from part a) between 5 and 6 ppm that shows the bound oleate and free oleate or oleic acid. c) Zoomed-in spectra (from part a) between 7.3 and 7.5 ppm that shows the free benzenethiol.

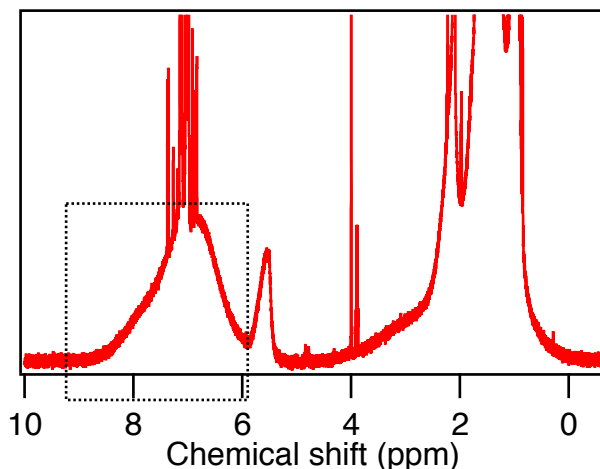


Figure 4.18. ^1H NMR spectrum of 174 μM suspension of partially benzenethiolate-capped CdSe (3.8 nm) in d-toluene. The spectrum is zoomed in to better show the broad benzenethiolate peak between 5.9-9 ppm (squared with dashed line).

These benzoate ligands are not necessarily bound to the surface of CdSe, but as shown in the previous section, can take part in both X-type or L-type exchange or Z-type displacement of native oleate/myristate ligands. Figure 4.18 shows the ^1H NMR spectrum of CdSe NCs sample after ligand exchange with benzenethiol. The broad peak between 5.9-9 ppm is indicative of bound benzenethiolate ligands. With this knowledge in hand, we start with analyzing the benzenethiol ligands that are bound either to the surface of NCs or formed a complex with Z-type Cd carboxylates. Figure 4.19 shows the mix benzenethiol species that are formed after each addition of benzenethiol (blue circles). Formation of these species has a similar trend to the formation of free carboxylic acid (or $\text{Cd}(\text{carboxylates})_2$), which suggests losing of carboxylates is coupled with the attachment of benzenethiolate; that is, most of the reaction consists of X-type exchange of carboxylate and Z-type displacement of cadmium carboxylate. PL and absorption data provide a further proof for the displacement of the Z-type Cd species. In figure 4.20 (a), spectra of CdSe NCs shows an increase in their absorption spectra upon addition of benzenethiol. Increase of the first and third excitonic peak is almost three times of their corresponding second excitonic peak

(Figure 4.20 b). This could be evidence of the removal of extra cadmium from the surface. Based on Figure 4.21 (b), PLQY is quenched completely ($PLQY < 0.1\%$) after the final addition of benzenethiol. Similar to previous sections, we compare these results to Figure 3.XX (a) and (c) (Chapter 3). for PLQY of smaller than 0.1%, we anticipate that about 40 ligands must be removed from the surface which counts for 40 benzenethiol and 40 carboxylate ligands. If that is the case, the other 80 free carboxylates were X-type exchanged (Figure 4.19, compare red, green and blue circles at $[BT]=14$ mM).

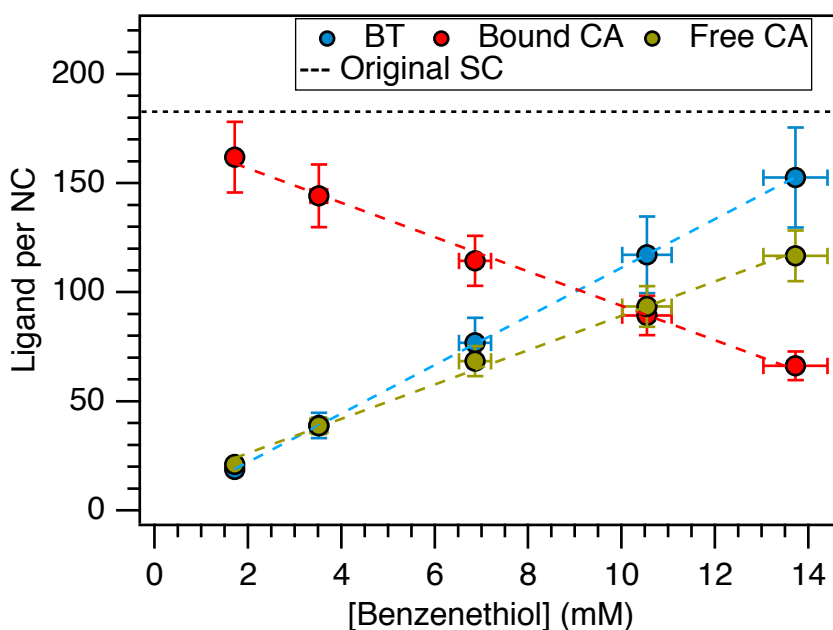


Figure 4.19. Number of ligands per CdSe NC, mixture of benzenethiolate ligand, X-type, L-type or attached to Z-type (blue circles), bound carboxylate (red circles), free carboxylate (green circles). Dashed line shows the original surface coverage with carboxylate native ligands. Dashed lines are guide to the eye.

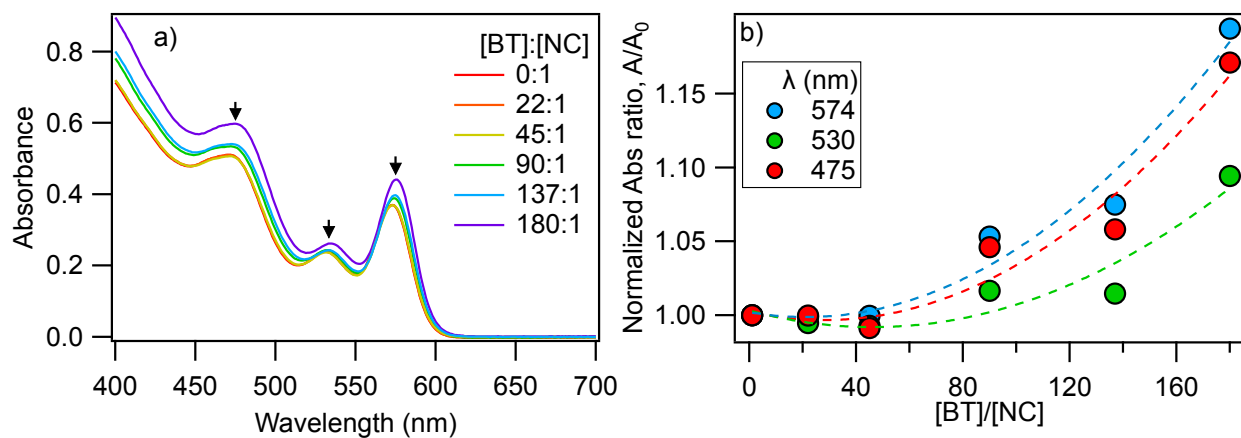


Figure 4.20. Absorption spectra of 1.3 μM CdSe NCs (3.8 nm) in presence of different concentration of benzenethiol in toluene (starting surface coverage of CdSe NCs: 4.1 ± 0.2 MA and OA, starting PLQY= 13%). Normalized absorbance ratios (from part a, shown with arrows) at 574 nm (blue circles), 530 nm (green circles), 475 nm (red circles) against the ratio of the concentration benzenethiol added to NCs. For example, at 574 nm (blue circles), the absorbance of each spectrum at 574 nm is divided by the absorbance of the NCs at 574 nm before addition of benzenethiol (red spectrum in part a). Dashed lines are guide to the eye.

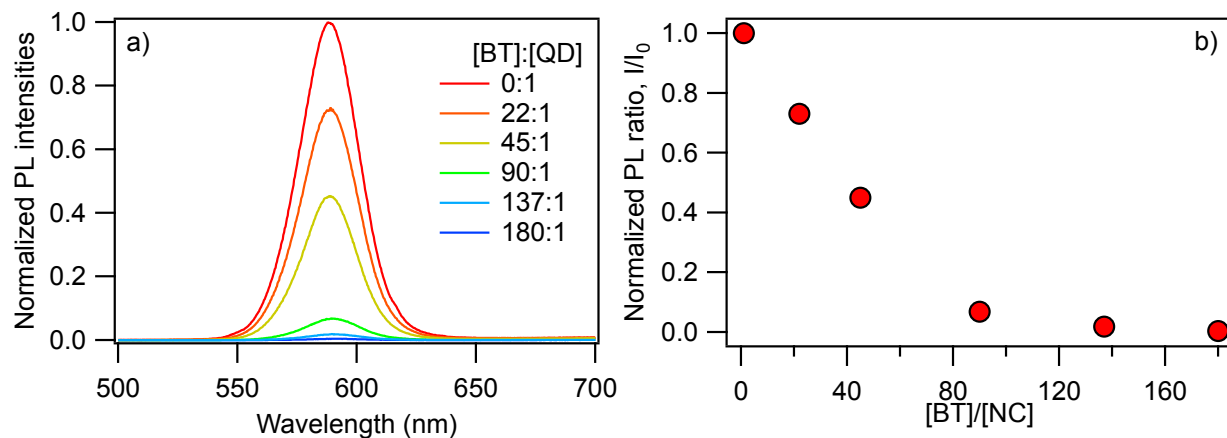


Figure 4.21. Photoluminescence spectra of 1.3 μM CdSe NCs (3.8 nm) in presence of different concentration of benzenethiol (starting surface coverage of CdSe NCs: 4.1 ± 0.2 MA and OA, starting PLQY= 13%). b) Normalized PL intensity (from part a) of CdSe NCs against the ratio of concentrations of benzenethiol added to NCs.

Now, there are about 30 ligands left that may have bound to the surface as L-type ligands. (the error on the last two data points in figure 4.17 are high and there is a chance that L-type binding occurred to a very small extent). Clean CdSe NC sample after the benzenethiol reaction, was analyzed and the surface coverage decreased to 98 ligands per NC, 54 of which are benzenethiolate

ligands (or partially thiol) and 44 are carboxylates (Table 4.2). This surface coverage is in agreement with the analysis of the titration of benzenethiol to CdSe NCs, where the exchange is a mixture of X-type exchange and Z-type displacement.

