

THE IMPACT OF SURFACE CHEMISTRY ON THE PHOTOPHYSICAL PROPERTIES OF
CADMIUM SULFIDE NANOCRYSTALS

By

Lisa M. Janes

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ABSTRACT

THE IMPACT OF SURFACE CHEMISTRY ON THE PHOTOPHYSICAL PROPERTIES OF CADMIUM SULFIDE NANOCRYSTALS

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In this dissertation, we study the complex nature of the surface in cadmium-rich CdS nanocrystals. We found that cadmium carboxylate complexes (CdX_2) act as Z-type ligands (Lewis acids) that passivate undercoordinated sulfur sites. To elucidate more information about these states, CdX_2 groups were displaced using *N,N,N',N'*-tetramethylethylenediamine (TMEDA), and monitoring using ^1H NMR and photoluminescence spectroscopies. Through these studies, we demonstrate the existence of two distinct binding sites, each with its own binding affinity for CdX_2 . These sites are under dynamic equilibria, and a two-site binding model was developed to provide a deeper understanding of the thermodynamics of the surface binding in CdS. Thermodynamic data shows that the entropic contribution is a significant difference between each binding site.

With a better understanding of the binding thermodynamics of each surface site in hand, we move to determine the role played by each defect site on the photophysical properties of CdS NCs. The absorption profiles of CdS NCs are altered upon the creation of surface defects. There is a direct correlation between the observed red shift of the excitonic peak with the creation of B_2 sites on the surface, as well as a correlation between the broadening of the $1\text{S}_e\text{-}2\text{S}_{3/2\text{h}}$ peak and the creation of B_2 sites. The creation of defects changes the surface polarization, resulting in changes in the absorption profile.

Furthermore, a direct correlation between the creation of each vacant site and its impact on the photoluminescence (PL) spectroscopy is discussed. Each site has its effect on PL emission, and B_2 vacancies are excellent exciton quenchers and are the primary cause of the energy shift seen in the

trap state emission. The trap state emission of CdS NCs was determined to be caused by two distinct trap states. The PL efficiency of each trap state is influenced by the cadmium to sulfur ratio on the surface and correlated to the creation of each surface defect. The excited-state lifetimes of both trap states and of the exciton recombination were probed throughout this study. Our results gave insight into the complex nature of the surface and its impacts on the photophysical NC properties. Overall, we determined that the creation of B₂ vacant sites significantly impacts the lifetime of each state. To have greater control over the photophysical properties of CdS NCs, B₂ vacant sites need to be capped with ligands. The impact of these discoveries presented in this thesis will provide greater understanding of CdS NC surface and better control of the surface.

**This thesis is dedicated to Matt, Mom, Dad, and Ricky.
Thank you for always believing in me.**

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LIST OF ABBREVIATIONS

B	Surface State
CBC	Covalent Bond Classification
CBM	Charge Balance Model
CdS	Cadmium sulfide
CdSe	Cadmium selenide
CdTe	Cadmium Telluride
CdX ₂	Cadmium Carboxylate
CW	Continuous Wave
DSSCs	Dye-sensitized Solar Cells
DOSY	Diffusion Ordered Spectroscopy
eV	Electron Volt
ICP	Inductively Coupled Plasma
ICP-OES	Inductively Coupled Plasma- Optical Emission Spectroscopy
IR	Infrared
<k>	Average Rate Constant
<i>K_{eq}</i>	Equilibrium Constant
LED	Light Emitting Devices
MO	Molecular Orbital
NC	Nanocrystal
NIR	Near- infrared
nm	Nanometer

NMR	Nuclear Magnetic Resonance
Pb(oleate) ₂	Lead oleate
PbS	Lead sulfide
PL	Photoluminescence
PLQY	Photoluminescence Quantum Yield
QD	Quantum Dot
SC	Semiconductor
TEM	Transmission Electronic Microscopy
TMEDA	<i>N, N, N', N'</i>-tetramethylethylenediamine
UV	Ultraviolet
Vis	Visible
XANES	X-ray Absorption Near Edge Structure
XES	X-ray Emission Spectroscopy
XPS	X-ray Photoelectron Spectroscopy
XRD	X-ray Diffraction

Chapter 1: Introduction

1.1 Semiconductor Nanocrystals

1.1.1 Introduction to Semiconductor Nanocrystals

Colloidal quantum-confined nanocrystals (NCs) are nanometer-size crystals that combine molecular properties with the characteristics of solid-state semiconductors (SCs).¹ Due to their highly tunable properties, NCs are outstanding candidates for applications involving photo-sensing, photovoltaics, bioimaging, storage and transport of energy, and solid-state lighting.^{2–11} NCs share the optical and chemical characteristics of solid-state SCs but significantly differ in the way these characteristics can be controlled chemically.

In contrast to their bulk counterparts, semiconductor NCs have large surface-to-volume ratios. They are typically composed of three components: core, shell, and the surface (interaction between core and shell). The core composition, consisting of inorganic semiconducting materials, usually determines most of the NC electronic properties.^{12,13} Colloidal NCs have a delocalized electronic structure that is typically restricted by quantum confinement effects, which leads to electronic excitations that are dependent on the size/shape of the NC core.^{14,15} Furthermore, quantum confinement effects lead to discrete energy levels and give the material optical properties similar to those associated with molecular materials.¹⁶ These inorganic cores are terminated with a shell composed of long-chain organic ligands that help stabilize the NCs and impact the optical properties of the NCs.^{17–20} Furthermore, these ligands allow the NC to suspend in non-polar solvents. Most notably, these shells can improve the photoluminescence quantum yield (PLQY) of the NCs through the reduction of non-radiative recombination.²¹ Lastly, the surface of the NC is where the core and shell meet. The surface makes unique contributions to the NC's photophysics but is also the most difficult part to control and characterize.

1.1.2 Semiconductor Properties and Quantum Confinement Effect

SC materials have a valence and conduction band.²² Since NCs are composed of many atoms, the number of atomic orbitals is very large and closely spaced in energy. These atomic orbitals are so energetically close together that they can be considered as a continuum of energy levels, otherwise known as an energy band. The valence band is composed typically of occupied bonding orbitals, and the conduction band is comprised of unoccupied anti-bonding orbitals. The difference in energy between the highest energy level in the valence band and the lowest energy level in the conduction band is the bandgap. In various semiconductor materials, bandgaps vary between 0 and 4.0 eV depending on the material. The excitation of a valence band electron into the conduction band creates an electron-hole pair, otherwise known as an exciton.^{23,24} The exciton is delocalized over a volume of space defined by the Bohr radius, which depends on the charge carriers' effective masses and on the dielectric constant of the material. In bulk materials, the Bohr radius is typically many orders of magnitude smaller than the crystal size (i.e. a few nanometers). Because of this, typical confinement effects in bulk SC can be ignored. However, when the crystallite sizes become smaller than the Bohr radius, the excitonic energies are affected. Quantum confinement occurs when the exciton is confined to volumes similar (or smaller) than the Bohr radius. Different materials will exhibit quantum confinement at different sizes than others because the Bohr radius is material dependent.¹⁶ Once this quantum confinement is experienced by material, the bandgap becomes inversely related to their diameter and allows NCs to have highly tunable properties.

1.1.3 Applications of SC NCs

Due to their high tunability, colloidal NC systems have been used in a variety of different applications, including (but not limited to): imaging, photovoltaic devices, displays, and lighting.^{4,6,8,8,11,25,26} In all these applications, NCs need to have long-term stability, large absorption

cross-sections, and high quantum efficiency. For NCs to be effectively used in the applications mentioned above, non-radiative processes need to be mitigated and controlled. One of the most common ways to tune and maintain NC stability and light absorption processes is to modify the NC surface.

NCs have great potential in bioimaging due to their tunable photoluminescence properties and high resistance to photobleaching.²⁵ NCs have varying emission wavelengths that can span across visible and near-infrared (NIR).²⁷ These different emission wavelengths can be excited with one broadband excitation source, which allows for colorful images.²⁸ However, the surface of NCs must be modified to interact with biological molecules through electrostatic or ligand-receptor interactions for them to be more suitable for biological functions.²⁹ Most recent studies on the synthesis of water-soluble silver sulfide quantum dots for cell imaging show favorable biocompatibility.²⁵ Many studies have also been done that offer the potential and applications of NCs as fluorescent probes. Most recently, molybdenum disulfide quantum dots (QDs) have been used as nanoprobe for the pre-diagnosis of cancer through bioimaging.³⁰

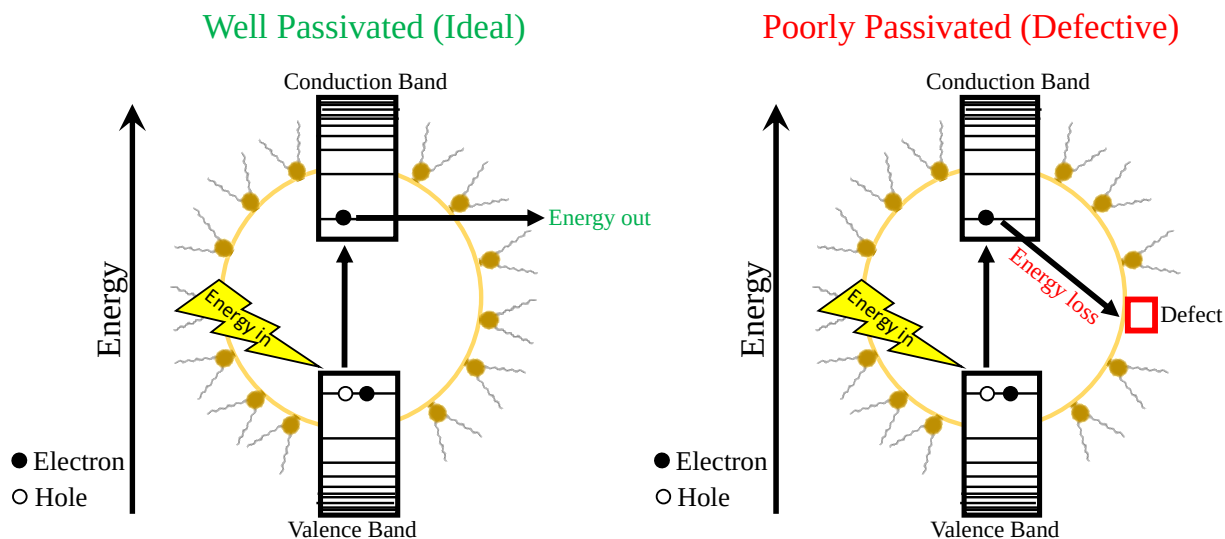
One of the most recognizable uses of colloidal NCs to the public is their use in light-emitting devices (LED).⁸ Also known as QD LEDs, these NCs have high color purity due to their highly narrow emission bands and have extremely high stability. A blue back LED panel is used to excite QD for green and red pixels. These NCs can be used for applications where a specific wavelength is needed because of their size tunability. Typically, II-VI NCs are used for QD LEDs such as CdSe, covering the visible spectrum (380 to 750 nm). Another application of NCs is in photovoltaic devices due to their photovoltaic properties. The most common use of NC-based photovoltaic devices involves the use of quantum dot-sensitized solar cells.^{2-5,31} NCs have been used in dye-sensitized solar cells (DSSCs), type II bulk heterojunctions, and Schottky diodes which

all rely on efficient charge separation.^{3-5,32,33} The primary efficiency loss mechanism of NC photovoltaics is through non-radiative recombination at the material interface.^{34,35} In NC-based QD DSSCs, electrons are injected into the wide-bandgap metal oxide electrode from the excited NC. Typically, cadmium chalcogenide NCs have been the most extensively studied, and effort has been focused on the development of the surface to best minimize electron recombination at the surface of the NC.^{34,36-38}

In all the applications mentioned above, the modification of the NC ligand shell surface is required. The need to understand the nature of the ligands at the surface is essential when controlling NC properties. The work presented in this thesis is an attempt to understand the complicated ligand surface relationship of NCs.

1.2 Nanocrystal Surfaces

The surface of NCs plays a vital role in their properties due to the high surface-to-volume ratio. Since most of the applications mentioned previously require the extraction of work from photoexcited NCs, an understanding of how to control the energetics and recombination pathways in NCs is necessary. In bulk semiconductors, non-radiative processes often occur at localized lattice defects,^{39,40} but for NCs non-radiative relaxation processes typically originate on the crystal's surface where low-lying electronic states are present.^{18,19,39-43} These low-lying electronic states can dramatically alter the electronic properties associated with the NC. To eliminate these undesirable low-lying electronic states, the origin and energetics of surface defects need to be understood.

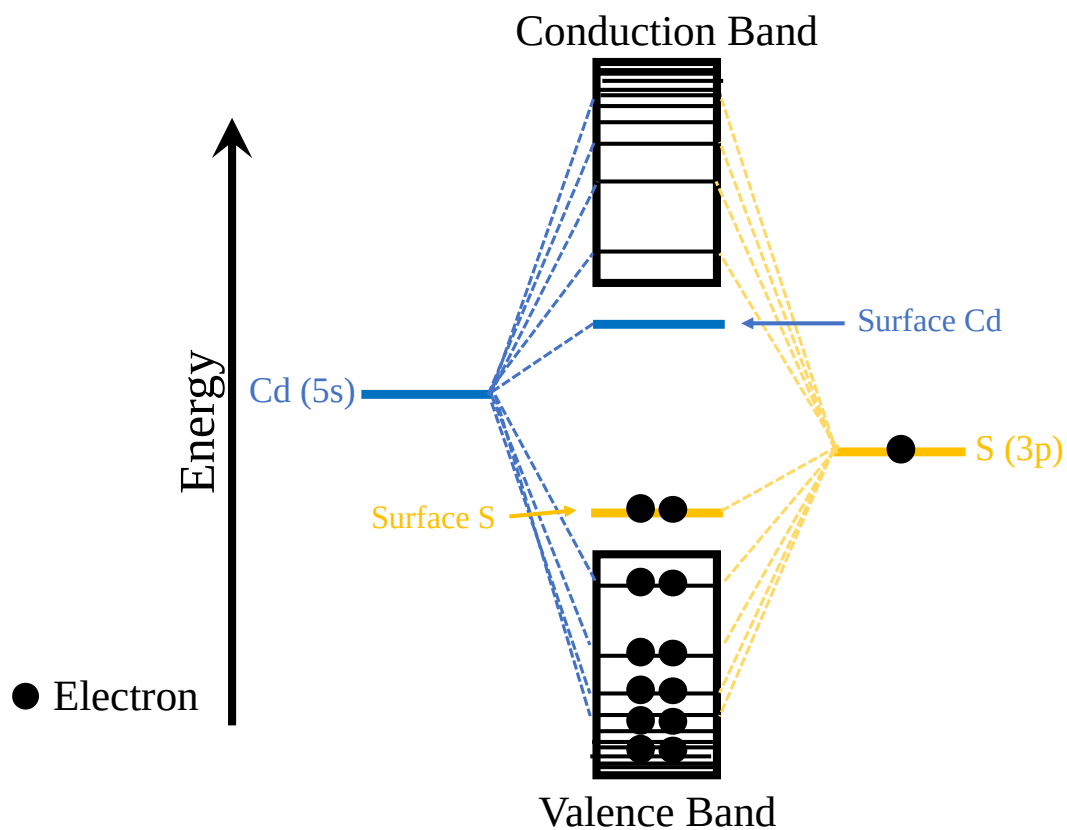


Scheme 1.1 Well passivated NC vs. a poorly passivated NC. Surface defects cause energy loss in the NC because of the defect acting as a charge carrier trap.