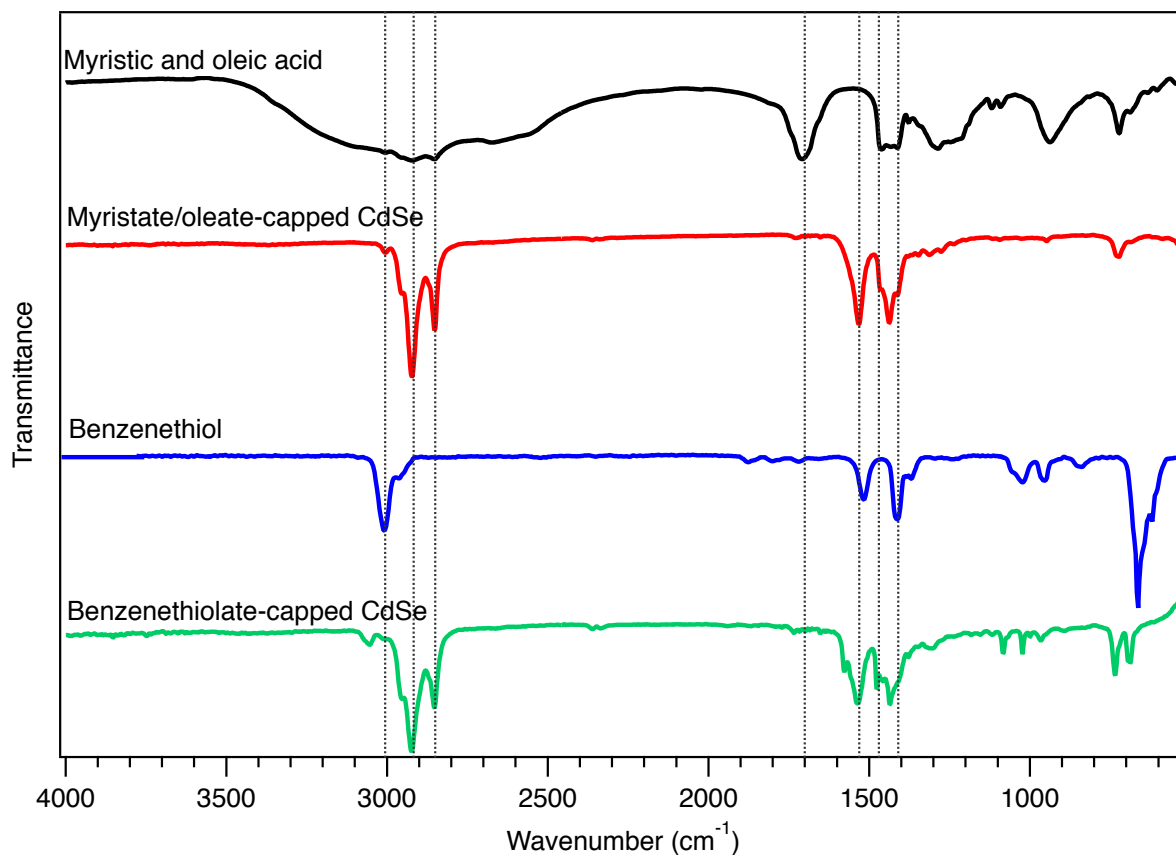


Figure 4.22. FTIR spectra of a mixture of myristic acid and oleic acid (black), myristate/oleate capped CdSe NCs (red), benzenethiol (blue), and benzenethiolate capped CdSe NCs (green).

4.7 Conclusion

The desired goal of the experiments explained in this Chapter is 100% X-type exchange of native ligands of CdSe NCs with other ligands. Subsequently, it would be of interest to compare the efficiency of Z-type displacement of these four different ligands with TMEDA as it would provide us with information about the binding affinity of Se surface site for cadmium with different ligands, how the equilibrium constants and optical properties depend on the surface chemistry. However,

as shown in table 4.2, there are two issues with these exchanges. Firstly, the exchanges are not 100% efficient and there is a significant amount of native ligand that remains on the surface of NCs in almost all cases. Secondly, the ligand coverage decreases significantly after the reaction and isolation of NCs. In Chapter 2, we discussed two different surface sites that are bound to Z-type Cd carboxylate ligands. The CdSe NCs sample that is used for titrations here has almost identical properties to the one discussed in Chapter 2. The theory calculations anticipate 32 surface sites in (111) facets and 62 surface sites on (100) facets. Therefore, the surface sites on (111) facets counts for 64 carboxylates. After the reaction with Oleylthiol, benzenethiol and benzoic acid and isolation of NCs, most of the Z-type ligands on the (111) facets are gone and moreover, because the ligands are not 100% exchanged, any comparison on the Z-type displacement efficiencies would not be meaningful.

To overcome this problem, we should find a way to block the Z-type displacement pathway when performing the X-type exchange. In order to do that, the L-type ligands used for X-type exchange should not be in the protonated form. Instead, if the deprotonated version of that ligand is used, the efficiency of X-type exchanged can be improved hypothetically. This deprotonated version can be a salt form of a tertiary amine ligand (bulky amines are weak at promoting the Z-type displacement).⁶ For instance, to do the exchange with benzenethiol, triethylammonium benzenethiolate salt can be used which forms an ion pair in the solution.

The other way to exchange the native ligands is to strip the Z-type surface ligands using TMEDA following by annealing the NCs with Z-type ligands (CdX_2 , X= benzoate, thiolate, benzenethiolate). Anderson *et al.* showed that the displacement of cadmium carboxylate ligand is reversible if it's performed at elevated temperature (240 °C) and by adding extra cadmium carboxylate and carboxylic acid.⁶ Lawrence *et al.* showed the reversibility of displacement of

cadmium benzoate from the surface of CdSe magic size NCs.³² To reach 100% exchange with the desired ligand, one must design similar experiments. If performed successfully, these samples can be used to further study the Z-type displacement equilibrium and its effect on the PLQY of NCs.

Table 4.2. Properties of CdSe samples after each ligand exchange reaction and with different capping ligands.

CdSe Sample	Total ligand/NC	Exchanged ligand/NC	Native ligand/NC	Total SC(nm⁻²)
MA/OA capped	184 ± 5	NA	184 ± 5	4.1 ± 0.2
MA capped	173 ± 5	(MA)	(OA)	3.8 ± 0.2
OA capped	170 ± 5	(OA)	(MA)	3.7 ± 0.2
OT capped	118 ± 5	(OT)	(OA+MA) 12± 5	2.6 ± 0.2
BA capped	130 ± 7	(BA)	(OA+MA) 61±5	2.8 ± 0.2
BT capped	98 ± 7	(BT)	(OA+MA)	1.7 ± 0.2

CdSe Sample	Exchanged ligand SC (nm⁻²)	Native ligand SC (nm⁻²)	PLQY%
MA/OA capped	NA	4.1 ± 0.2	13 ± 1
MA capped	3.5 ± 0.2	0.3 ± 0.1	11 ± 1
OA capped	3.5 ± 0.2	0.3 ± 0.1	10 ± 1
OT capped	2.3 ± 0.2	0.3 ± 0.1	0.4 ± 0.1
BA capped	2.6 ± 0.3	1.3 ± 0.1	5 ± 1
BT capped	2.2 ± 0.3	1 ± 0.1	0.1 ± 0.1

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Chapter 5: Ligand Exchange and Surface Chemistry of CdS NCs

5.1 Introduction

In Chapter 2 and 3, the key role of Z-type ligands (CdX_2) on the surface chemistry of CdSe NCs was investigated. It was shown that two different surface sites are exposed to the surface of NCs upon removal of Z-type ligands. It was also shown that creation of these surface traps was correlated to the PL quenching efficiency. Although this study provided critical information about the surface chemistry of CdSe NCs, it would be interesting to check if the conclusions can be extended to other II-IV semiconductor NCs. It is well known that semiconductor systems with different atoms (metal, chalcogen or both) have different photophysical properties.¹⁻⁴ Table 5.1 compares the band position and band gap peripheries for bulk CdSe and CdS semiconductors. CdS has a higher band gap than CdSe and this is still true when they are in the confined regime. For example, for a given size, CdS NCs have a higher band gap than CdSe NCs and they have different valence band and conduction band positions as well. CdS NC is also one of the most commonly studied materials that has a great potential for photo-emissive applications.⁵⁻⁹

Table 5.1. Electronic properties of CdSe and CdS bulk semiconductors

Bulk Semiconductor	Band Gap (eV)	Valence Band (eV)	Conduction Band (eV)
CdSe	1.74	-5.7	-3.96
CdS	2.46	-6.5	-4.04

These values were obtained from ref. (10)

So far, there have been multiple studies on properties of NC core (without the organic ligand shell) and their associated quantized excitonic states.¹¹⁻¹⁶ However, the surface chemistry of most semiconducting NCs are poorly understood. As explained in Chapter 1, understanding the creation of defects on the surface of NCs is of great importance. The defects that often form due to poor passivation of NC surfaces with organic ligands, are typically probed indirectly by monitoring the

quenching of the exciton emission signal. The states associated with these surface defects are usually dark and cannot be probed directly.

CdS NCs are exceptional in that their trap states lead to efficient radiative recombination. Trap states are known to be the distribution of mid-gap states, and they are located in a lower energy than the band gap and so their emission signal has a broad feature due to the vibrational coupling of the trap states. In the case of CdS NCs with a large band gap, these trap states fall in the visible region (Figure 5.1). Hence, the trap emission itself can be used to directly monitor the changes in the trap states by changing the moiety around the surface.

Initial studies on the CdS system were mainly focused on trap PL states and their characterization using low temperature PL and PL lifetime measurements.^{8,17-20} It was determined that trap PL is due to the trapping of charge carriers (electron or hole) followed by their recombination at the surface of NCs.^{5,21} The Kambhampati group investigated the surface chemistry of CdS NCs by studying the low temperature emission of trap states.²²⁻²⁵ They modeled the surface of CdS using a semi-classical electron transfer approach as the behavior of trap states could not be explained by fundamental deep-trap model. In their model, the surface defects are considered as a fundamental electron state of the system. In this approach though, the role of ligands that are bound to the surface of CdS NCs, and the surface lattice and surface reconstructions were not considered.

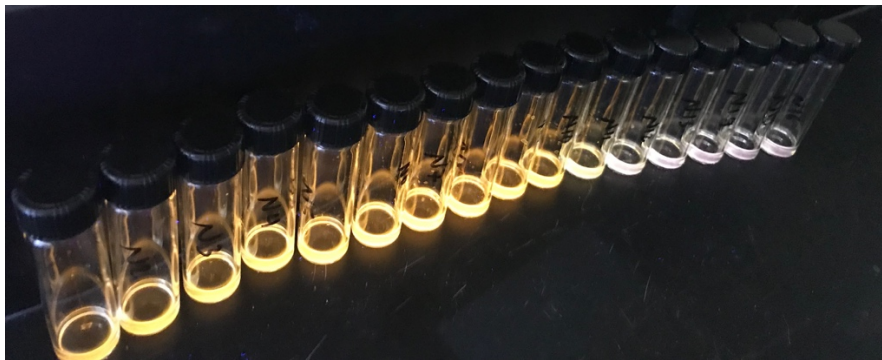


Figure 5.1. Suspensions of 3.5 nm CdS NCs with an increasing amount of TMEDA (from right to left). This figure shows as more trap states are created, the dominant color of emission of excited CdS NCs becomes orange.

In this Chapter, we investigated the surface chemistry of CdS NCs with specific focus on zinc-blende CdS NCs capped with long-chain carboxylate ligands. Similar to CdSe NCs that studies before, these CdS NCs have a non-stoichiometric cadmium-rich surface, cadmium carboxylate groups (CdX_2) covering the surface. Similar to Chapter 2 and 3, we deliberately created traps on the surface of CdS NCs by displacing these CdX_2 groups, and monitored this process using ^1H NMR spectroscopy. Then we studied the impact of the removal of CdX_2 on the PLQY of the excitonic and trap states. Moreover, we correlated the change in the PLQY of exciton and trap to specific sulfur (S) sites at the surface of CdS NCs.

5.2 Experimental Section.

5.2.1 Chemicals

Cadmium nitrate tetrahydrate ($\text{Cd}(\text{NO}_3)_4 \cdot 4\text{H}_2\text{O}$, 98%), oleic acid (90%) octadecene (ODE, 90%), N, N, N',N',-tetramethylethylene-1,2-diamine (TMEDA, 99%), myristic acid (>99%), ferrocene (Fc, 98%), sulfur (99.98%) were purchased from Sigma Aldrich. Ethyl acetate (HPLC grade), toluene (ACS grade), sodium hydroxide (>98%), anhydrous methanol (HPLC grade) were purchased from Macron Fine Chemicals. Ethyl acetate was degassed by bubbling nitrogen for 2 h

and dried over molecular sieves for at least two days prior to use. Oleic acid was degassed through 3 cycles of vacuum/purge with nitrogen and kept under nitrogen atmosphere just prior to use. Ferrocene was recrystallized from methanol solutions. Toluene and pentane were dried using an alumina distill columns. TMEDA was stored in the glovebox and taken out for sample preparation. Other chemicals were used as received.

5.2.2 Synthesis of Cadmium Myristate

The synthesis of cadmium myristate was detailed in Chapter 2, Section 2.2.4.

5.2.3 Synthesis and Purification of Cadmium Sulfide NCs

Cadmium sulfide was prepared by adopting literature protocols.²⁶ 5.67 g (10 mmol) cadmium myristate, 0.16g (5 mmol) sulfur powder and 630 mL octadecene were placed in a 1 L three-neck round bottom flask equipped with a water condenser. The flask was degassed in three cycles of 20 min each, then heated to 240 °C over 7 min. Heat was maintained until the desired size was reached (5 min for 3.3 nm and 20 min for 3.5 nm), which was checked by taking the absorption of a diluted aliquot of the reaction suspension. Heat was consequently removed and 30 mL (96 mmol) of degassed oleic acid were injected over 20 min while the flask was allowed to cool down to room temperature, followed by continuous stirring for 15 h under nitrogen flow. Octadecene was then removed by vacuum (50-70 mTorr) distillation at 130 °C, after which 20 mL dry toluene was added to the yellow concentrated and impure NCs suspension, which was finally transferred into four test tubes and centrifuged for 20 min at 6000 rpm. The supernatant was transferred in 1 mL portions into test tubes, and 10 mL ethyl acetate was added to each tube to precipitate the NCs. After centrifugation at 6000 rpm, the supernatant was removed and the NCs resuspended in 1 mL of

toluene; the entire cleaning cycle was repeated four times. Finally, 10 mL ethyl acetate was added to each test tube (with only the particles), followed by sonication for 15 s. The test tubes were then centrifuged (6000 rpm) and the supernatant removed. The NCs were dried over nitrogen for 24 h, and then suspended in *d*-toluene to make a 86 μ M stock solution of NCs, as assessed by UV-Vis spectroscopy, following the empirical calibration curve established by Peng et al.

5.2.4 Optical Spectroscopy

Absorption spectra are collected on a UV-Vis spectrophotometer (Shimadzu, UV-2600) in 1 nm increments, using 1 cm pathlength quartz cuvettes. Spectra were measured in toluene after the toluene background was subtracted. Continuous wave (CW) photoluminescence (PL) measurements were performed using a 0.55 m focal length spectrometer (iHR550, f/6.4, 150 grooves/mm grating blazed at 500 nm) equipped with a CCD detector (Horiba Symphony II nitrogen cooled deep depleted CCD), and exciting at 375 nm using a tungsten lamp coupled to a 0.32 m focal length monochromator (Horiba iHR320, f/4.1, 600 grooves/mm grating blazed at 500 nm). PLQY were measured with an absolute PL quantum yield spectrometer (Hamamatsu Quantaaurus, C11347), using toluene suspensions prepared as described below and exciting at 375 nm.

5.2.5 Sample Preparation for ^1H NMR and PL.

d-Toluene solutions of TMEDA were prepared to cover a range of concentrations from 0.01 M to 6.7 M (neat TMEDA). Mixtures of CdSe NCs and TMEDA in *d*-toluene were prepared, each containing 600 μ L of 86 μ M CdS NCs ([CdS NC] = 78 μ M), 30 μ L of a given TMEDA solution ([TMEDA] varying from 0.1 mM to 303 mM, or about 1:1 to 1:3900 CdS NC: TMEDA ratios)

and 30 μL of 5.7 mM ferrocene solution ($[\text{Fc}] = 0.27 \text{ mM}$); each sample was allowed to equilibrate after mixing by waiting 30 min prior to measurements. ^1H NMR spectra were collected on an Agilent DDR2 500 MHz NMR spectrometer equipped with 7600AS 96 sample auto-sampler running VnmrJ 3.2A, using a 45° pulse angle / 10 s relaxation time sequence and 32 scans. Spectra were analyzed using MestreNova (Mestrelab Research S.L.) and Igor Pro 7.05 (Wavemetrics). Samples for photoluminescence (PL) spectra were prepared by diluting 30 μL aliquots from each NMR sample to 2.03 mL with toluene.

5.2.6 Ligand Coverage and Surface Coverage Calculations

The Calculation of cadmium carboxylate ligand coverage of CdS NCs is very similar to that of CdSe NCs, which was described in Chapter 2. We assume identical displacement behavior of oleate and myristate ligands by TMEDA as they behave almost identically with regards to exchange reactions.²⁷ We use oleate peak as a probe to monitor the displacement of the total carboxylate ligands by TMEDA.

5.3 CdX₂ Displacement from CdS NCs

The absorption and photoluminescence spectra of clean suspensions of CdS NCs (without any free ligand) before and after addition of TMEDA ($[\text{TMEDA}]: [\text{NC}] = 0:1$ and $4000:1$) are shown in Figures 5.2 and 5.3 for 3.5 and 3.3 nm CdS NCs respectively. TMEDA alters both the absorption and PL peaks of CdS. As can be seen in Figures 5.2 and 5.3, the PLQY of CdS NCs converges to zero with addition of TMEDA and the absorption spectra decrease. A similar study for CdSe didn't show an appreciable change in absorption spectrum of CdSe NCs (Figure 2.1). This comparison suggests a difference between the surface chemistry behaviors of CdS and CdSe systems upon

ligand displacement by TMEDA. Similar to Chapter 2, we began this study by analyzing the Z-type ligand displacement using ^1H NMR spectroscopy.

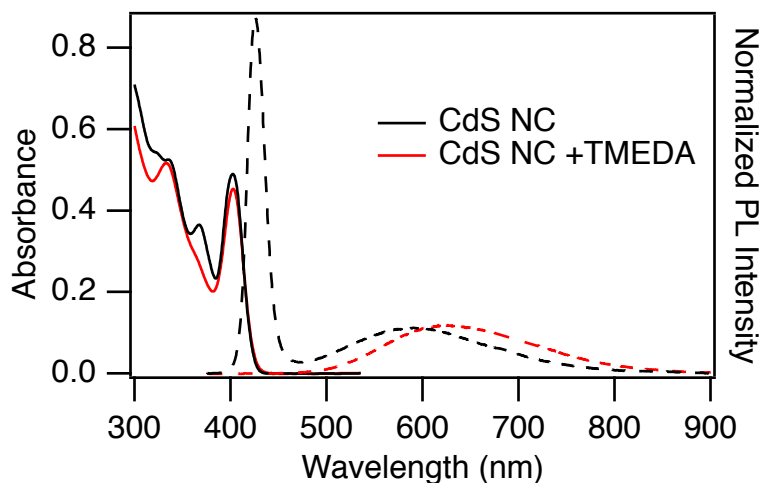


Figure 5.2. Absorption (solid) and photoluminescence (dashed) of 3.5 nm CdS NCs ($1 \pm 0.1 \mu\text{M}$) before (black) and after (red) addition of TMEDA (4.5mM), illustrating the impact of displacing CdX_2 complexes from the surface of CdS NCs.

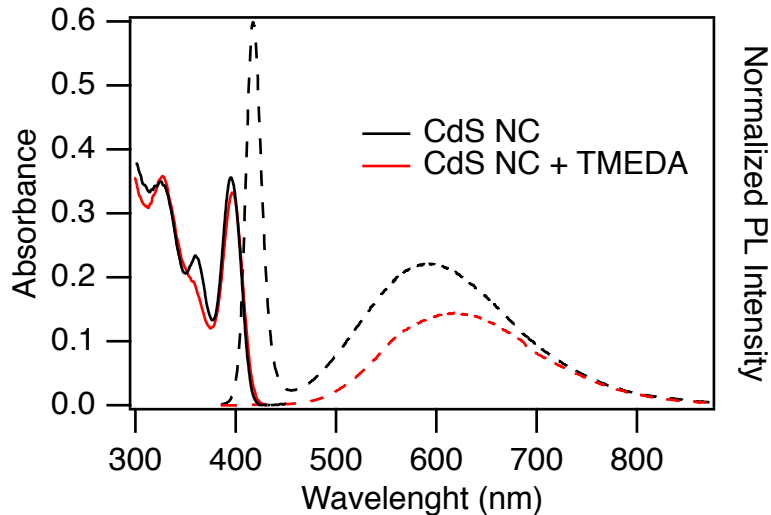


Figure 5.3. Absorption (solid) and photoluminescence (dashed) of 3.3 nm CdS NCs ($1 \pm 0.1 \mu\text{M}$) before (black) and after (red) addition of TMEDA (3.6 mM), illustrating the impact of displacing CdX_2 complexes from the surface of CdS NCs.