The NC surface is composed of two different parts: the inorganic crystal lattice and the ligand shell. The inorganic lattice is affected by the material crystal structure, exposed facets, and the NC morphology that result from energy minimization of the surface during synthesis.⁴⁴ Depending on the synthetic conditions, different morphologies can be achieved. For example, when carboxylate ligands are used during CdSe synthesis, a zinc blende structure is obtained, but when phosphonate ligands are used the material forms in the wurtzite crystal structure.⁴⁵ The material crystal structure, facets, and morphology are essential characteristics that directly define and impact the surface's coordination environment. The ligand shell composes the other half of the NC surface and can also affect its structure and reactivity. Ligand-based properties such as binding properties and charges of the ligands can be controlled to help understand their impact on the surface photophysics. To fully define the NC surface, two different factors thus need to be considered: the dynamic equilibria between the NC surface and solvated species and the heterogeneity across the surface, both of which will be discussed in this thesis.

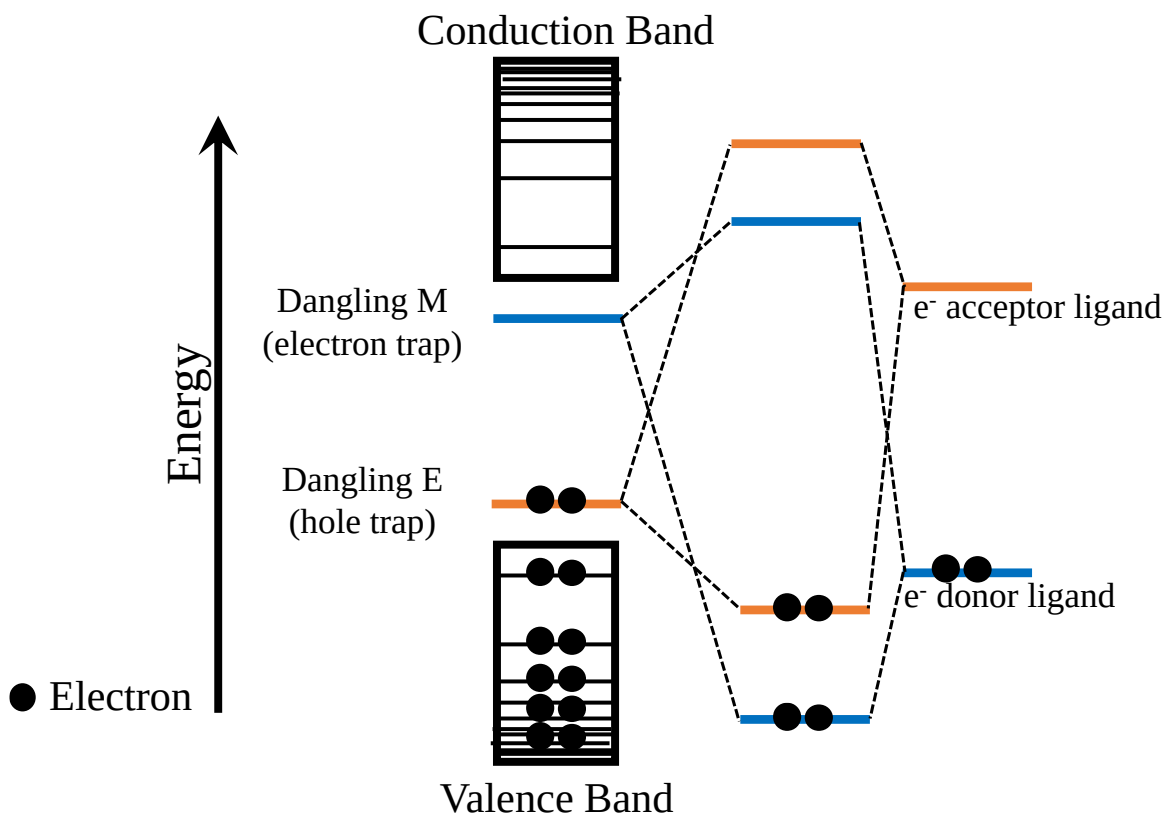
1.3 Molecular Orbital Theory and Surface States

As stated previously, semiconductor NCs combine properties of both bulk materials and molecules. More specifically, NCs combine the crystalline structure of bulk semiconductors on a molecular scale. Because NCs have a large surface-to-volume ratio, a larger proportion of the atoms reside on the surface rather than within the NC, and since electronic carriers are delocalized across the whole NC, the energetics of the surface need to be studied. The atoms on the surface have different energy levels than the atoms residing within the NC. The PLQY of cadmium chalcogenide NCs can be altered depending on the synthesis method and through the addition of ligands during the synthesis.^{18,42,46–53} Though the NC structure is complex, molecular orbital (MO) theory can provide a simplified model of the valence band and conduction band of NCs. Since this thesis focuses on CdS NCs, this will be our example to discuss surface defects. Sulfur atoms are more electronegative than cadmium and lie lower in energy in the MO diagram, and the valence orbitals of sulfur will dominate the valence band. Due to the NC's surface, the atoms at the surface are often under-coordinated, which leads to mid-gap energy states, as depicted by the energy diagram in Scheme 1.2. These open sites that are under-coordinated are otherwise known as “dangling bonds”. Filled sulfur orbitals, higher in energy than the valence band, act as hole traps, and empty cadmium orbitals, lower in energy than the conduction band, act as electron traps.



Scheme 1.2 Molecular orbital diagram of metal chalcogenide NCs surface without any surface passivation.

To passivate these dangling bonds, the surface needs to be adequately terminated by ligating species. These species move the surface electronic states far from the lowest delocalized excited-state energy (as shown in Scheme 1.3) and improves the PLQY.^{14,40,43,54–56}



Scheme 1.3 Molecular orbital diagram of metal chalcogenide NCs surface with surface passivation.

However, the ability to control the NC surface's behavior is often limited by the fact that their structure is highly complex, with characteristics varying from NC to NC in the same ensemble and from facet to facet. Surface ligands are also reactive and can exhibit complicated dynamics across the surface, and part of this thesis aims to model the behavior of such surface ligands.^{42,57–62}

1.4 Modeling the NC Surface: CBM vs. CBC Model

Throughout the history of colloidal NCs, models of the surface have evolved, and as the understanding of the NC surface expanded, many different ligands have been investigated.^{63–65} The earliest NC surface chemistry models were purely based on how the NCs were synthesized, with trialkylphosphines being one of the first capping ligands used.⁶⁶ As our understanding of how ligands affect the electronic properties of NCs, it was determined that carboxylic acids are better

than trioctylphosphine ligands.⁶⁷ The importance of ligands lies in the fact that they ensure charge neutrality of metal-rich NCs.^{49,68} Two prevalent models are employed to help with the characterization of the surface non-stoichiometric NCs: the charge-orbital balance model (CBM) and the covalent bond classification (CBC).

1.4.1 Charge-Orbital Balance Model (CBM)

The CBM accounts for any extra ions at the non-stoichiometric NC surface regardless of whether they are metal or non-metal. The following formula can be used to help describe the charge balancing within the system:

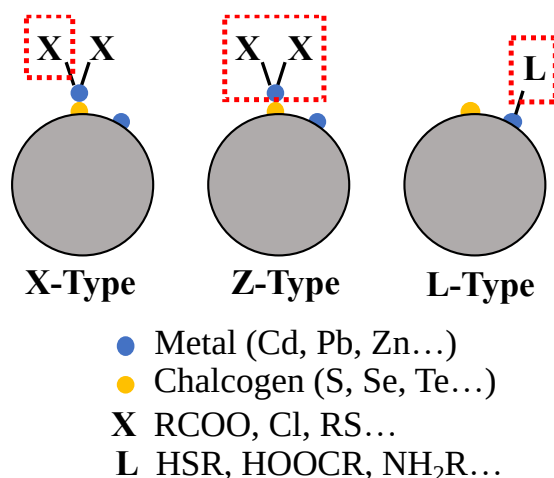
$$N_{exc} = \sum_i N_i q_i \quad \text{eq. 1.1}$$

N_{exc} represents the number of excess electrons in the system, N_i is the number of ligands or atoms of the NCs, and q_i is their oxidation states (assuming atoms and ligands are in their thermodynamically most favorable oxidation states).⁶⁹ If applied to the system studied in this thesis, CdS, Cd and S oxidation states would be +2 and -2, respectively. For any anionic ligands, the oxidation state would typically be -1, and for any non-ionic ligands the oxidation state would be 0. A Cd-rich NC with N extra Cd atoms would then require $2N$ anionic extra species (i.e. carboxylate or halides) to ensure charge neutrality. This model can be applied to doped NC systems as well; however, this will not be addressed here since the NC used in this thesis were not doped.

1.4.2 Covalent Bond Classification Model (CBC)

The CBC model was initially proposed for organometallic compounds but has been adapted to the surface of NCs.⁷⁰ The inorganic core and ligand shell described as neutral entities, with the core of the NC consisting of an equal number of ions of each polarity ($\text{Cd}^{2+} = \text{S}^{2-}$). Ligands are classified by how many electrons they donate: X-type ligands are one-electron donors in their neutral form, L-type ligands are two-electron donors (often phosphines, amines, or thiols), and Z-type ligands

are two-electron acceptors (CdX_2 , ZnX_2 , etc.). There is a covalent bond between the ligands and surface atoms, and the electrons within that bond are shared equally between the ligand and surface atoms.



Scheme 1.4 Covalent Bond Classification model for ligands used in surface passivation of metal chalcogenide nanocrystals.

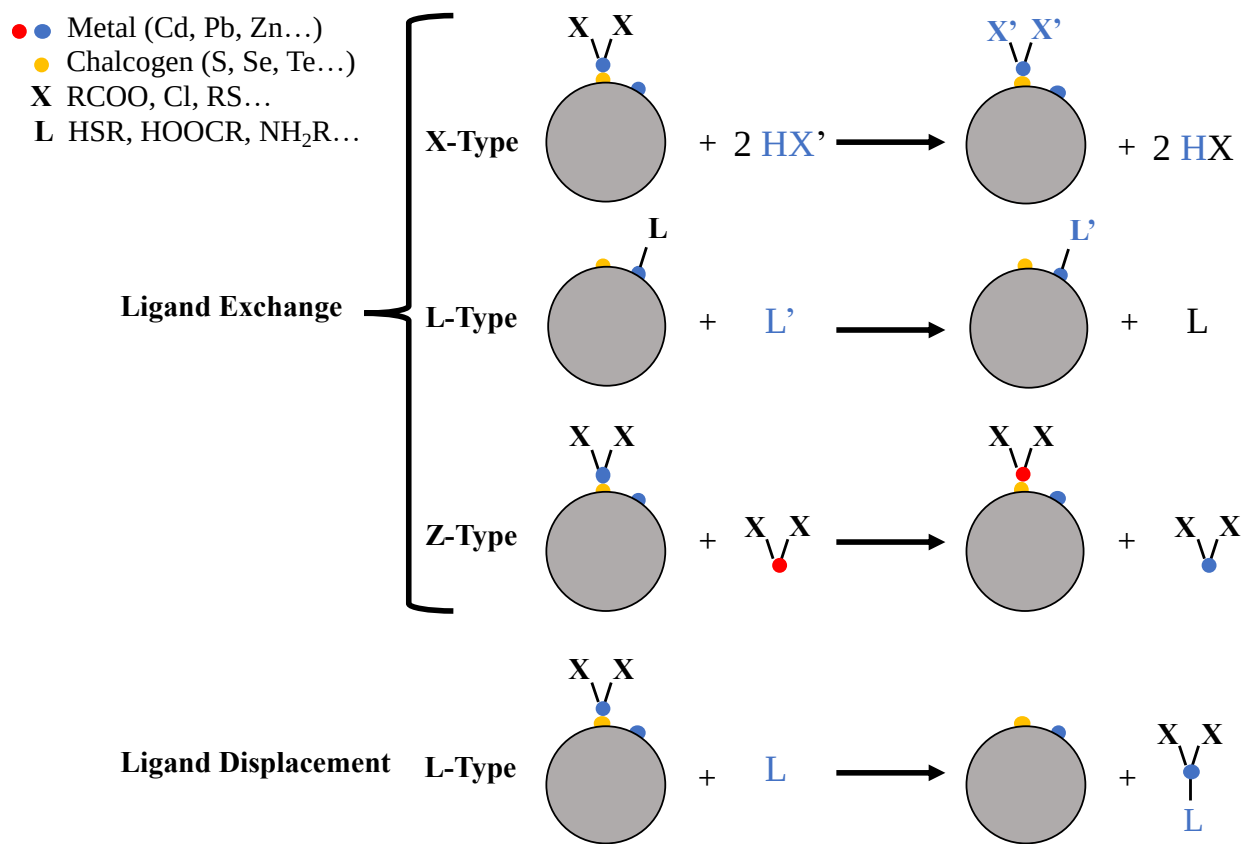
For our example of Cd-rich CdS NCs, we assume a neutral core of CdS (Cd atoms = S atoms) and CdX_2 complexes act as Z-type ligands on the surface. The sulfur atoms share their electron to the Z-type ligand removing most surface traps. Sulfur serves as a Lewis base, and the Z-type ligand acts as a Lewis acid.

1.5 Ligand Exchange on the NC Surface

1.5.1 Generic Ligand Exchange Motifs

For NCs to have a wide span of applications, ligands need to be exchangeable depending on the desired application. Typically, during synthesis, long-chain ligands are used to ensure good size distribution and reduce NC aggregation, but these are not the most useful for all kinds of NC applications and need to be exchanged for more suitable ligands. Furthermore, the ligand exchange

process can reduce surface states and improve surface passivation. There are three different types of ligand exchanges shown in Scheme 1.5.

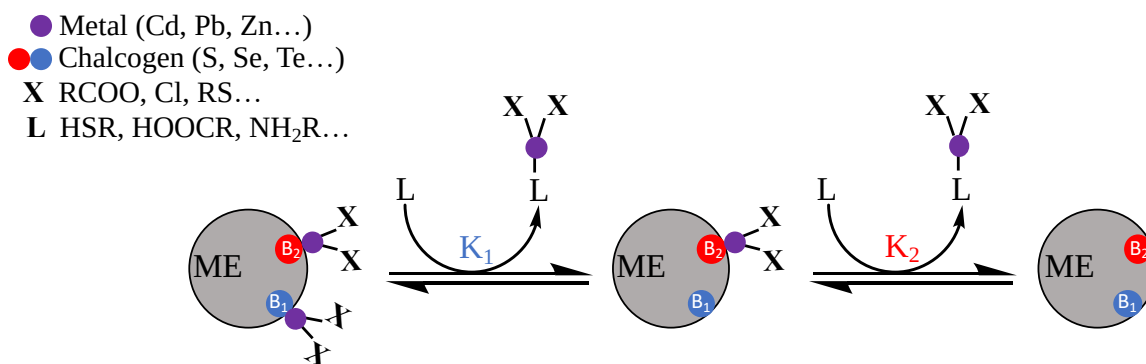


Scheme 1.5 Different types of ligand exchange and displacement at the NC surface.

These ligand exchange processes come with their own set of complications and the possibility of an undesired pathway for ligand exchange. X-type ligand exchange has been extensively studied for various materials and is accompanied by other ligand exchange processes.^{46,71–74} In all these processes, it is possible that the ligand is displaced entirely from the surface, creating a surface defect. Amines are known to create these defects through etching.⁷⁵ Furthermore, the removal of Z-type ligands from the surface leads to the creation of deep surface traps known for quenching photoluminescence. Because of this, many studies have been done on this type of ligand displacement.^{18,42,60,62,76–78}

1.5.2 Z-type Displacement on Metal Chalcogenide NCs

Z-type ligand displacement has been a significant focus in the field since Anderson et al. showed that Z-type displacement could be promoted by using Lewis bases (L-type ligands), and that the result of this displacement is the creation of surface defects.⁷⁹ This displacement is a direct cause of equilibrium shifting through the addition of the L-type ligand to promote an L-Z complex formation. The surface defects created from this displacement have been correlated to a decrease in PLQY and identified as hole traps. To better understand the vacant sites created after Z-type displacement, Beaulac⁶² and Hens⁷⁸ used L-type displacement to probe the surface of CdSe NCs chemically. In these experiments, the NC surface was perturbed by adding various L-type reagents, such as *N, N, N', N'*-tetramethane-1,2-diamine (TMEDA), benzylamine, and *n*-butylamine. During these titrations, the concentrations of free and bound ligands were monitored using ¹H NMR spectroscopy. From ¹H NMR analysis, a two-site displacement isotherm was proposed to describe the NC surface equilibrium, as shown by Scheme 1.6.



Scheme 1.6 L-Type promoted Z-type displacement from the NC surface.

Z-type ligands bind to two different sites on the NC surface, B₁ and B₂, and each site has its equilibrium constants, K₁ and K₂. Each site also has its quenching efficiency, and both sites contribute to binding heterogeneity across the NC surface. Similar work has been carried out in

PbS NC by various groups.^{77,80–82} The Dempsey group has recently discovered that TMEDA-promoted Pb(oleate)₂ also follows a two-site binding isotherm but shows significant differences in binding sites with size.⁷⁷ Through this study, they were able to show that Z-type ligands at vertex sites are more labile than those at edge sites. Though the surface of CdSe and PbS has been studied extensively, not much has been studied on CdS in terms of the experiments described above.

1.5.3 CdS NCs

This thesis focuses on studying the surface and impacts of surface defects on CdS NCs. Systems with different atoms have different photophysical properties.^{16,40,83,84} For example, bulk CdSe SCs have a band gap that is smaller than that of bulk CdS NCs, 1.74 eV and 2.46 eV respectively, and this band gap difference is still true when they are in the confined region.⁸⁵ For a given size, CdS NCs will have a larger band gap than CdSe NCs and will differ in their positioning of the valence and conduction bands. CdS NCs have been studied extensively for photo-emissive applications, however, not much has been studied on the impact of the surface on photophysical properties.^{86–89} We chose to focus on CdS NCs in this thesis for two major reasons: 1) to see if the conclusions previously reached for CdSe NCs^{62,78} can be applied to other II-IV SC NCs and 2) to better understand the impact of surface defects on the photophysics of trap states within the NC ensemble. CdS NCs are unique in the fact that their trap states lead to radiative recombination since CdS NCs have a large band gap with trap states that fall in the visible region. Both excitonic and trap emission can be monitored to correlate changes in the surface to changes in the photophysical properties of the NC. Other studies have focused on characterization of trap PL states, however most studies ignore the role of ligands on the surface.^{35,43,86,88,90–95} Through disturbing the surface as described earlier, a more complete picture of the impact of surface defects on photophysical properties can be created.

1.6 NC Characterization

1.6.1 Characterization of Optical Properties

To typically characterize NCs, transmission electronic spectroscopy (TEM), inductively coupled plasma analysis (ICP), and ultraviolet visible spectroscopy (UV-Vis) techniques are employed. Brus was the first to propose a method to calculate the size of NCs based on the effective mass approximation model.²² More recently, empirical models have been developed to calculate the size of chalcogenide NCs from optical data if the NCs absorption wavelength at the lowest excitonic peak is known.^{13,96} It is also now possible to determine the concentration of NCs from the absorption spectrum of the NCs.⁹⁶ The methods mentioned here rely on models created from TEM, ICP, and UV-Vis data and will be utilized throughout this work.

1.6.2 Characterization of the NC Surface

The NC surface's characterization can be organized into different categories based on what part of the surface they probe: capping-ligands, the interface between ligand and lattice, or the surface's electronic structure. There are many techniques to help investigate each component mentioned above, and a select few will be discussed in this section.

To probe the capping-ligands, ¹H NMR techniques are often used to help quantitatively describe the surface of the NC.^{97,98} Furthermore, the use of ¹H NMR techniques can distinguish between bound and free ligands within the NC sample. Ligands bound to the NC surface have broad linewidths, whereas free ligands have sharp and distinct linewidth (since free ligands have faster-tumbling rates than bound ligands).^{97,99–103} Also, chemical shifts of bound ligand are generally shifted downfield due to electrons being deshielded from the NC core. With the addition of an internal standard, the concentrations of bound and free ligands can be determined quantitatively, which allows for binding isotherms to be calculated.^{46,62,76–78} To further investigate the capping-ligands,

thermogravimetric analysis and calorimetry can be used to determine the ligands' binding strengths.^{104–106} ^1H NMR is also beneficial because it is a non-destructive technique to help identify the capping-ligands.

Tools commonly used to probe the inorganic/organic interface typically include photoelectronic techniques, vibrational spectroscopies, TEM, ICP, and computational methods. Infrared (IR) and Raman spectroscopies are also effective modeling ligand binding on the NC surface.¹⁰⁷ IR methods are easy to use and are most helpful when combined with other techniques such as X-ray techniques. X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS) are used to determine the stoichiometry, oxidation states, and the NC's crystalline structure. However, these measurements are mainly qualitative and cannot identify the number of ligands on the surface. Without this quantitative analysis, the binding behaviors of ligands cannot be accurately determined. High-resolution TEM imaging has been used to gain insight into the attachment between fused wurtzite CdSe NC lattices.¹⁰⁸

DFT calculations, X-ray methods, and optical spectroscopies such as UV-Vis and photoluminescence (PL) spectroscopy can be used to elucidate more about surface-based electronic states. DFT calculations can predict the formation of electronic states based on surface chemistry without any influence from the surrounding media. This method becomes even more powerful when paired with experimental results. XPS, X-ray emission spectroscopy (XES), and X-ray absorption near edge structure (XANES) can provide sensitive measurements on the oxidation states of surface atoms, which provides more information on the nature of the formation of mid-gap states.^{109,110} UV-Vis spectroscopy is employed to study the impact of surface states on the exciton through changes in absorption (such as red or blue shifts, gains or losses in absorption, or appearance of new features) and is used to characterize NCs after ligand exchange, surface

charging, surface oxidation, and other chemical alterations.^{111–116} PL spectroscopy is a fundamental tool used to analyze surface defects through steady-state PL, time-resolved PL, and PL quantum yields. Any changes in these spectra (PLQY loss, shortening of emission lifetime, loss of steady-state PL) indicates the formation of defect states that creates trap states. If the surface states created are emissive, PL spectroscopy can provide additional information on them.^{117–119} The combination of ^1H NMR, UV-Vis, and PL spectroscopy will be used throughout the work presented here to help elucidate the characteristics and effects of surface defects on CdS NCs.

1.7 Thesis Structure

The complexity of CdS surface chemistry and its effect on the optical properties of the NC is studied within this thesis. In Chapter 2, the equilibria of ligand displacement and the creation of surface defects on the surface of CdS are discussed by analyzing NMR spectra. Chapter 3 explores the impact of surface sites on light absorption. Chapter 4 correlates the creation of surface defects to changes in steady-state light emission. Chapter 5 investigates the multi-exponential excited-state dynamics of CdS after creating surface defects.

Through these studies, we demonstrate the existence of two distinct binding sites, each with its own binding affinity for CdX_2 and each site is under dynamic equilibrium with the surface. We find that the creation of one type of binding site on the surface greatly impacts the NC photophysical properties. To tailor NCs to specific applications this surface defects needs to be properly controlled.

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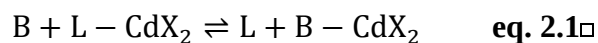
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Chapter 2: Insight into the Complexity of the CdS NC Surface: Stability of Z-Type Ligands

2.1 Introduction

As discussed earlier, the presence of surface defects causes energy losses, and to effectively prevent these energy losses the NC surface needs to be characterized. These undesired energetic losses can be mitigated by precise control of the surface of these nanocrystals.^{1,2} However, the surface of NCs is challenging to control because of the complexity of the surface, which can vary from NC to NC, and facet to facet.³⁻⁶ Furthermore, the system is further complicated because surface ligands are highly labile and can move between different surface sites.

In the studies presented here, we focused on continuing the previous research on zinc-blende CdSe NCs to a new system, zinc-blende CdS NCs.^{7,8} These NCs have a nonstoichiometric cadmium-rich composition coming from the presence of neutral cadmium carboxylate (CdX_2) complexes on the surface. To better describe the surfaces of NCs, a model based on CdSe from Owen and collaborators has been employed.⁹⁻¹¹ In this model, CdX_2 complexes on the surface are considered Lewis acid acceptors (Z-type ligands in CBC) that bind to unpassivated selenium, surface sites, passivating the surface of the NCs.^{9,12} These surface-bound complexes can be displaced by an acid/base exchange reaction:



where B is a generic Lewis-basic site on the surface of CdSe and L is a soluble Lewis base (L-type ligand in CBC). Displacement of CdX_2 from the surface lowers the PLQY of CdSe NCs due to new surface sites that enhance non-radiative relaxation through hole-trapping process.^{10,11} Previously, using the general Z-type ligand exchange process in eq 2.1 and ^1H NMR studies, it was demonstrated that two different sites are present on the surface of CdSe modeled best through a two-site displacement isotherm, and each site has its impact on the PLQY of CdSe NCs. These two sites have different binding affinities to CdSe as well as different excitation relaxation

mechanisms.^{7,8,13} Most recently, Dempsey and co-workers have also applied a Z-type ligand exchange process and quantitative ^1H NMR to study the surface of PbS nanocrystals and found that there are multiple distinct surface sites with different reactivities.¹⁴ In terms of CdS NCs, a majority of studies have primarily been interested in studying trap PL states and their characterization using low-temperature PLQY and lifetime measurements.^{15–19}

Quantitative ^1H NMR has not been readily employed, but rather the surface of CdS NCs has been investigated through monitoring changes in trap state emission. The Kambhampati group has modeled the surface of CdS NC using a semi-classical electron transfer approach and considered surface defects as a fundamental electronic state, ignoring the role of surface ligands.^{20–23}

We aimed to study the effects of surface ligands on zinc-blende CdS NCs through Z-type ligand displacement to determine the type of surface sites present on these NCs. CdS NCs, much like the previously studied CdSe NCs, are obtained from carboxylate precursors and have a cadmium-rich composition arising from CdX_2 complexes on the surface. Our results show that two distinct binding sites occur on the surface, and each has its own intrinsic thermodynamic stability.

2.2 Experimental Details

2.2.1 Chemicals

Cadmium nitrate tetrahydrate ($\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, 98%), oleic acid (90%), octadecene (ODE 90%), *N, N, N', N'*-tetramethylethylenediamine (TMEDA, 99%), myristic acid (>99%), and ferrocene (Fc, 98%) were purchased from Sigma-Aldrich. Ethyl acetate (HPLC grade), toluene (ACS grade), sodium hydroxide (>98%), and anhydrous methanol (HPLC grade) were from Macron Fine Chemicals. Sulfur powder (99%) was purchased from Spectrum Chemicals. d-Toluene was purchased from Cambridge Isotope Laboratories (CIL). Ethyl Acetate was degassed by bubbling nitrogen for 2 hours and dried over molecular sieves for two days. Oleic acid was degassed using

three cycles of vacuum/purge with nitrogen. Ferrocene was recrystallized from methanol solutions. Toluene was dried using alumina stills. TMEDA was stored in the glove box and taken out to prepare samples. All other chemicals were used as received.