The ^1H NMR spectra of 3.5 and 3.3 nm CdS NCs, with and without TMEDA, are shown in Figure 5.4 and 5.5 respectively. The top spectra ($[\text{TMEDA}]=0$) in Figure 5.4a and 5.5a show the spectra

of 3.5 and 3.3 nm CdS without any free ligands. Integration of intensities of the bands associated with bound carboxylates (methyl groups at 1 ppm) are of interest as these bands should represent the total of all ligands on the surface of NC. The concentration of carboxylate ligands is calculated by comparing the methyl peak with ferrocene at 4 ppm and yields values of 192 ± 5 and 154 ± 5 carboxylate ligands per NCs for 3.5 and 3.3 nm CdS NCs respectively. As discussed in Chapter 2 (Section 2.3), these amounts correspond to 96 ± 3 ($\sim 2.5 \text{ nm}^{-2}$) and 77 ± 3 ($\sim 2.3 \text{ nm}^{-2}$) CdX_2 complexes per NC for 3.5 and 3.3 nm CdS NCs respectively. The values for surface coverage are given in Table 5.1. These surface coverages are slightly higher than those of CdSe NCs (compare with Table 2.1). One possible reason is the smaller radius of sulfur comparing to selenium atoms, which presumably allows for higher density of ligands per unit area.

Moreover, before addition of TMEDA, all carboxylate ligands are bound to the surface of CdS NCs which is indicated by the broad band at 5.7 ppm in Figure 5.4 and 5.5 (top spectra). This peak is assigned to the vinyl peak of oleate ligands. Upon addition of TMEDA, the sharp peak at 5.4 ppm appears that is indicative of free CdX_2 ligands. Since the ratio of bound to free CdX_2 ligands in vinyl region are almost identical to those ratios of methyl region, the vinyl peak is used as a probe for ligand displacement.

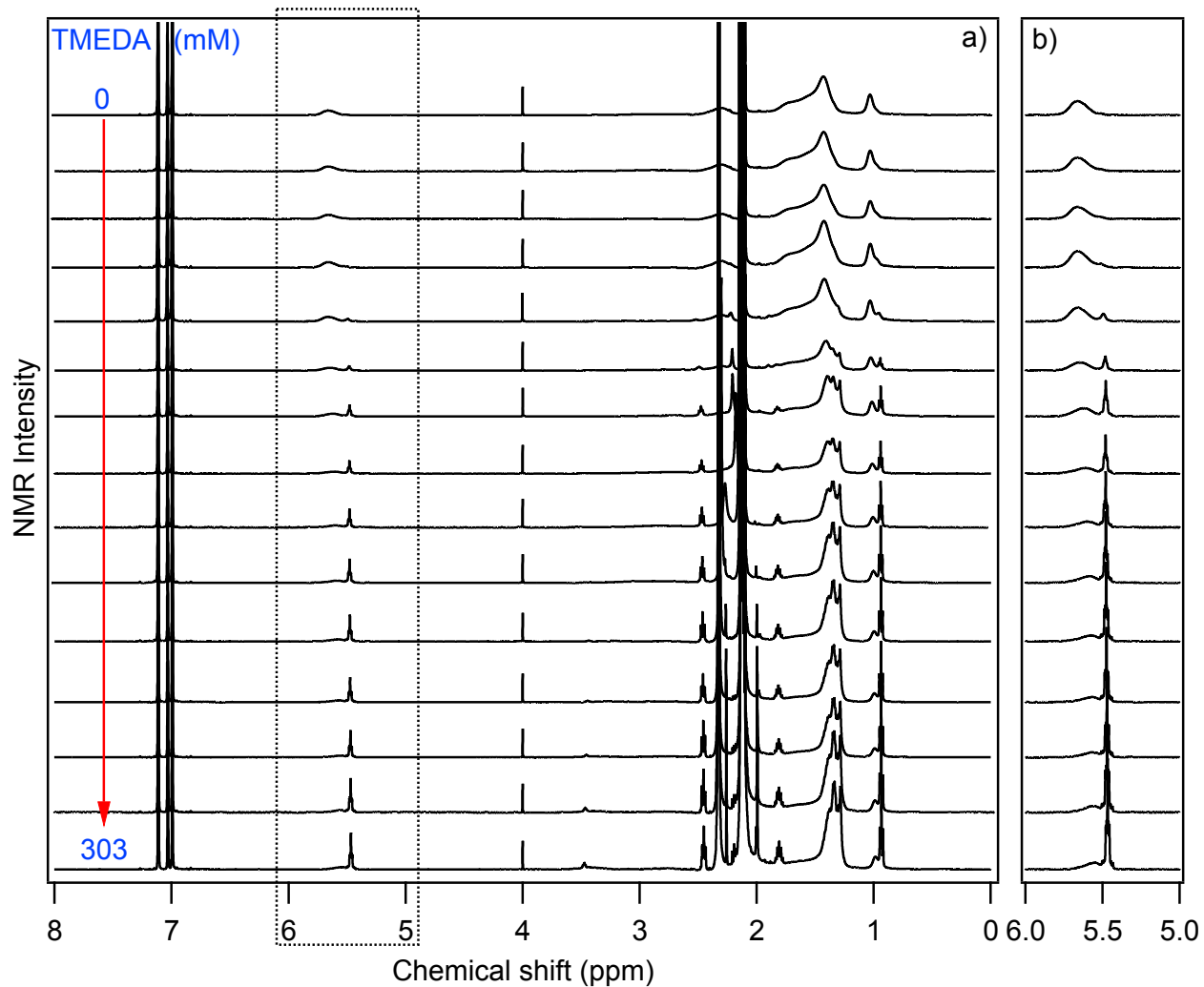


Figure 5.4. NMR Spectra of 3.5 nm CdS NCs (78 μM in *d*-toluene) in presence of different concentrations of TMEDA (b) Zoomed-in spectra (from panel (a)) between 5 and 6 ppm showing the bound (broad peak) and free (sharp peak) cadmium carboxylates (CdX_2).

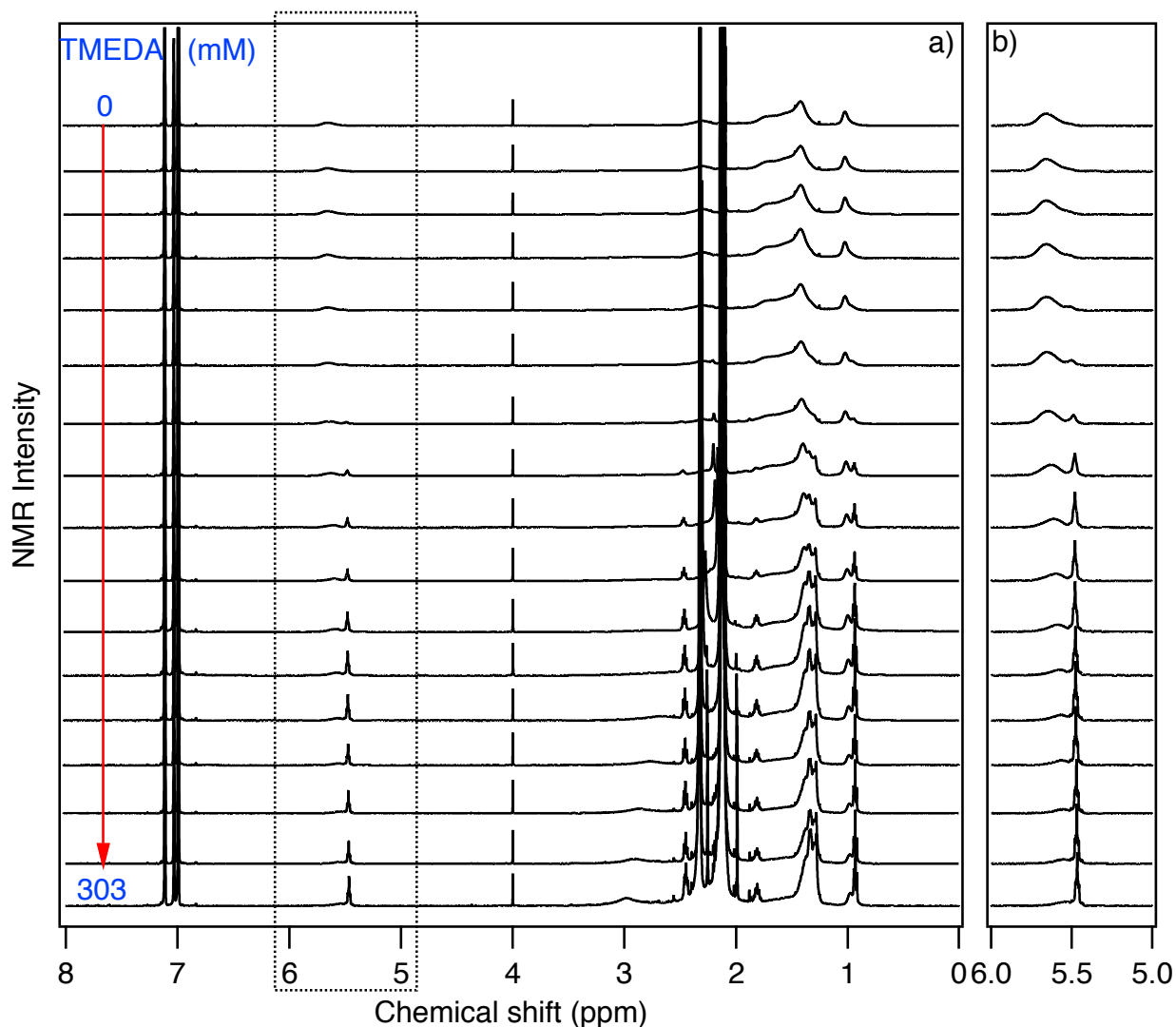


Figure 5.5. NMR Spectra of 3.3 nm CdS NCs (78 μM in *d*-toluene) in presence of different concentrations of TMEDA (b) Zoomed-in spectra (from panel (a)) between 5 and 6 ppm showing the bound (broad peak) and free (sharp peak) cadmium carboxylates (CdX_2)

Upon addition of TMEDA to CdS NCs suspensions in both cases (3.5 and 3.3 nm), the decrease in the intensity of the broad peak at 5.7 ppm is correlated to increase in the sharp peak at 5.4 ppm so that the total number of bound and free ligands per NC remains constant. This is better seen in Figures 5.6 and 5.7 for bound and free ligands in 3.5 and 3.3 nm CdS NCs. In both 3.5 and 3.3 nm CdS NCs suspensions, upon addition of 50 mM TMEDA, ($[\text{TMEDA}]: [\text{NC}] = 641$), almost half of

the CdX_2 groups are removed from the surface of CdS NCs while the further addition of 250 mM TMEDA has a lower impact in CdX_2 removal from the surface of CdS NCs. This is not surprising though, as we already discussed the same behavior upon removal of CdX_2 from the surface of CdSe NCs.