2.2.2 Synthesis of Cadmium Myristate

Cadmium myristate was synthesized by adapting a literature protocol.²⁴ In a typical synthesis, 15 mmol of cadmium nitrate tetrahydrate was weighed and transferred to a 500 mL beaker with 150 mL of anhydrous methanol. The solution was sonicated until all the solids were dissolved. In a 2 L round-bottom flask, 30 mmol of NaOH and 30 mmol of myristic acid were added to 1.5 L of anhydrous methanol. The mixture of NaOH and myristic acid was heated to 40°C for 5 minutes and then sonicated until a single-phase sodium myristate solution was formed. This solution was transferred to a 2 L round-bottom flask and stirred. While the solution was stirring, the cadmium nitrate solution was added dropwise to the sodium myristate over 3 hours. After all the cadmium nitrate was added, the solution was stirred for 24 hours under ambient conditions. The product was filtered and washed five times with anhydrous methanol and air-dried for 24 hours. The dried product was crushed and transferred to a 250 mL round bottom flask, sealed, and vacuumed dried for 24 hours.

2.2.3 Synthesis and Purification of CdS NCs

Cadmium sulfide was prepared by adapting a literature protocol.²⁵ 10 mmol of cadmium myristate and 5 mmol sulfur powder were placed in a 3-neck round-bottom 1 L flask with 630 mL of octadecene. The flask was degassed with 3 (20 minutes) cycles of vacuum/purge with nitrogen. The flask was then heated to 240 °C over 7 minutes and the heat was maintained until the NC size was about 3.4 nm, which was checked by taking an aliquot of the suspension and checking its absorption profile. To get the desired size, the excitonic absorption peak was tracked through the

synthesis. Around 1 mL of the synthesis mixture was removed from the suspension and diluted with 1 mL toluene and placed into a cuvette. The absorption profile was taken of the sample and the excitonic absorption peak was identified. The peak energy and width were found, and the size of the nanocrystal was found from a method from Peng and co-workers (an application developed for the Apple iPhone was used called “QD Calc”).²⁶ Once the excitonic peak was positioned around 400 nm and the desired size was obtained, the heat was removed and 96 mmol of degassed oleic acid was injected over 20 minutes while the flask content reached room temperature and the suspension was stirred over nitrogen for 15 hours. Octadecene was removed through vacuum distillation (50 mTorr) at 130 °C until 20 mL was left. Once most of the solvent was removed, 20 mL of dry toluene was added. The toluene suspension was divided into four different test tubes and centrifuged for 20 minutes at 6000 rpm. The supernatant was then transferred in 1 mL portions into new test tubes, and 10 mL of ethyl acetate was added to precipitate the NCs from the suspension. The test tubes were then centrifuged for 10 minutes at 6000 rpm, and the supernatant was removed. The solid NC at the bottom was resuspended in toluene and sonicated for 10 minutes. This cleaning process was repeated five times to remove all unbound ligands. After the last cleaning, the solid NC at the bottom of the test tube was dried over nitrogen for 24 hours and then suspended in dry d-toluene to make an 85 μ M solution, as determined from by UV-vis spectroscopy following the empirical calibration curve established by Peng et al.²⁶

2.2.4 Optical Spectroscopy

Absorption spectra were collected on a Shimadzu UV-2600 UV-Vis spectrophotometer in 1 nm increments, using a 1 cm path length quartz cuvette with a toluene background subtraction. Continuous-wave (CW) photoluminescence (PL) measurements were performed using a 0.55 m focal length spectrometer (iHR550, f/6.4, 150 grooves/nm 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/nm grating blazed at 500 nm). PLQY were measured with a PL quantum yield spectrometer (Hamamatsu Quantasaurus, C11347), using toluene suspensions prepared as described below and exciting at 375 nm.

2.2.5 Transmission Electron Microscopy

TEM images were recorded on a JEOL 2200 FFS microscope operating at 200 keV. Formvar-coated copper grids (Ted Pella) were used as NC supports for TEM. Suspensions of CdS NCs in toluene were drop-casted on the TEM grid, and images were analyzed using ImageJ.

2.2.6 Sample Preparation for ^1H NMR and PL Spectroscopies

Solutions of TMEDA in d-toluene were prepared with a range of concentrations from 0.01 to 6.7 M (neat TMEDA). Mixtures of CdS NCs and TMEDA were prepared in d-toluene. Each solution contained 600 μL of 77 μM CdS NCs ($[\text{CdS}]=70 \mu\text{M}$), 30 μL of TMEDA sample, and 30 μL of 4.2 mM ferrocene solution ($[\text{Fc}]=0.19 \text{ mM}$). After initial mixing, each sample was given 30 minutes to reach equilibrium. ^1H NMR spectra were collected on an Agilent DDR2 500 MHz NMR spectrometer equipped with 7600AS 96 sample autosampler running VnmrJ 3.2A, using a 45° pulse angle/ 10 s relaxation time sequence and 32 scans. Spectra were analyzed using MestreNova (Mestrelab Research SL) and Igor Pro 7.05 (Wavemetrics). To prepare for PL measurements, 30 μL of each NMR sample was taken and diluted with 2 mL of toluene.

2.2.7 Ligand Concentration and Surface Coverage Calculations

To determine the surface coverage of CdX_2 on the surface of CdS NCs, the terminal methyl ($-\text{CH}_3$) peak at 1 ppm was integrated and referenced to the integration of the ferrocene protons at 4 ppm. CdX_2 complexes are either cadmium myristate or cadmium oleate in this study. The concentration

determined was for the total carboxylates present in the system. However, due to charge compensation, the actual concentration of CdX_2 is half of what was determined. The ligand coverage was then calculated by taking the concentration of CdX_2 and dividing it by the concentration of NCs and the surface area of the NCs. Further details are given in the SI 2.1.

2.3 CdX_2 Displacement from CdS NCs

The absorption and PL spectra of a clean suspension of CdS NCs before the addition of TMEDA are shown in Figure 2.1

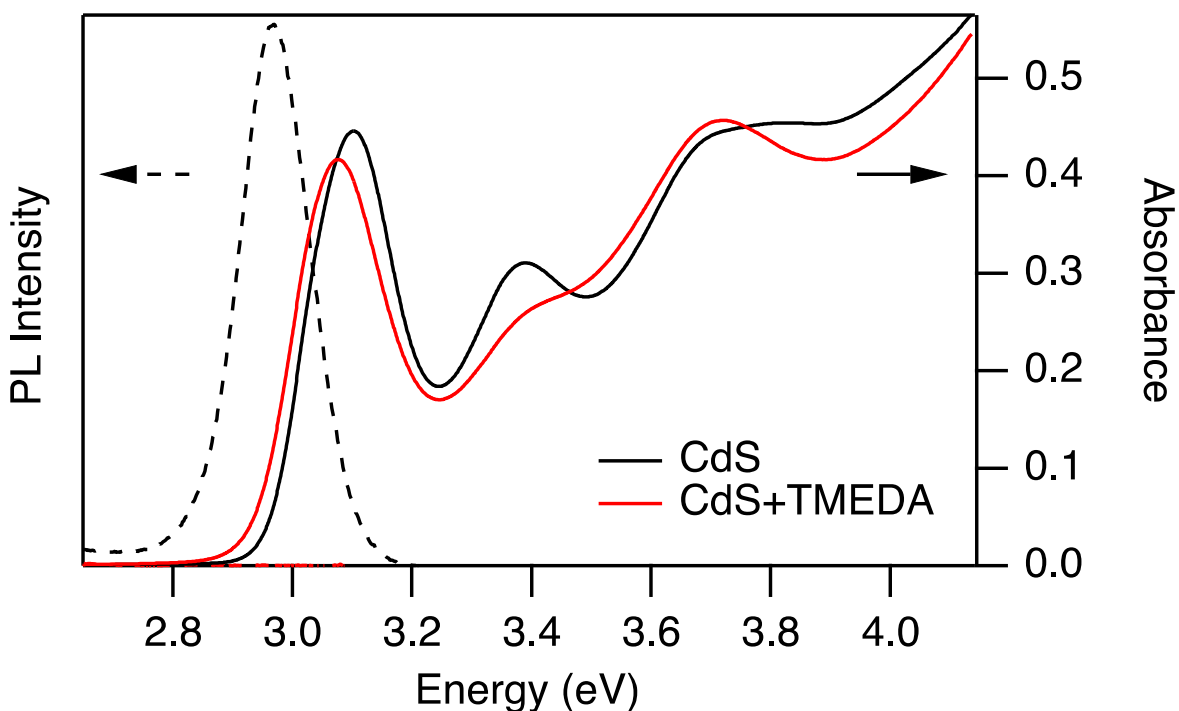


Figure 2.1 Absorption (solid) and photoluminescence (dashed) of 3.4 nm CdS NC ($1.0 \mu\text{M}$) before (black) and after (red) addition of TMEDA (303.6 mM).

Upon adding 4500 equivalents of TMEDA per NC, the PLQY of the exciton is practically quenched. There are two notable changes in the absorption of CdS: (1) a red shift of the lowest excitonic absorption peak and (2) a blue shift of the 2nd absorption peak. This change both in PLQY and absorption is seemingly linked to the displacement of CdX_2 groups from the surface of CdS

quantified by ^1H NMR. Figure 2.2(a) shows the ^1H NMR spectra during the gradual addition of TMEDA to a suspension of CdS NCs in d-toluene. The ^1H NMR spectra give detailed information about ligands bound to the NC surface and ligands freely diffusing in solution. Integrating the terminal methyl ($-\text{CH}_3$) groups at one ppm with respect to a ferrocene reference gives a surface coverage of approximately $2.9 \pm 0.2 \text{ nm}^{-2}$ (see SI 2.2 for calculations details).

Looking closely at the ^1H NMR spectra in Figure 2.2, before any TMEDA has been added, all carboxylate species are bound to the NC's surface (as indicated by the 1.0 ppm broadened resonances in Figure 2.2(b)).

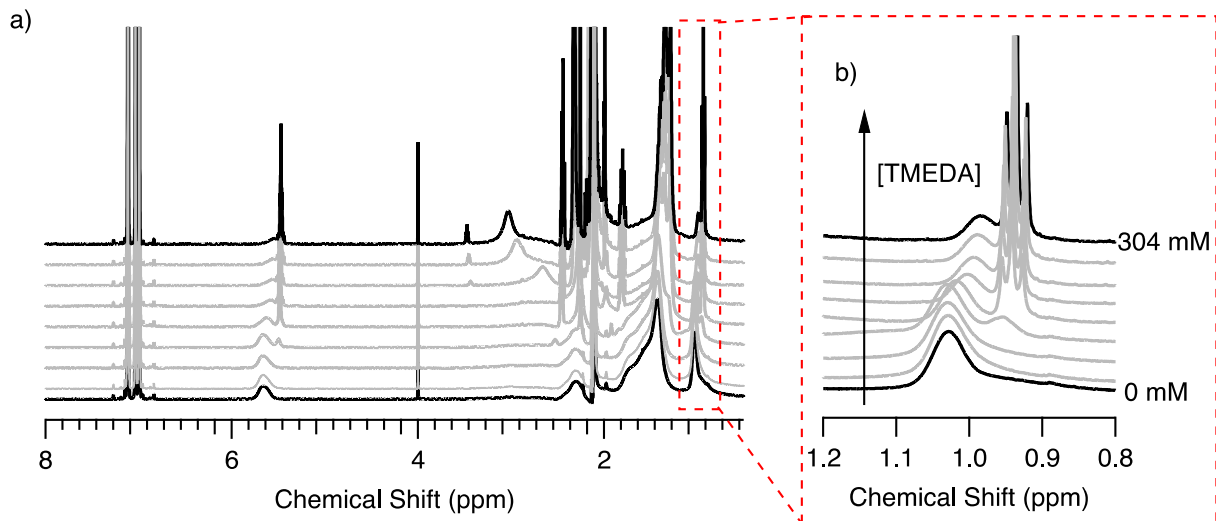


Figure 2.2 (a) ^1H NMR spectra of 3.4 nm CdS NCs ($67 \mu\text{M}$) with various amounts of TMEDA added. (b) HNMR showing the difference between bound (0.97 ppm) and free (1.0 ppm) cadmium carboxylates.

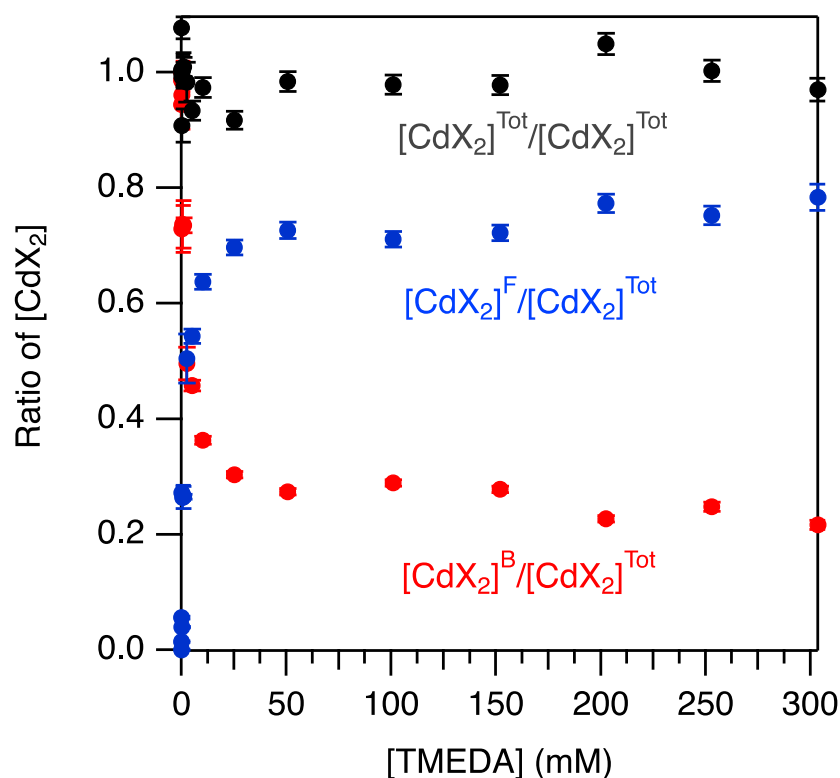
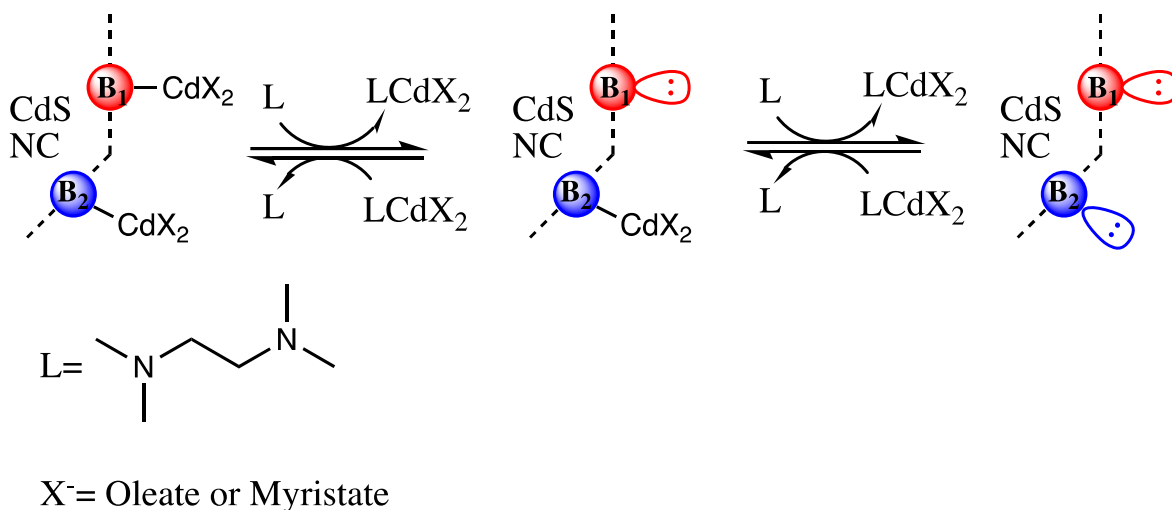


Figure 2.3 Ratio of the total (gray), free (blue), and bound (red) CdX_2 groups as a function of added TMEDA.