In Chapter 2, we showed that this non-monotonic behavior of CdX_2 removal is due to the existence of two separate equilibria associated to ligand displacement from two different surface sites. Using a similar analysis here, we calculate the equilibrium constant of each equilibrium and number of each surface sites for two different size of CdS NCs.

Table 5.2. Properties of different CdS samples, $T=293.15$ K.

NC diameter (nm)	[NC] (μM)	[CdX_2] (mM)	[CdX_2]/[NC] (N_{tot})	Surface Coverage (CdX_2/nm^2)
3.3 ± 0.2	78 ± 2	6 ± 0.5	77 ± 3	2.3 ± 0.2
3.5 ± 0.2	78 ± 2	7.5 ± 0.6	96 ± 4	2.5 ± 0.2

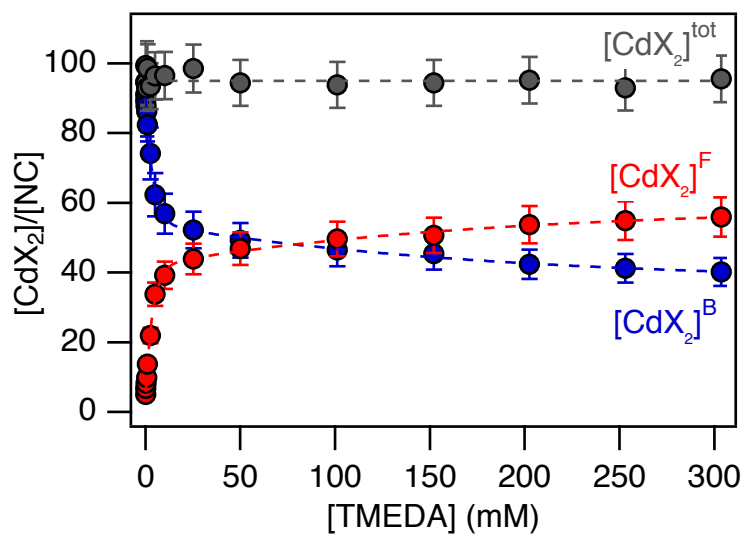


Figure 5.5. Total number of CdX_2 groups (gray circles) per CdS NC(3.5 nm), number of CdX_2 groups bound to the surface of CdS NCs (blue circles), and number of CdX_2 groups displaced by TMEDA from the surface of CdS NCs (red circles).

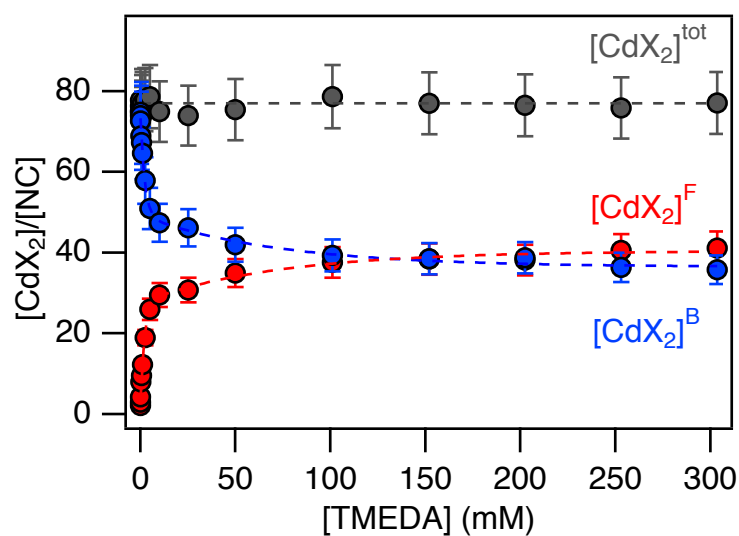


Figure 5.6. Total number of CdX_2 groups (gray circles) per CdS NC (3.3 nm), number of CdX_2 groups bound to the surface of CdS NCs (blue circles), and number of CdX_2 groups displaced by TMEDA from the surface of CdS NCs (red circles).

5.4. Analysis of the Ligand Exchange Equilibrium.

In previous section, we calculated the number of free (L-CdX₂) and bound CdX₂ (B-CdX₂) for each addition of TMEDA for both 3.5 and 3.3 nm CdS NC samples. The concentration of free TMEDA (L) is calculated by subtracting the [L- CdX₂] from the total TMEDA that was added to the suspension of CdS NCs. In Figures 5.8a and 5.9a, values of [NC]/[B-CdX₂] are plotted against the $\phi = [L]/[L- B-CdX_2]$, and eq 2.10 in Chapter 2 is used to fit the data. The outcome of the fits is summarized in Table 5.2. N_{tot} is the total number of ligands/NC before addition of TMEDA ($\phi = 0$). N₁ and N₂ are the two different binding sites with equilibrium constants of K₁ and K₂ respectively. The N₁:N₂ ratios for both cases are roughly about 1:1. However, this number depends on the synthesis and preparation method. Similar to CdSe study in Chapter 1, the values of K₁ are smaller than K₂ values by two orders of magnitude. However, these values are smaller than that we observed for CdSe, meaning that regardless of the type of binding site, the displacement of CdX₂ from the surface of CdS is easier than from the surface of CdSe. By plugging in these fit parameters into eq.2.12 and 2.13 in Chapter 2, the number of CdX₂ removed from N₁(B₁) and N₂ (B₂) sites are calculated and plotted against TMEDA concentration (Figure 5.8b and 5.9b) for both 3.5 and 3.3 nm CdS respectively. The total number of actual and calculated CdX₂ that is removed from the surface of CdS are also plotted in Figures 5.8(b) and 5.9(b). The model works excellent for the equilibrium of CdX₂ at the surface of 3.5 and 3.3 nm CdS NCS.

Table 5.3. CdS NC surface-related data, obtained from analysis of titration experiments, T=293.15 K

NC diameter (nm)	N ₁ %	N ₂ %	(N _{tot})	K ₁	K ₂
3.3 ± 0.2	43	57	77 ± 3	0.4 ± 0.3	374 ± 209
3.5 ± 0.2	48	52	96 ± 4	0.4 ± 0.1	262 ± 45

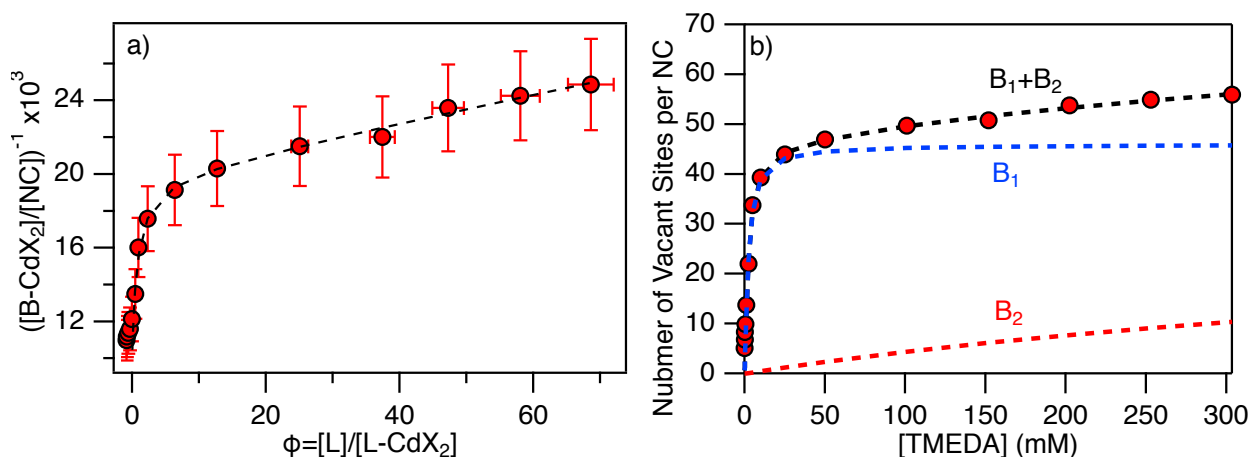


Figure 5.8. a) TMEDA titration of 3.5 nm CdS NCs (78 μM in *d*-toluene), modeled with eq.2.10 in Chapter 2 (black dashed line). b) Calculated number of vacant sites at the surface of the 3.5 nm CdS NC sample, for each type of site, B_1 : blue, B_2 : red, all sites: black. Data for the total number of open sites, equivalent to the number of CdX_2 ligands that are removed from each surface site as a function of added TMEDA, is shown by the red circles.

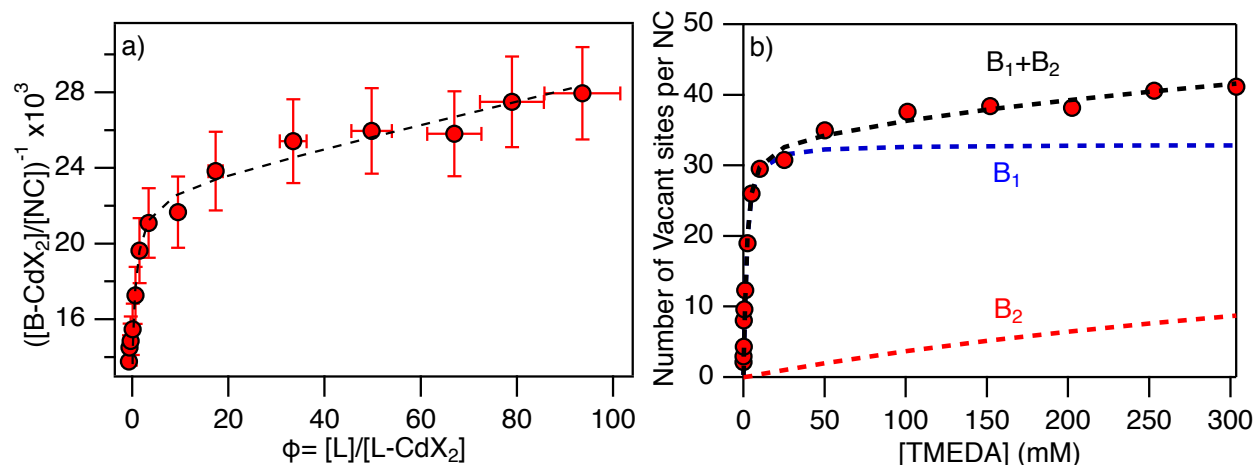


Figure 5.9. a) TMEDA titration of 3.3 nm CdS NCs (78 μM in *d*-toluene), modeled with eq.2.10 in Chapter 2 (black dashed line). b) Calculated number of vacant sites at the surface of the 3.3 nm CdS NC sample, for each type of site, B_1 : blue, B_2 : red, all sites: black. Data for the total number of open sites, equivalent to the number of CdX_2 ligands that are removed from each surface site as a function of added TMEDA, is shown by the red circles.