As more TMEDA is added, the decrease in the integrated broad resonance at 1.05 ppm is matched by the increased integrated area of the sharp band at 0.9 ppm, as shown in Figure 2.2(b). This sharp feature at around 1 ppm is associated with carboxylate species unbound from the CdS surface (and are labeled as “free”).^{7,8,14,27–29} The nature of this displacement has been discussed previously.^{7–9,14} This change indicates an L-type displacement of CdX_2 through complexing with TMEDA (a soluble Lewis base, TMEDA in this case). The CdX_2 complex behaves as a Lewis acid (Z-type ligand) and is in a dynamic exchange between the NC surface and TMEDA. As previously seen, the behavior of this displacement cannot be described using a single-site binding model but requires the existence of two different sites, each with their own free energy of binding.^{7,8,14}

Initial displacement of CdX_2 happens with only 5 mM of TMEDA added, but the addition of 300 mM TMEDA has almost no impact on overall displacement, as shown in Figure 2.3. This behavior can be described effectively through a two-site binding model, as shown in Scheme 2.1. Much like what has been seen with CdSe ,^{7,8} there are two distinct binding sites, each with its associated free energy of binding and role in the photophysics of CdS .



Scheme 2.1 Two-site binding model showing surface exchange equilibria between the two sites, B_1 and B_2 , respectively.

2.4 Analysis of the Ligand-Exchange Equilibrium

To start analyzing the equilibrium above, we simplify our system to a single binding site as given by eq. 2.1. In this scenario, there is a single Lewis acidic surface-site (B) that is either occupied by a CdX_2 complex or vacant and is in dynamic exchange with a free Lewis base (L). The equilibrium constant for this process is given by:

$$K_{eq} = \frac{[\text{B}-\text{CdX}_2][\text{L}]}{[\text{B}][\text{L}-\text{CdX}_2]} = \frac{[\text{B}-\text{CdX}_2]}{[\text{B}]} \phi \quad \text{eq. 2.2}$$

$$\phi = \frac{[\text{L}]}{[\text{L}-\text{CdX}_2]} = \frac{[\text{L}_0]}{[\text{L}-\text{CdX}_2]} - 1 \quad \text{eq. 2.3}$$

The process monitored through ^1H NMR as shown in Figure 2.2 is the reversal of the equilibrium reaction given by eq. 2.1. Instead of looking at this equilibrium process in terms of displacing

CdX₂ from the surface, we are describing the binding of the CdX₂ complex onto the surface. However, analyzing the equilibrium in this nature is simpler. Larger equilibrium constants mean it is harder to displace CdX₂ from the surface with TMEDA (stronger NC-CdX₂ bonds). In eq. 2.2, ϕ denotes the ratio of free (unbound) TMEDA vs. bound TMEDA and is obtainable from ¹H NMR analysis (Figure 2.2) by using the initial concentration of TMEDA ([L₀]) added into the system. To find the total number of binding sites per NC, N, the sum of the occupied ([B – CdX₂]) and vacant sites ([B]) are taken:

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

where [NC] is 67 μM as obtained through UV-Vis spectroscopy. Through combining eq. 2.2 and 2.4, an equation to describe the equilibrium process in terms of measurable quantities is given:

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

From eq. 2.5, a plot of $\frac{[NC]}{[B - CdX_2]}$ vs. ϕ , as given in Figure 2.4, should yield a line with a slope of $\frac{1}{N \cdot K_{eq}}$.

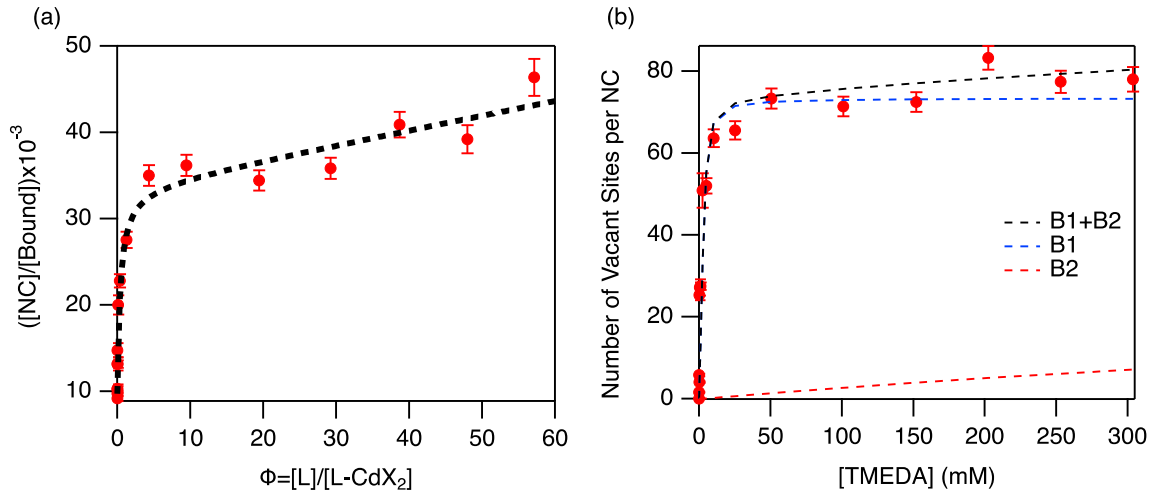
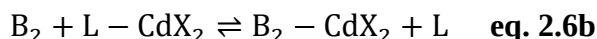
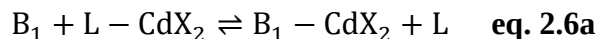


Figure 2.4. (a) TMEDA titration of 3.4 nm CdS NCs (67 μM in d-toluene), modeled with eq 2.10 (dashed black line). (b) The calculated number of B1 (dashed blue line), B2 (dashed red line), and total (dashed black line) vacant sites on the surface of the 3.4 nm CdS sample. The calculated number of sites is equivalent to the number of CdX₂ removed from the surface of CdS (shown in red circles).

As shown in Figure 2.4(a), the data is not linear which means there are two different regimes of displacement, and the assumption of a single binding site cannot fully explain the mechanism of CdX₂ displacement, so a two-site equilibrium is used. This same two-site model was used for previous surface studies done on CdSe and the same derivation will be used here.⁸ These exchange reactions can be defined using two types (B₁ and B₂) of open and occupied sites:



Using the formalism described in eq. 2.2, the equilibrium constants for each reaction are given by:

$$K_1 = \frac{[B_1 - CdX_2][L]}{[B_1][L - CdX_2]} = \frac{[B_1 - CdX_2]}{[B_1]} \phi \quad \text{eq. 2.7a}$$

$$K_2 = \frac{[B_2 - CdX_2][L]}{[B_2][L - CdX_2]} = \frac{[B_2 - CdX_2]}{[B_2]} \phi \quad \text{eq. 2.7b}$$

The ¹H NMR data does not allow us to distinguish between B₁ and B₂ sites but does give us information on the total concentration of TMEDA-bound CdX₂ (L-CdX₂) and surface-bound CdX₂ (B-CdX₂) species. The total concentration of bound CdX₂ is composed of the number of CdX₂ bound to site 1 and site 2:

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

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

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

The coupled exchange reactions can be described as shown in eq. 2.10, which follows the same form as eq. 2.5 above:

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

The data in Figure 2.4(a) was fitted using eq. 2.10, giving values for N₁, N₂, K₁, and K₂ shown in Table 2.1.

Table 2.1 3.4 nm CdS Surface-Related Data from TMEDA Titration experiments, $T=293.15$ K.

Trial	N₁	N₂	K₁	K₂	N_{tot}
1	73 ± 2	30 ± 5	0.1 ± 0.1	201 ± 100	103 ± 5
2	78 ± 3	35 ± 5	0.3 ± 0.1	330 ± 128	113 ± 6
3	51 ± 2	41 ± 5	0.1 ± 0.1	380 ± 100	92 ± 5
Average	67 ± 4	35 ± 5	0.2 ± 0.1	304 ± 191	102 ± 9

Trial	[NC] (μM)	[CdX₂] (mM)	Surface Coverage (CdX₂/nm²)
1	66 ± 2	6.7 ± 0.3	2.8 ± 0.3
2	70 ± 2	7.7 ± 0.3	3.0 ± 0.3
3	66 ± 2	7.0 ± 0.1	2.9 ± 0.3
Average	67 ± 3	7.1 ± 0.4	2.9 ± 0.3

With the equilibrium constants and number of distinct sites determined, individual analysis of each equilibrium process can be done. To deconvolute the individual equilibrium binding of the respective sites, the direct occupancy of each site is related to the ratio of the total TMEDA added:

$$\frac{B_i}{[NC]} = \frac{N_i \cdot \phi}{\phi + K_i}, i = 1, 2 \quad \text{eq. 2.11}$$

$$[L]_o = \frac{N_{tot}(\phi^3 + \phi^2) + (N_1 K_1 + N_2 K_2)(\phi^2 + \phi)}{\phi^2 + (K_1 + K_2)\phi + K_1 K_2} [NC] \quad \text{eq. 2.12}$$

The displacement of CdX₂ from each site (B₁ and B₂) is plotted in Figure 2.4(b).

The outcome of the ligand exchange analysis is summarized in Table 2.1. N₁ and N₂ are two different binding sites on the surface of CdS with their respective equilibrium constants of K₁ and K₂, respectively. The number of N₁ sites on the surface is approximately 1.5 times greater than the number of N₂ sites on the surface. Similar to what has been reported for similar studies on CdSe NCs, the value of K₁ is smaller than K₂ by about two orders of magnitude, which is related to the energy of binding CdX₂ to these two sites.^{7,8} This signifies that ligands bound to any N₁ site are much easier to remove than those bound to the N₂ sites. This analysis shows that at around 50 mM TMEDA, the full displacement of CdX₂ from B₁ sites is achieved, whereas at this same point in

the titration, less than 10% of B₂ sites have been de-coordinated. The same surface analysis was done on two different sizes of CdS (3.7 nm and 4.0 nm) and are shown in the supporting information (SI 2.8.2). There is seemingly no discernable trend between the numbers of the two sites and NC size, however the equilibrium constant of binding to either a N₁ or N₂ site is similar. Ligands bound to any N₁ site regardless of size would be much easier to remove than those bound to N₂ sites.

2.5 Thermodynamics of Surface Site Binding

To further understand the binding affinity of CdX₂ to the two different surface binding sites of CdS NCs, temperature-dependent ¹H NMR was performed. These studies allow to define the thermodynamic difference between the binding sites by modulating the equilibrium of the CdX₂ reactions. Two TMEDA concentrations (5 and 304 mM) were selected, representing points in the titration where one of the two exchange reactions dominates the overall equilibrium. According to these temperature-dependent studies, the displacement of CdX₂ from the surface becomes more spontaneous at lower temperatures, indicating that this process is exothermic (and that the binding of CdX₂ on the surface of CdS NCs is endothermic, relative to the TMEDA- CdX₂ species). To quantify the enthalpy change of this process, a van't Hoff analysis was done on the temperature dependent ¹H NMR:

$$\frac{d \ln(K_{eq})}{d(T^{-1})} = -\frac{\Delta H}{R} \quad \text{eq. 2.13}$$

Figure 2.5 shows the van't Hoff analysis for the temperature-dependent ¹H NMR studies. The enthalpy of binding is temperature independent, as shown by the linear behavior of the equilibrium at different temperatures.