5.5. Impact of Specific Surface Vacancies on Optical Properties of CdS

The absorption spectra of 3.5 and 3.3 nm CdS NCs after each addition of TMEDA are shown in Figure 5.10a and 5.11a respectively. The change in the absorption of three excitonic peaks of 3.5 and 3.3 nm CdS is shown in Figure 5.10b and 5.11b respectively. For 3.5 nm CdS NCs, the change

in the first (403nm) and third (336 nm) excitonic peaks are very similar and overall the absorption is decreasing. The second excitonic peak (368 nm) shows a similar trend to the first (403nm) and third (336 nm) peaks but it is more shifted down (by $\sim 25\%$). For 3.3 nm CdS however, both first (395 nm) and second (360 nm) excitonic peaks are decreasing by 10% and 15% respectively while the third excitonic peak (326 nm) remains rather constant. In both cases the third excitonic peak has the least amount of change upon TMEDA addition while the second excitonic peak is most affected. The change (decrease and disappearance of the peak) in the absorption of second excitonic peak in both sizes of CdS NCs is most likely due to removal of the CdX_2 group from the surface. Similar change in the second excitonic peak upon removal of CdX_2 group from the surface of CdSe is previously reported.²⁸ However, changes in the magnitude of the first and third excitonic peaks don't show similar trends which is most likely due to the orbital mixing of the ligands with the surface Sulfur (S) atoms. The slight red shifts (1-2 nm) are perhaps arising from the same effect.

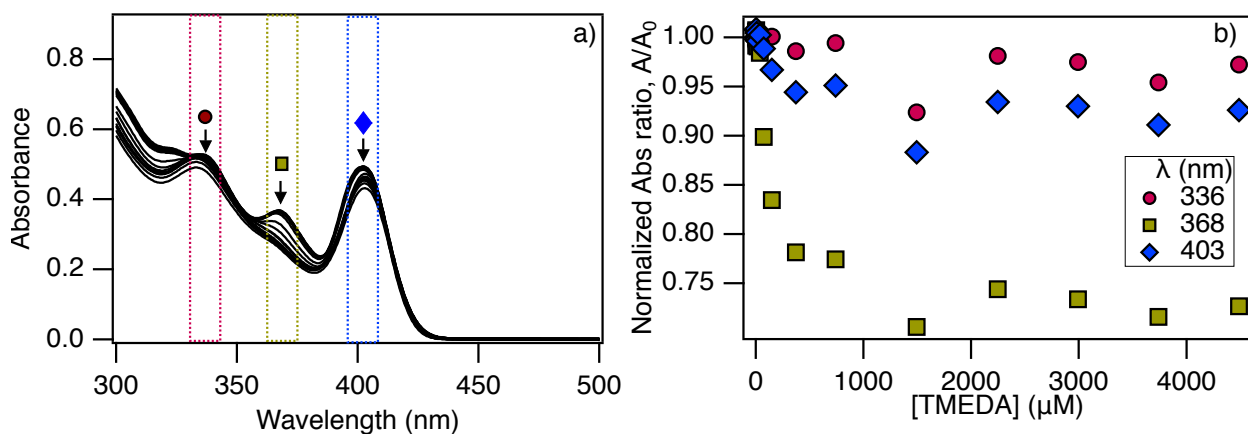


Figure 5.10. a) Absorption spectra of 3.5 nm CdS NCs ($1 \pm 0.1 \mu\text{M}$) in presence of different concentration of TMEDA. b) Normalized absorbance ratios (from part a, shown with arrows) at 336 nm (red circles), 368 nm (yellow squares), 403 nm (blue diamonds) against the ratio of the concentration of TMEDA added to NCs. For example, at 403 nm (blue diamonds), the absorbance of each spectrum at 403 nm is divided by the absorbance of the NCs at 403 nm before addition of TMEDA.

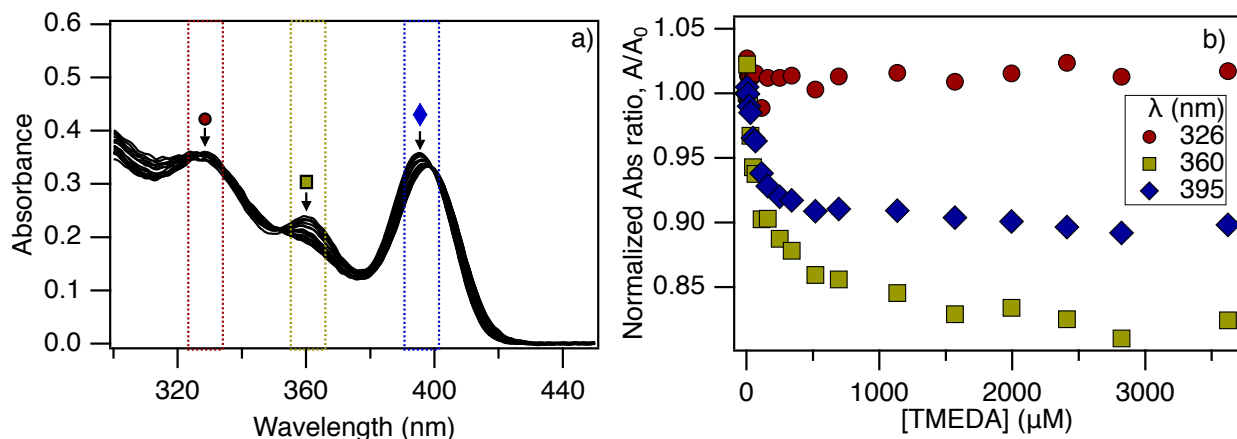


Figure 5.11. a) Absorption spectra of 3.3 nm CdS NCs ($1 \pm 0.1 \mu\text{M}$) in presence of different concentration of TMEDA. b) Normalized absorbance ratios (from part a, shown with arrows) at 326 nm (red circles), 360 nm (yellow squares), 395 nm (blue diamonds) against the ratio of the concentration of TMEDA added to NCs. For example, at 395 nm (blue diamonds), the absorbance of each spectrum at 395 nm is divided by the absorbance of the NCs at 395 nm before addition of TMEDA.

Due to the change in the absorption spectra of CdS NCs upon addition of TMEDA, all recorded PL spectra are corrected for the change in the absorption at the excitation wavelength. In PL measurements, CdS NCs were excited at 375 nm. Hence the total integration of each spectra is divided by the corresponding absorption peak at 375 nm. Table 5.3 shows the PLQY of each CdS sample and the portions of PLQY for exciton and trap. Note that the trap PLQY for 3.3 nm CdS NCs is twice that of 3.5 nm CdS NCs. Figure 5.12a and 5.13a show the PL spectra of 3.5 and 3.3 nm CdS NCs upon addition of TMEDA. In both cases, after addition of TMEDA, the exciton emission peak (~ 415 nm) decreased and by addition of 1 mM TMEDA (~ 1000 eq more NCs), the exciton PLQY is completely quenched. By contrast, the corresponding trap PLQY increases till the addition of 1 mM TMEDA (shown in Figures 5.12a and 5.13a with solid lines). For 3.5 nm CdS NCs more additions of TMEDA causes red shifts in trap peak by 40 nm and subsequently the magnitude of the trap peak decreases (shown in Figure 5.12a with dashed lines). For 3.3 nm CdS NCs with more additions of TMEDA, the shift (~ 40 nm) in trap peak was observed while the PLQY of trap was increasing (TMEDA ~ 0.2 mM), then the magnitude of trap peak decreased.

Table 5.4. CdS NCs PL data, prior to TMEDA treatment, T=293.15 K.

NC diameter (nm)	Total PLQY (%)	Exciton PLQY (%)	Trap PLQY (%)
3.3 $\pm$ 0.2	29 $\pm$ 0.5	9 $\pm$ 0.2	21 $\pm$ 0.4
3.5 $\pm$ 0.2	20 $\pm$ 0.5	9 $\pm$ 0.2	11 $\pm$ 0.3

The evolution of the PLQY of exciton, trap and total intensities (trap + exciton) are plotted against added TMEDA in Figures 5.12b and 5.13b for 3.5 nm and 3.3 nm CdS respectively. For better characterizing the PL quenching efficiency, the Stern-Volmer plots for change in the PLQY of the exciton, trap and the total PLQY, are shown in Figures 5.12c and 5.13c for 3.5 and 3.3 nm CdS respectively. In these plots, the reciprocal of the PL intensities is normalized to the PL intensity in the absence of TMEDA (I_0). In both cases, the change in total PLQY is similar to the trap PLQY (Figures 5.12c and 5.13c, red and yellow circles) which shows that the total PLQY is dominated by the trap emission.