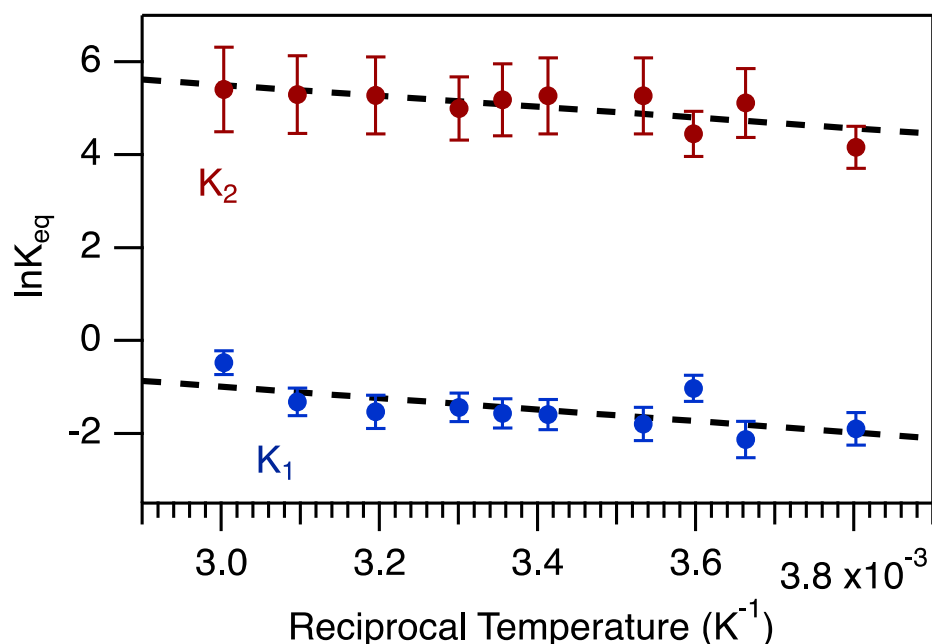


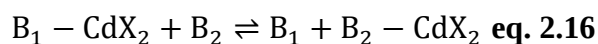
Figure 2.5 Temperature dependence of K_1 and K_2 for 3.4 nm CdS NCs. Red circles: [TMEDA]=304 mM, Blue circles: [TMEDA]=5 mM.

The enthalpy of each binding process is determined from the van't Hoff formalism (the slope of the fit). The Gibbs free energies for each process are obtained from the equilibrium constants found in Table 2.1, and entropy was found from there, as shown in eqs. 2.14 and 2.15:

$$\Delta G_i = -RT \ln(K_i) \quad \text{eq. 2.14}$$

$$\Delta S_i = (\Delta H_i - \Delta G_i) \cdot T^{-1} \quad \text{eq. 2.15}$$

It is important to note that the thermodynamic data obtained for each binding site is with respect to the formation of CdX₂-TMEDA complexes and not purely to the binding of CdX₂ to the surface of the NC. However, by subtracting the first two equilibrium equations established earlier (eq. 2.6a and eq. 2.6b), we can obtain the overall equilibrium expression of:



This equilibrium expression is now independent of the nature of the Lewis base used to displace CdX₂ from the surface. By subtracting the thermodynamic parameters obtained from the initial van't Hoff analysis, we can gain insight into the direct difference in enthalpic terms associated with the two binding sites, B₁ and B₂, as summarized in Table 2.2. The overall binding of CdX₂ to the surface is nearly isenthalpic between the two different sites. The stark difference between the two sites is due to the entropic contribution: the stability of the B₂-CdX₂ complex is mainly due to the larger entropy of CdX₂ bound to that site.

Table 2.2 Thermodynamic parameters for CdX₂ Exchange with TMEDA of CdS NCs. (3.4. nm)

Trial	ΔH_1 (kJ/mol)	ΔH_2 (kJ/mol)	ΔS_1 (J/mol•K)	ΔS_2 (J/mol•K)	ΔG_1 (kJ/mol)	ΔG_2 (kJ/mol)
1	10 ± 4	10 ± 3	17 ± 4	77 ± 3	5 ± 1	-13 ± 1
2	11 ± 10	9 ± 5	26 ± 1	77 ± 5	3 ± 1	-14 ± 2
3	7 ± 2	10 ± 1	2 ± 2	78 ± 2	7 ± 2	-13 ± 2
Average	9 ± 11	10 ± 6	15 ± 5	77 ± 6	5 ± 2	-13 ± 3

Trial	$\Delta\Delta H_{2-1}$ (kJ/mol)	$\Delta\Delta S_{2-1}$ (J/mol•K)	$\Delta\Delta G_{2-1}$ (kJ/mol)
1	0 ± 5	60 ± 5	-18 ± 2
2	-2 ± 11	51 ± 5	-17 ± 3
3	3 ± 2	76 ± 3	-20 ± 3
Average	0.3 ± 12	62 ± 8	-18 ± 11

The temperature-dependent studies above indicate that the TMEDA-induced CdX₂ displacement reaction is endothermic. Through comparison of the enthalpic and entropic terms of binding CdX₂ to the surface of the NC for each site reveals the reasoning for the large thermodynamic stability of the B₂-CdX₂ complex. The affinity of B₂ for CdX₂ relative to the B₁ site is an entropic effect (much like what was seen in previous studies on CdSe NCs where the average entropy difference between each site was 92 J mol⁻¹ K⁻¹).⁸ The striking similarity in entropy is arguably reasonable

since both systems (CdSe vs. CdS) are zinc-blende crystal structures so the organization of the facets is similar. In previous studies done on CdSe NCs in our group, it was determined that each type of defect site can be correlated to a specific facet. Zinc-blende NCs are typically described in terms of two most stable facets, the (100) and the (111) facet.⁸ The full details of binding of each facet are fully described in previous work.⁸ From this work, it was determined that the (111) facets have a lower density of dangling bonds and vacancies created on (100) facets lead to the creation of midgap states.⁸ The B₂ vacant sites are hereby assigned to vacancies on the (100) facet and due to the large thermodynamic stability of CdX₂ complexes on B₂ vacancies it is reasonable to assume that at equilibrium the (100) facet is fully covered. The low coverage of the (111) facet, the facet with B₁ vacancies, is related to the structure of the cadmium carboxylate complex and the sterics of binding to these sites, as described in work done Saniepay et al. the thermodynamics of CdX₂ binding favors full coverage on the (100) facet due to entropic effects.⁸

However, a surprising result is seen when the enthalpic terms of binding are compared. Regardless of if CdX₂ binds to a sulfur or selenium site, the process is endothermic and the enthalpic difference of binding between each site is similar (binding to a B₂ site was 13 kJ mol⁻¹ for CdSe NCs).⁸

To help rationalize the small energetic differences in binding to the surface of CdS vs. CdSe, we use Polar Covalence to help us with a “back-of-the-envelope” calculation to quantify bond energies.³⁰ This calculation assumes that the covalent bond energy of a compound “A-X” can be calculated by considering two main resonance forms: A-X and A⁺ and X⁻.

The first scenario will have covalent bond energy of E_c , and the ionic structure will have ionic bond energy of E_i . The total bond energy, E_{ax} , of the compound can be calculated as a weighted sum of the ionic and covalent bond energies:

$$E_{ax} = t_c E_c + t_i E_i \quad \text{eq. 2.15}$$

Since we are assuming that only those two forms exist, according to Resonance Theory, the blending coefficients, t_c , and t_i , should add up to unity:

$$1 = t_c + t_i \quad \text{eq. 2.16}$$

To find the covalent bond energy (E_c), the geometric mean of the homonuclear covalent bond energies (E_{aa} and E_{xx}) can be used:

$$E_c = \frac{R_c}{R_o} \sqrt{E_{aa} E_{xx}} \quad \text{eq. 2.17}$$

$$R_c = R_a + R_x \quad \text{eq. 2.18}$$

This geometric mean includes a correction to compensate for the actual bond distance relative to the covalent bond radii's sum. If the A-X bond were purely covalent, the bond distance would be the sum of the two covalent radii (R_c) of A and X, R_a and R_x . The real bond distance is slightly different from if it were two purely covalent species. This is considered by taking the ratio of the covalent radii with the observed bond length, R_o .

The ionic bond energy (E_i), is related to Coulomb's Law and is inversely related to the experimental bond length:

$$E_i = \frac{382 \frac{\text{kcal} \cdot \text{\AA}}{\text{mol}}}{R_o} \quad \text{eq. 2.19}$$

Now, it is necessary to find the coefficients, t_c , and t_i . The ionic resonance form contribution, t_i , can be found in the partial charges on A and X in the ground state are known, δ_A and δ_x respectively:

$$t_i = \frac{|\delta_A| + |\delta_x|}{2} \quad \text{eq. 2.20}$$

The partial charges in the ground state are related to the electronegativities of the individual atoms compared to the electronegativity of the whole molecule:

$$\delta_{A \text{ or } X} = \frac{\chi_m - \chi_{A \text{ or } X}}{1.57 \sqrt{\chi_{A \text{ or } X}}} = \frac{\chi_m - \chi_{A \text{ or } X}}{\Delta \chi_{A \text{ or } X}} \quad \text{eq. 2.21}$$

where χ_m is the molecular electronegativity, χ_A is the electronegativity of the free atom A, and $\Delta\chi_A$ is the change of electronegativity in atom A when a unit of charge is added. To find the molecular electronegativity, χ_m , we find the geometric mean of the electronegativities of the individual atoms:

$$\chi_m = \sqrt{\chi_A \chi_x} \quad \text{eq. 2.22}$$

Table 2.3 Parameters for Sanderson Bond Calculation.^{30,31}

CdX (X=S or Se)	CdS	CdSe
R_{Cd} (Å)	1.49	1.49
R_x (Å)	1.05	1.17
R_o (Å)	2.57	2.69
E_{aa} (kcal/mol)	30.4	30.4
E_{xx} (kcal/mol)	65.9	53.8
χ_{Cd}	1.978	1.978
χ_x	2.957	3.014

Using this calculation, we get bond dissociation energies for CdS and CdSe to be 60 kcal/mol (251 kJ/mol) and 56 kcal/mol (234 kJ/mol), respectively. The resulting calculated energies are so similar because the ionic and covalent bonding energies are similar due to similar atomic radii and electronegativities between sulfur and selenium. This calculation supports the slight difference that we see in the enthalpy of binding to the surface and supports the idea of a small difference between the two surfaces. The amount of energy needed to remove CdX₂ from a sulfur or selenium surface site is very similar. This calculation also supports the idea of CdX₂ binding to a B₁ or B₂ vacancies as being less endothermic because the bond between a Cd and S atom is stronger than that of Cd and Se atom. The binding of CdX₂ to a S site would release more energy than it does to Se site, making the process less endothermic. In other sizes of CdS (see SI), we see a similar trend where

the difference in binding between the two sites is largely related to entropic affects, however there is no noticeable different in these parameters with size.

2.6 Conclusions

Through a general ligand process described previously for CdSe NCs,^{7,8} we have demonstrated the existence of two different sites on the surface of zinc-blende CdS NCs. We have used a model commonly used to correlate types of surface defects and their corresponding energetics of binding to the surface. From this model, we determined the existence of two distinct binding sites on CdS surface, each with their own intrinsic thermodynamics of binding. The nature of CdX₂ binding to each facet was determined, and through thermodynamical analysis of surface binding, a detailed model of surface composition was created. We determined that it is much easier to remove a CdX₂ complex from a B₁ site than it is from a B₂ site. It was also determined that the difference in stability between the two sites is due to entropic effects. The similarity in the enthalpic terms of binding for CdSe and CdS was further supported through Sanderson bonding calculations. Based on the results in this chapter, it can be determined that most vacant sites that are left on the surface after synthesis are B₁ vacant sites. The impact of these defect states on the photophysical properties of CdS will be explored in later chapters.

APPENDIX

SI 2.1 NMR Characterization of CdS NCs Capping Ligands

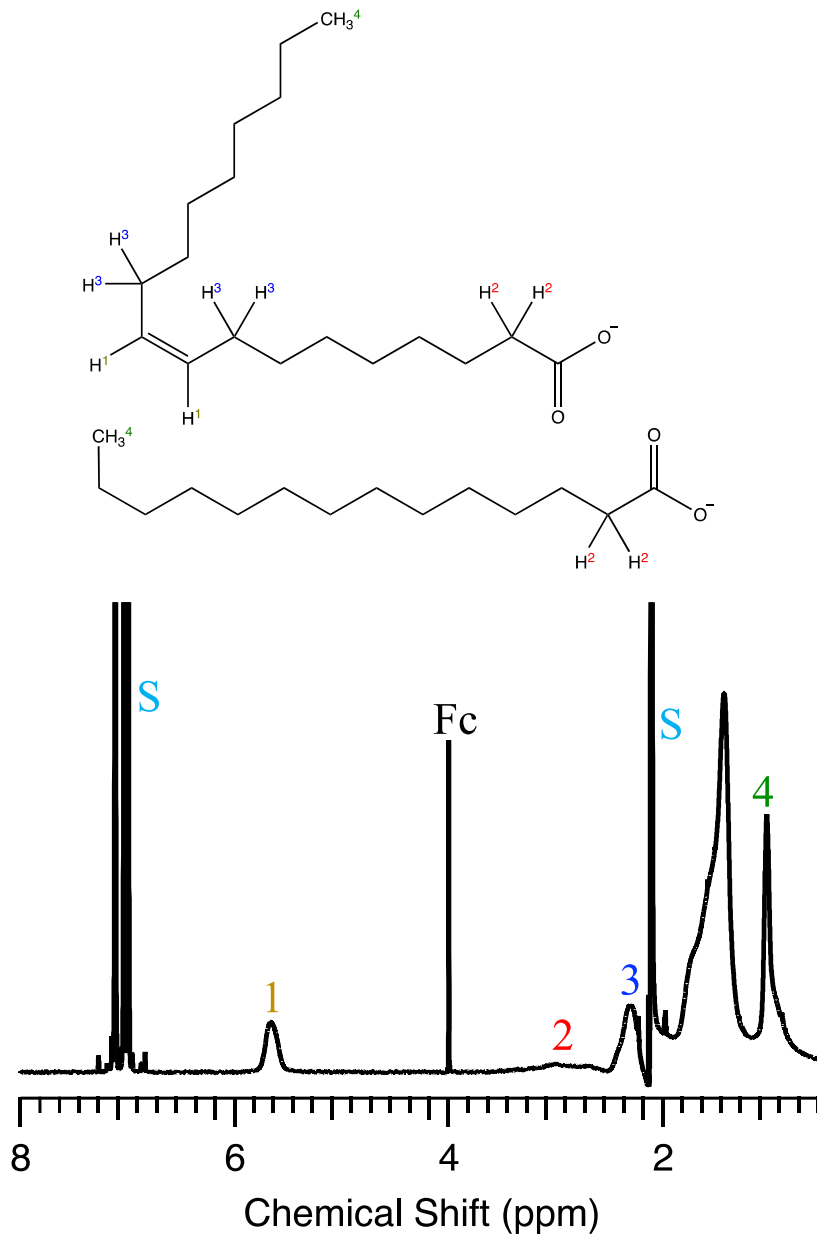


Figure SI 2.1 ^1H NMR spectrum of a clean suspension of CdS NCs ($67\ \mu\text{M}$) capped with oleate/myristate ligands. The chemical assignment of each peak is labeled. The protons not shown are associated with the peak between 1.2-2.2 ppm. Fc represents the internal standard, ferrocene. S represents solvent, which is d-toluene at 2.1 and 7.1 ppm.

SI 2.2 Calculation of Surface Coverage and Concentration

In a 20 mL vial, 600 μL of 65 μM CdS (3.4 nm) suspension in d-toluene was mixed with 30 μL of d-toluene and 30 μL of ferrocene solution in d-toluene (4.62 μM) and transferred to an NMR tube. Ferrocene is used as an internal standard, and the integration of the methyl peak was compared to the integrated signal of ferrocene, which was set to 10. The ^1H NMR was taken with 32 scans and a 30-second relaxation delay. The calculation for the ligand concentration and ligand coverage per NC is shown below:

$$[\text{Methyl}] = [\text{Ferrocene}] * \frac{\#H_{\text{ferrocene}}(10)}{\#H_{\text{methyl}}(3)} * \frac{\int \text{methyl}}{\int \text{ferrocene}}$$

The concentration of all carboxylate ligands is: $[\text{Carboxylates}] = [\text{methyl}] = 14.5 \text{ mM}$.

Assuming each cadmium is attached to two carboxylates (for charge-neutrality reasons), the concentration of cadmium carboxylate (CdX_2) is:

$$[\text{CdX}_2] = 7.3 \text{ mM}$$

Finally, assuming CdS is a spherical nanocrystal ($d=3.4 \text{ nm}$, $r=1.7 \text{ nm}$), on average, the surface area of each particle is:

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

$$A = 36.3 \text{ nm}^2$$

And the surface coverage for the 0.067 mM CdS is:

$$\frac{7.3 \text{ mM}}{0.067 \text{ mM} * 36.3 \text{ nm}^2} = 3.0 \text{ nm}^{-2}$$

SI 2.3 NMR Fitting Analysis

When TMEDA is added to a sample of CdS NCs, the NMR peaks corresponding to the methyl groups on both myristate and oleate are split into a broad and sharp peaks.⁸ This splitting of the peak indicates both free and bound CdX_2 on the surface of the NC. To capture all ligands' behavior

on the NC surface, the methyl peaks between 0.8 and 1.2 ppm are used for fitting and calculating the ratio of bound to free ligands. The sum of the bound and free ratio is normalized to the total number of carboxylates for that sample (which was discussed in SI 2.2).

For both the titration NMR spectra and the temperature-dependent NMR, the combinations of Gaussian and Lorentzian fits were used to find the total integration. The total area of the fits under the bound and free peaks was summed, and the ratio of bound and free CdX_2 was found.

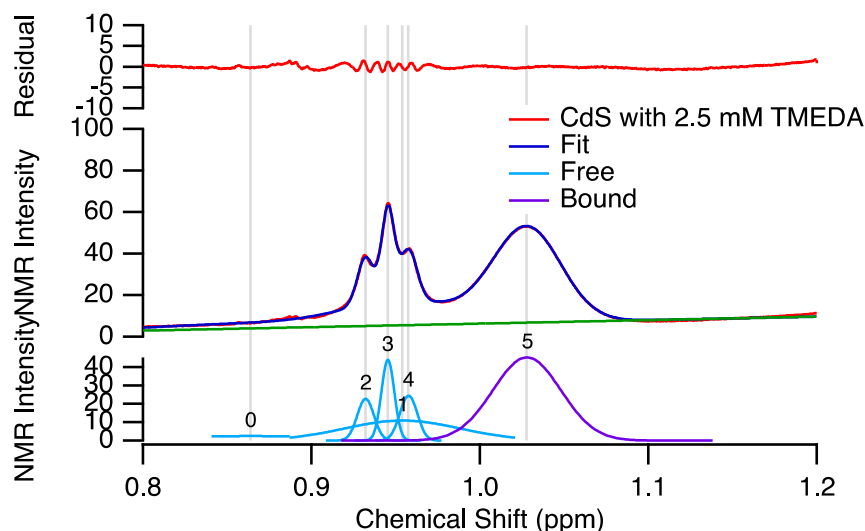


Figure SI 2.2 A sample of the fitting procedure used to deconvolute free and bound CdX_2 from 3.4 nm CdS NC surface with 2.5 mM TMEDA added.

Table SI 2.1 Fitting results from Gaussian and Lorentzian fit for 3.4 nm CdS with 2.5 mM TMEDA added.

Free	Bound	Total
2.33 ± 0.14	2.29 ± 0.01	4.62 ± 0.15

$$[\text{Methyl}](\mu\text{M}) = 0.194 \text{ mM} * \frac{10}{3} * \frac{4.62}{0.223} = 6.63 \text{ mM}$$

$$\int \text{Total} = \int \text{Free} + \int \text{Bound}$$

$$[\text{Free}] \text{ or } [\text{Bound}] = \frac{\int \text{Free or Bound}}{\int \text{Total}} \cdot [\text{Methyl}]$$

$$[\text{Free}] = \frac{2.33}{4.62} \cdot 6.63 \text{ mM} = 3.43 \pm 0.3 \text{ mM}$$

$$[\text{Bound}] = \frac{2.29}{4.62} \cdot 6.63 \text{ mM} = 3.29 \pm 0.2 \text{ mM}$$

SI 2.4 Methyl vs. Oleate NMR Fitting

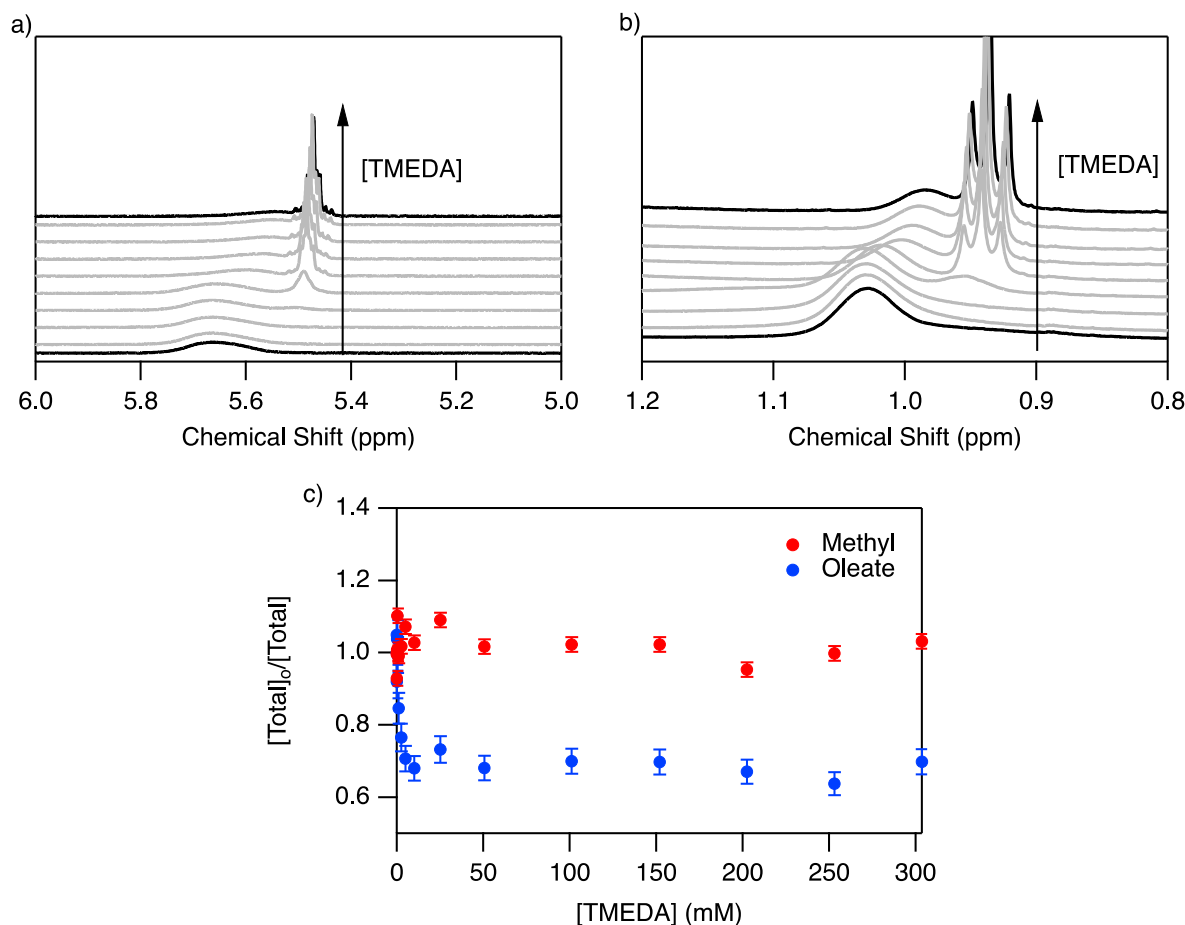


Figure SI 2.3 a) NMR spectra of 3.4 nm CdS (67 μ M) with varying amounts of TMEDA between 5.0-6.0 ppm. This area of the NMR represents the signal from the oleate ligands. b) NMR spectra of 3.4 nm CdS with varying amounts of TMEDA between 0.8-1.2 ppm, representing the signal from the methyl groups of both myristate and oleate. c) Comparison of the fittings of the methyl and oleate peak throughout the titration.

Typically, when the surface is analyzed, the oleate NMR peak around 5.0-6.0 ppm is analyzed for information due to the clear, separated peaks.^{7,8,14} However, in CdS, the oleate peak is too broad to be analyzed reliably. That is why for this study, the methyl peak was analyzed for all fittings. The methyl peak tracks both myristate and oleate ligands during the titration, whereas the oleate peak is only sensitive to oleate ligand displacement. Due to greater reliability and less error on methyl fitting, this was used throughout the paper.

SI 2.5 Displacement of CdX_2 on Other 3.4 nm Samples

SI 2.5.1 Displacement of CdX_2 from CdS NCs

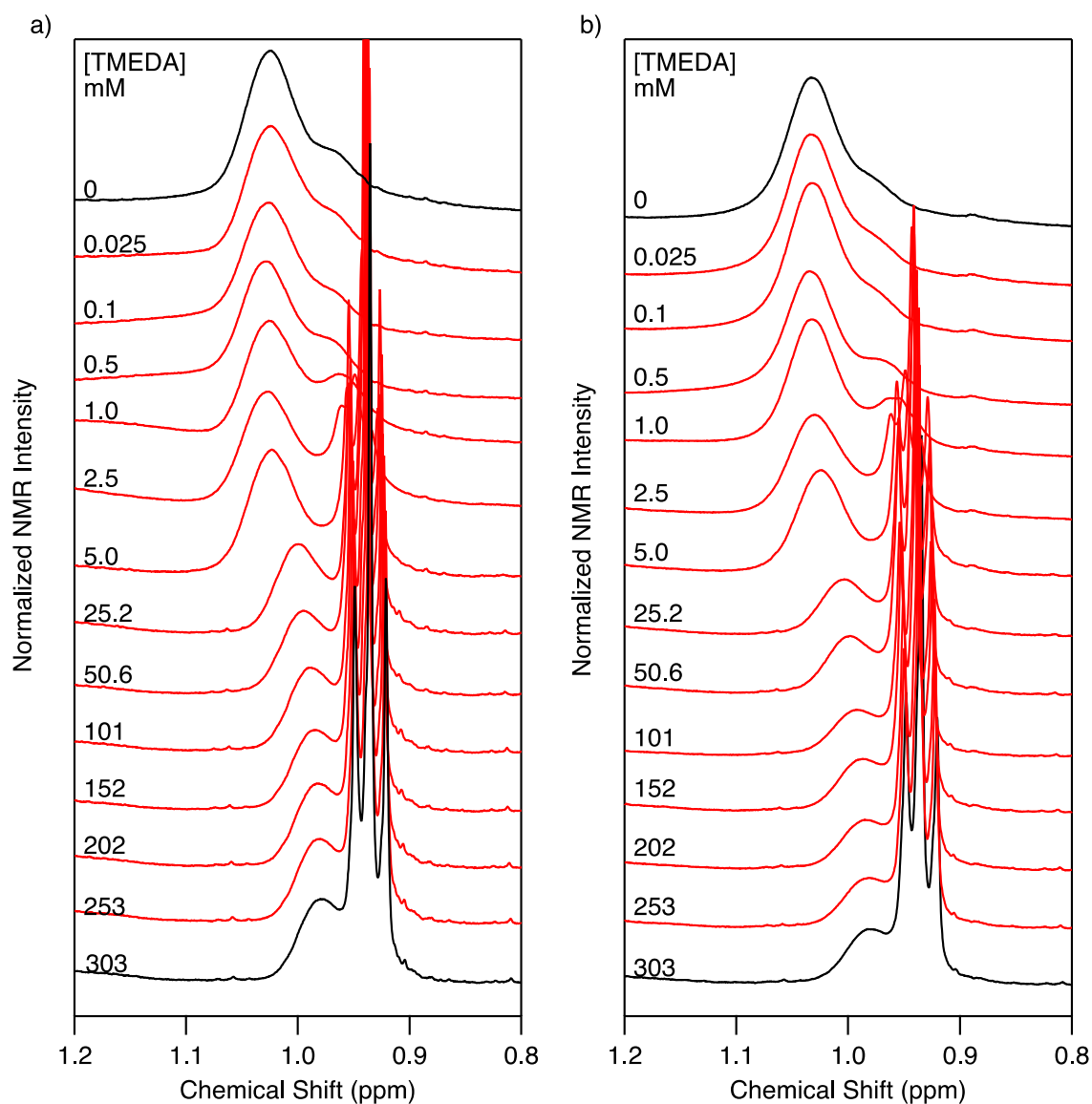


Figure SI 2.4. a&b) ^1H NMR spectra of 3.4 nm CdS NCs (67 μM) with various amounts of TMEDA added for panel a and b, respectively.