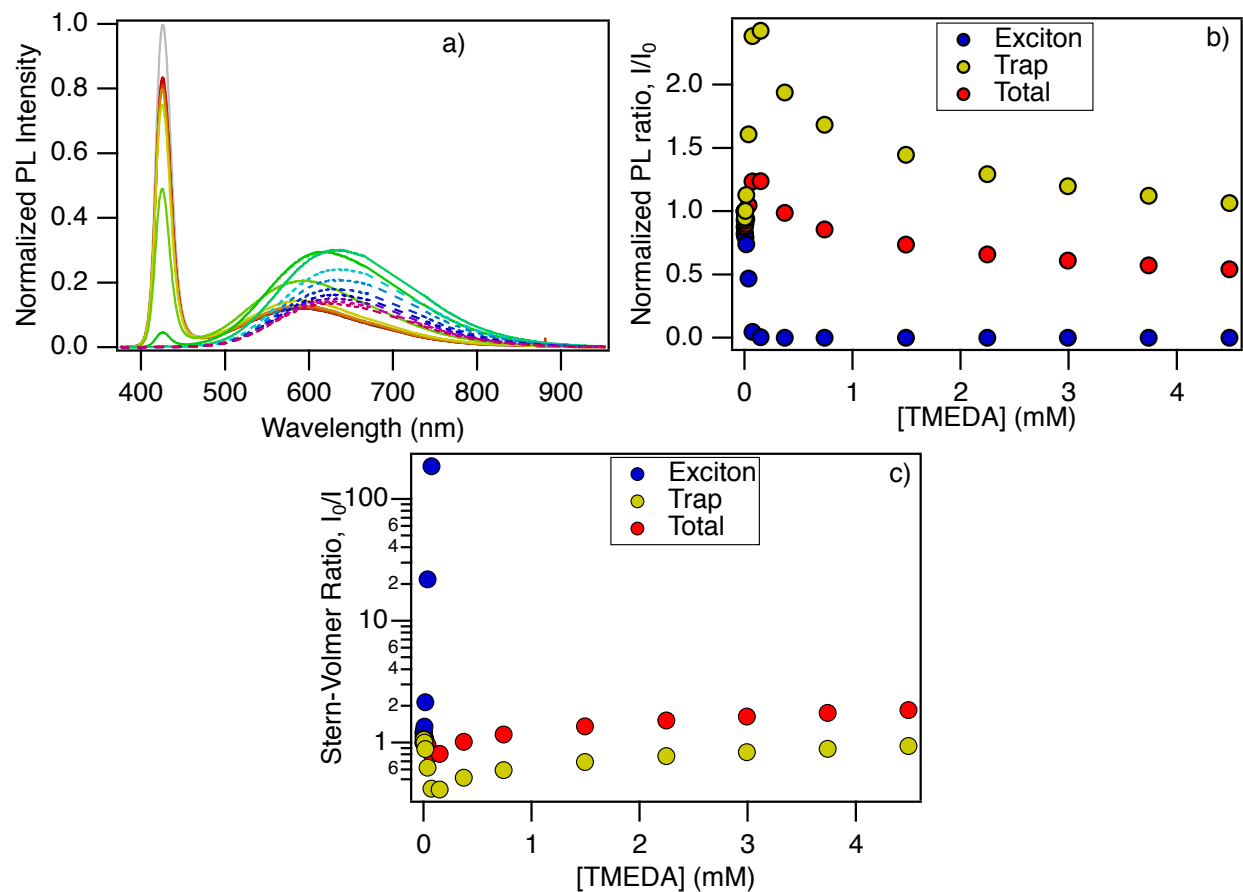


Figure 5.12. a) PL spectra of 3.5 nm CdS NCs ($\sim 1.0 \pm 0.1 \mu\text{M}$), with varying amounts of TMEDA (0 -4.5 mM). b) Normalized PL intensity of 3.5 nm CdS NCs (from part a). Intensities are normalized to the integrated PL intensity of the CdS NCs with no TMEDA (I_0), at exciton emission peak (424 nm, blue circles), trap emission peak (600 nm, yellow circles), and total emission (trap + exciton, red circles), after baseline subtraction. (c) Quantification of the TMEDA-induced CdS NC PL quenching (from part b) are reported as the Stern-Volmer ratio, I_0/I .

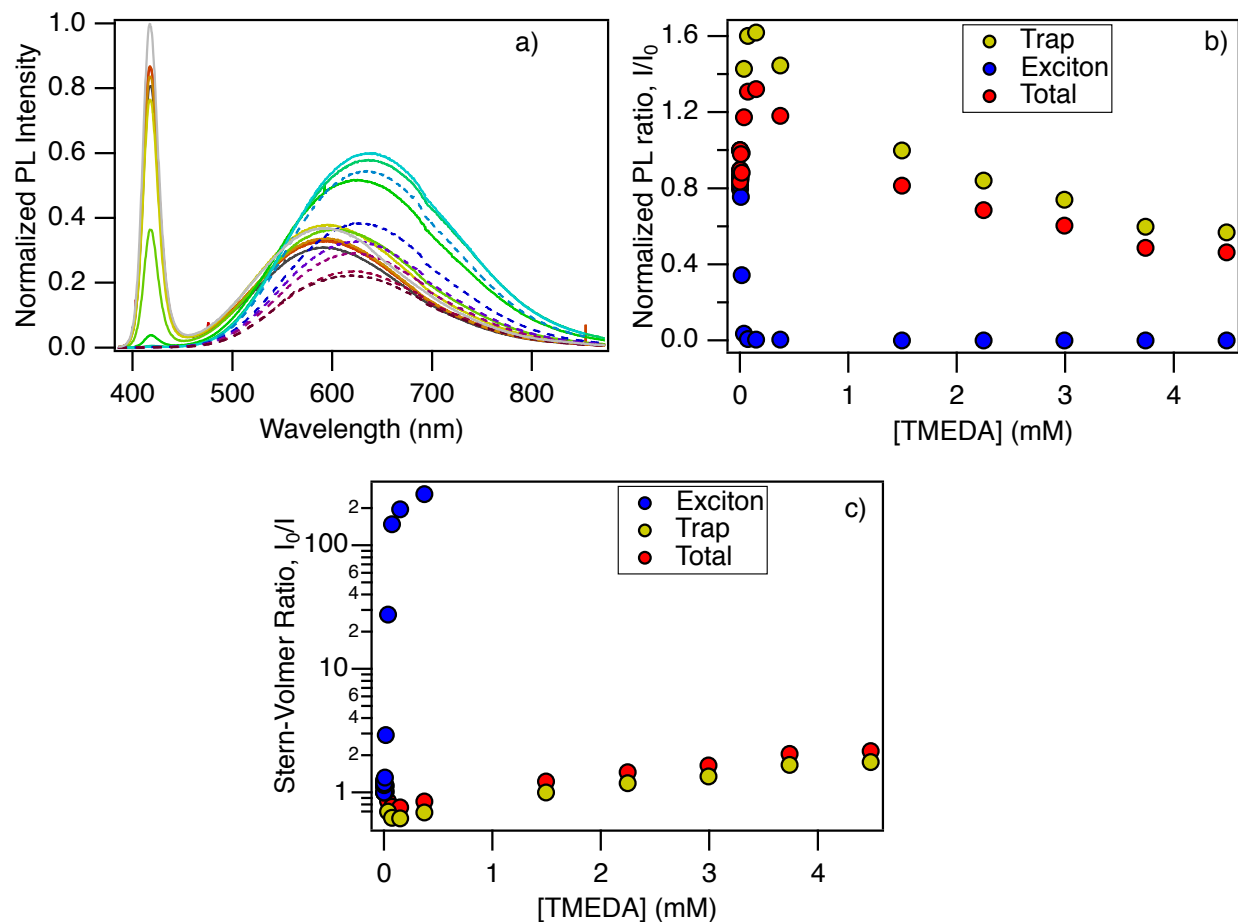


Figure 5.13. a) PL spectra of 3.3 nm CdS NCs ($\sim 1.0 \pm 0.1 \mu\text{M}$), with varying amounts of TMEDA (0 -4.5 mM). b) Normalized PL intensity of 3.3 nm CdS NCs (from part a). Intensities are normalized to the integrated PL intensity of the CdS NCs with no TMEDA (I_0), at exciton emission peak (415 nm, blue circles), trap emission peak (630 nm, yellow circles), and total emission (trap + exciton, red circles), after baseline subtraction. (c) Quantification of the TMEDA-induced CdS NC PL quenching (from part b) are reported as the Stern-Volmer ratio, I_0/I .

5.6 Correlation Specific Facet Vacancies with Photo-luminescence Quantum Yields: Dark versus Bright NC

In previous sections the impact of TMEDA on the displacement of CdX_2 was characterized. Similar to the CdSe study in Chapter 3, we can directly correlate the PL quenching efficiencies to the

formation of two types of surface defects (labelled B_1 and B_2 here). Figure 5.14a and 5.15a show the correlation of PL quenching efficiency of total PLQY to B_1 and B_2 surface defects for 3.5 and 3.3 nm CdS NCs. By contrast to what we observed in Chapter 3 for CdSe NCs (section 3.3, Figure 3.2), it is difficult to conclude the exact effect of each surface defects on PL quenching efficiency of CdS NCs. This is due the fact that the total emission in CdSe NCs is mainly composed of excitonic PL (trap emissions are insignificant), as opposed to the total emission in CdS NCs which is composed of exciton and trap emissions. Therefore, we plot the correlation of PL quenching efficiencies of exciton and trap to surface defects separately in Figures 5.14b and 5.14 c for 3.5 nm CdS NCs and in figure 5.15b and 5.15c for 3.3 nm CdS NCs.

The correlation of PL quenching efficiency of the excitonic PL with the formation of specific surface sites (shown for the first eight data points) is similar to what we observed for CdSe NCs. That is, B_2 sites are more efficient at quenching the excitonic PL of CdS NCs. (the ratio of Stern - Volmer for B_2 quenching converges to infinity while the ratio of Stern -Volmer for B_1 quenching is only about 20, Figures 5.14b and 5.15b).

The correlation of PL quenching efficiency of trap to B_1 and B_2 surface defects are shown in Figures 5.14c and 5.15c. Although there are differences in the magnitudes of the Stern-Volmer ratios between 3.5 and 3.3 nm CdS, in both cases, the similar trend is observed for quenching of CdS NCs by B_1 and B_2 defects. It seems that B_1 sites are responsible for the initial increase in trap PLQY (note the negative slope of B_1 vacancies), and B_2 sites are responsible for quenching the trap emission. We also point out that the decrease in trap emission is associated with a red-shift in in trap emission, therefore, these analyses would not be sufficient to draw a conclusion on the exact picture of traps on the surface of CdS.

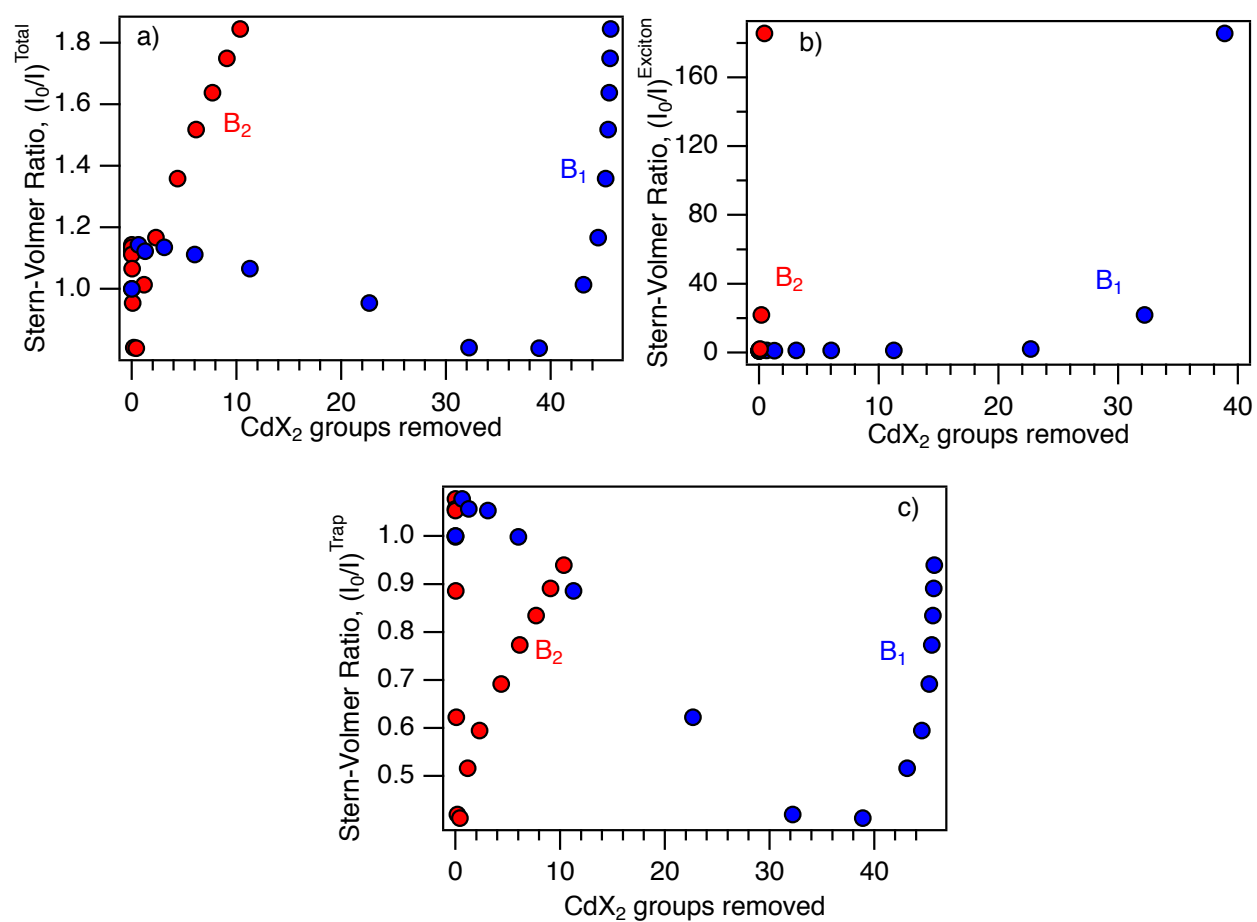


Figure 5.14. CdS NC (3.5 nm) PL quenching efficiencies of each type of vacancies, as induced by displacement of CdX_2 by TMEDA on a) total PLQY (trap and exciton), b) exciton PLQY, and c) trap PLQY.

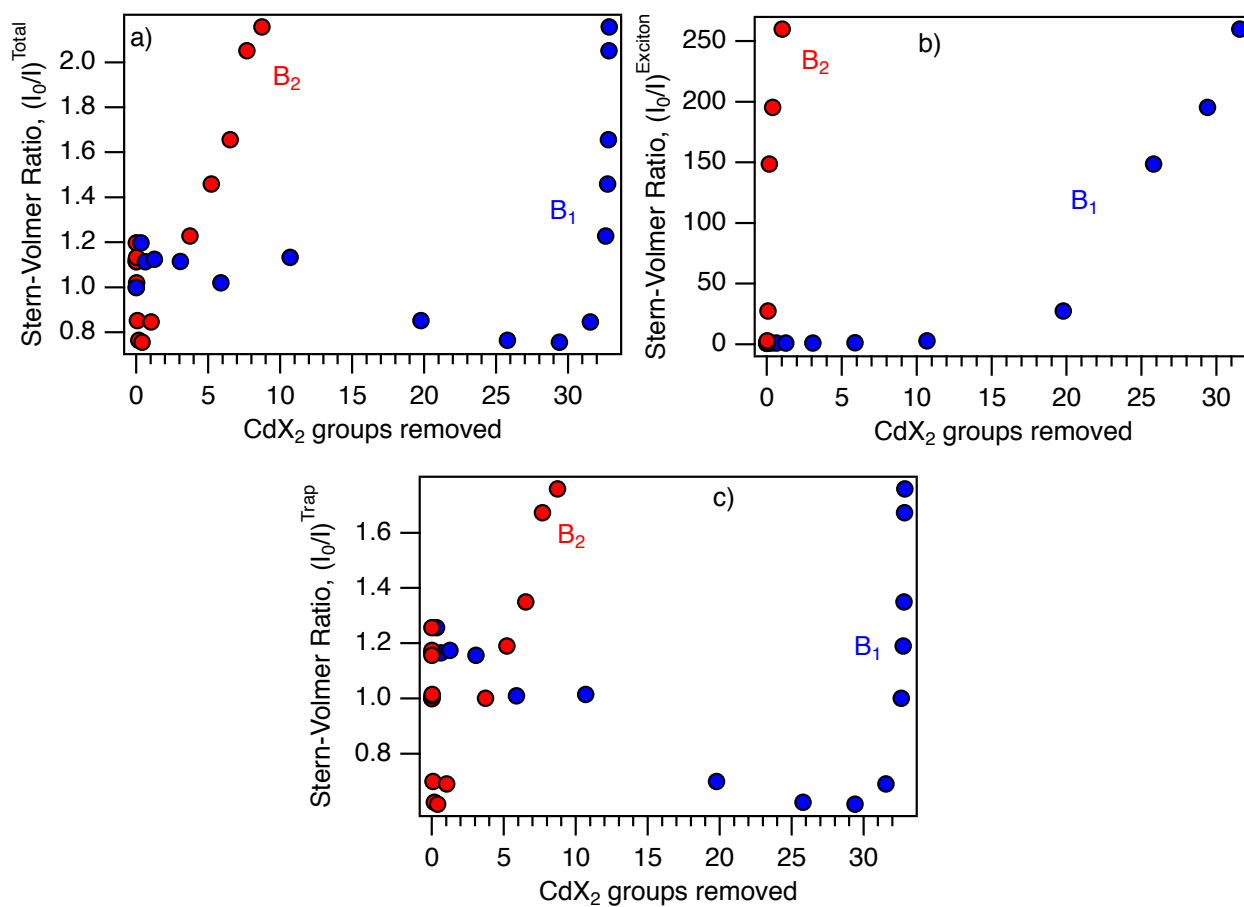


Figure 5.15. CdS NC (3.3 nm) PL quenching efficiencies of each type of vacancies, as induced by displacement of CdX_2 by TMEDA on a) total PLQY (trap and exciton), b) exciton PLQY, and c) trap PLQY.

5.7 Conclusion

In conclusion, zinc-blende CdS NCs showed two different surface defects that (similar to CdSe study, Chapter 2) that could attribute to (100) and (111) facets and B₂ defects (on (100) facets) are responsible for excitonic PL quenching. However, PLQY of CdS is mostly dominated by the trap PL and from the correlation of trap PL to the formation of surface defect it seems that both defects are responsible for change in trap PL. However, more analysis needs to be done to obtain a clear picture about the surface defects on CdS NCs.

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Chapter 6: Concluding Remarks

The aim of this research was to understand the complexity of the surface of II-VI NCs and their effect on the optical properties of NCs. To achieve this goal, various zinc blende CdS and CdSe NCs capped with carboxylate ligands were prepared and their surface chemistry was studied using ligand exchange experiments analyzed by a combination of NMR techniques along with PL and UV-Vis absorption spectroscopies.

Initially, the equilibria from Z-type ligand displacement on the surface of CdSe NCs was investigated. It was demonstrated that there are two different surface sites on the surface of CdSe NCs where they have different binding affinity towards the Cd-based Z-type ligands. A model was developed to calculate the number of each surface site and their corresponding binding equilibrium constants. To investigate the nature of the differences between the two binding sites, thermodynamics studies were carried out by using temperature dependent NMR. Two TMEDA concentrations were carefully selected, each corresponding to a regime where one of the two exchange reactions dominates the overall equilibrium. Van 't Hoff analysis on temperature dependent equilibria showed that the origin of the difference between the two surface sites are due to the entropic effect. This arises from the different crystal facets of semiconductor NCs. The Zinc blende crystal structure is mainly comprised of two facets; (100) and (111). Se surface sites in (111) facet are 3-coordinated while in (100) there are 2-coordinated. The geometry of (100) allows for the better overlapping of these atoms with Cd-X₂ Z-type ligands. Using a combination of the number of binding sites obtained from our model, and packing density of atoms in zinc blende CdSe systems, we calculated the total number of surface defects and later estimated number of binding sites on (111) facets.

To correlate different surface defects to PL quenching efficiency of NCs, we obtained PLs of diluted corresponding NMR samples (with TMEDA) which we studied earlier.

We had shown the amount of the displacement of Z-type ligands by TMEDA. As TMEDA is not the actual PL quencher and actually indirectly quenches the PL of NCs by displacing the Z-type ligands and create surface traps, we eliminated the TMEDA in the equation and directly correlated the PL quenching efficiencies to individual surface defects. This correlation showed the PL quenching efficiency of defects created at (100) sites are larger by two orders of magnitude compare to that of (111) surface defects.

Following these findings, an interesting study would have been the investigation of different X-type ligand exchanges with various types of ligands with different sterics and functional groups which would be helpful in understanding two important aspects in X-type ligand exchanges. Firstly, elucidating complexities such as undesired ligand exchange pathways leading to incomplete X-type exchanges. Secondly, comparison of displacement of CdX_2 with various X ligands and their effects on the optical properties of NCs. Deep understanding of these subjects is crucial in designing more efficient ways of making NCs for different applications.

To this end, we experimented the X-type ligand exchange with oleic acid, Oleylthiol, benzoic acid and benzenethiol. These X-type reactions were accompanied by displacement of Z-type ligands which we studied by a combination NMR, PL and UV-Vis absorption spectroscopy techniques. We also suggested ligand exchange strategies that most likely lead to 100% X-type exchange. Although this study shed light on some complexities in X-type exchanges, however, more controlled experiments needs to be done.

Finally, we switched gears and moved to a different semiconducting NCs system, CdS. We chose similar synthesis to that of CdSe to prepare a zinc blende CdS with the same capping ligands to compare the nature of different surface defects in these two systems. Using the model, we developed for CdSe, we investigated the different surface defects on the surface of CdS NCs.

Similar to CdSe NCs, there are two different sulfur surface defects on CdS NCs with ligand binding equilibrium constants that are two orders of magnitude apart, however, these equilibrium constants are 50-60% smaller than those of selenium on CdSe with similar sizes. This finding suggests that it is easier to remove Z-type ligands from the surface of CdS. We also correlated the different surface defects to the PL quenching efficiency of CdS NCs. Not only surface defects from (100) facets are responsible for the PL quenching of CdS NCs, but also defects from (111) facets change the trap PL by contributing to the energy of trap states and shifting the trap energies. The exact reason behind this phenomenon is yet to be understood which requires further analysis of the PL of trap states. Low temperature PL also provides useful information about the mechanism of charge trapping at the surface.