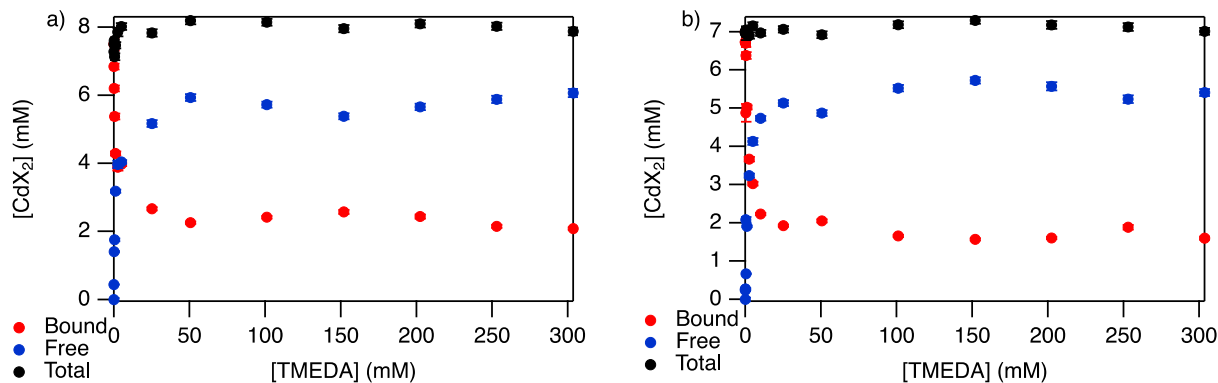


Figure SI 2.5 a&b) Total (gray), free (blue), and bound (red) CdX_2 groups as a function of added TMEDA for other 3.4 nm samples, for panel a and b, respectively.

SI 2.6. Analysis of TMEDA Addition

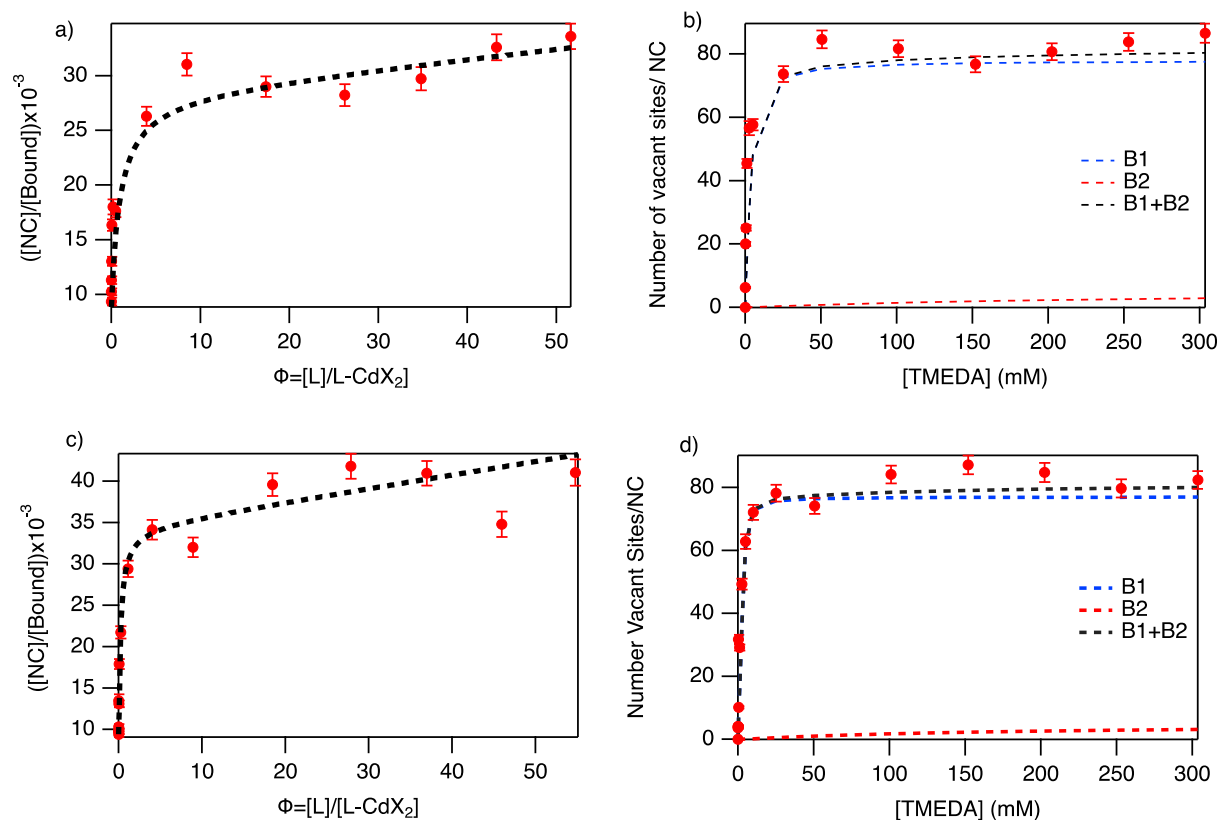


Figure SI 2.6 a&c) TMEDA titration of 3.4 nm CdS NCs ($67 \mu\text{M}$ in d-toluene), modeled with eq. 2.10. b&d) Calculated number of B1 (blue), B2 (red), and total (black) vacant sites on the surface of 3.4 nm CdS samples. The calculated number of sites is equivalent to the number of CdX_2 removed from the surface of CdS (shown in red circles).

SI 2.7 Temperature-Dependent HNMR Measurements

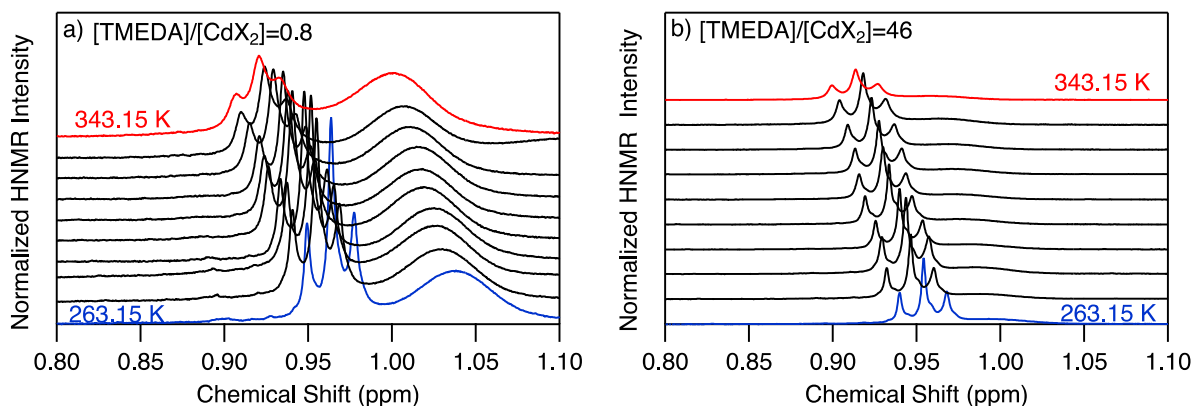


Figure SI 2.7 Temperature-dependent HNMR of 3.4 nm CdS (trial 1, main figures in Chapter 2) with a) 5 mM TMEDA and b) 304 mM TMEDA.

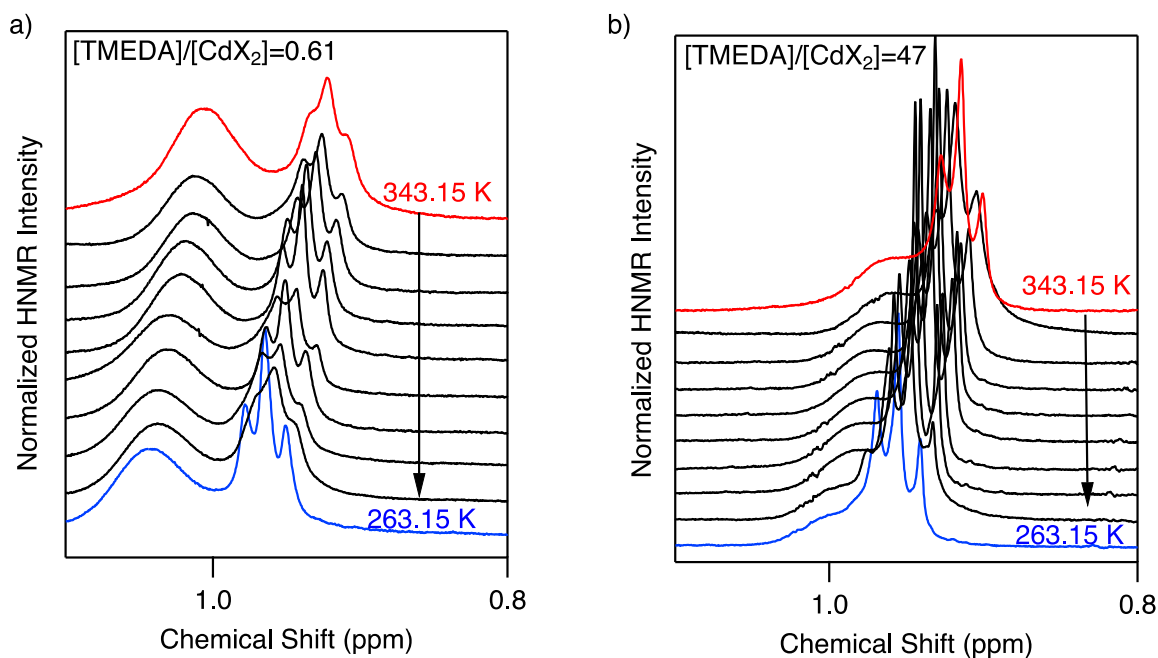


Figure SI 2.8 Temperature-dependent HNMR of 3.4 nm CdS (67 μM, trial 2) with a) 5 mM TMEDA and c) 304 mM TMEDA. Figures b and d show the change in concentration of free and bound CdX₂ at different temperatures.

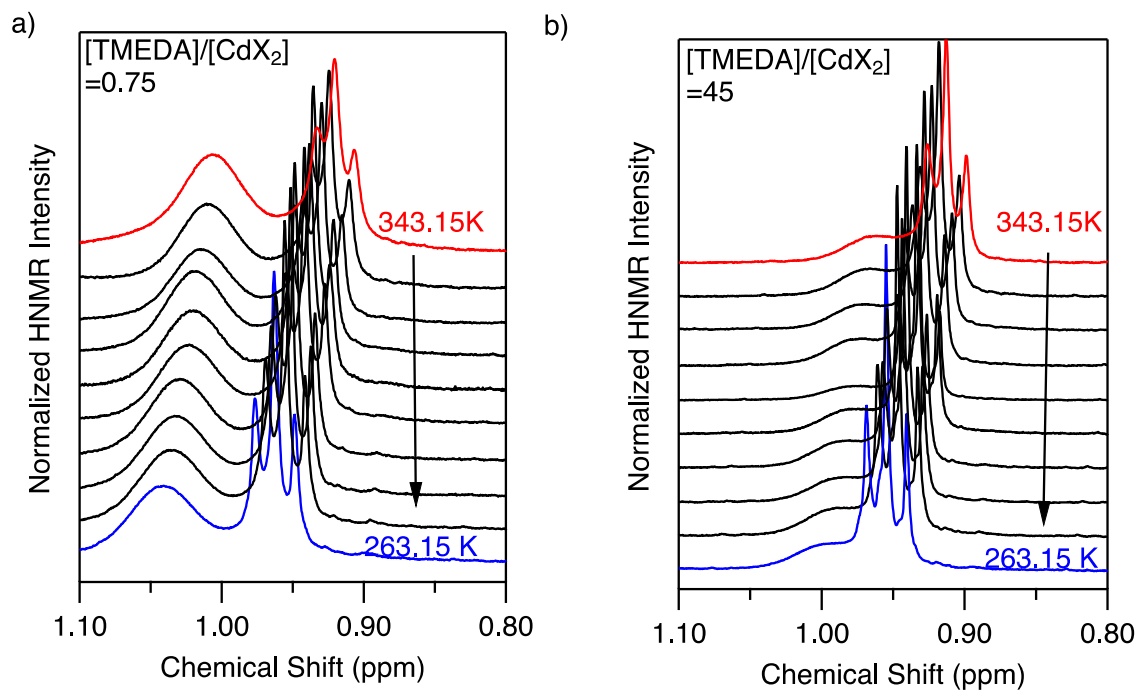


Figure SI 2.9 a) Temperature-dependent HNMR of 3.4 nm CdS (67 μ M, trial 3) with a) 5 mM TMEDA and c) 304 mM TMEDA. Figures b and d show the change in concentration of free and bound CdX_2 at different temperatures

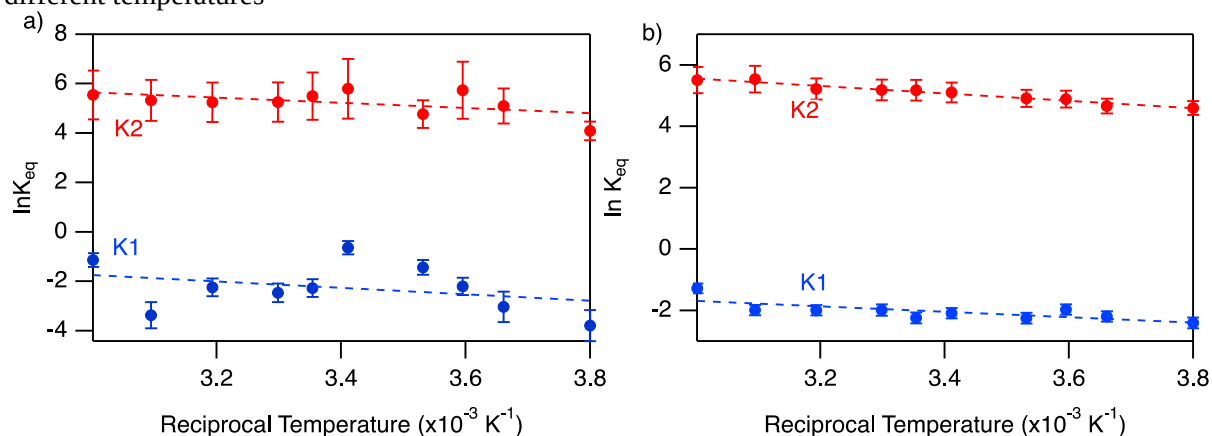


Figure SI 2.10 a) Temperature dependence of K_1 and K_2 for 3.4 nm CdS NCs (trial two and trial 3). Red circles: $[\text{TMEDA}] = 304$ mM, Blue circles: $[\text{TMEDA}] = 5$ mM

SI 2.8 Displacement of CdX₂ on other sizes of CdS NCs

SI 2.8.1 Displacement of CdX₂ from CdS NCs on other sizes

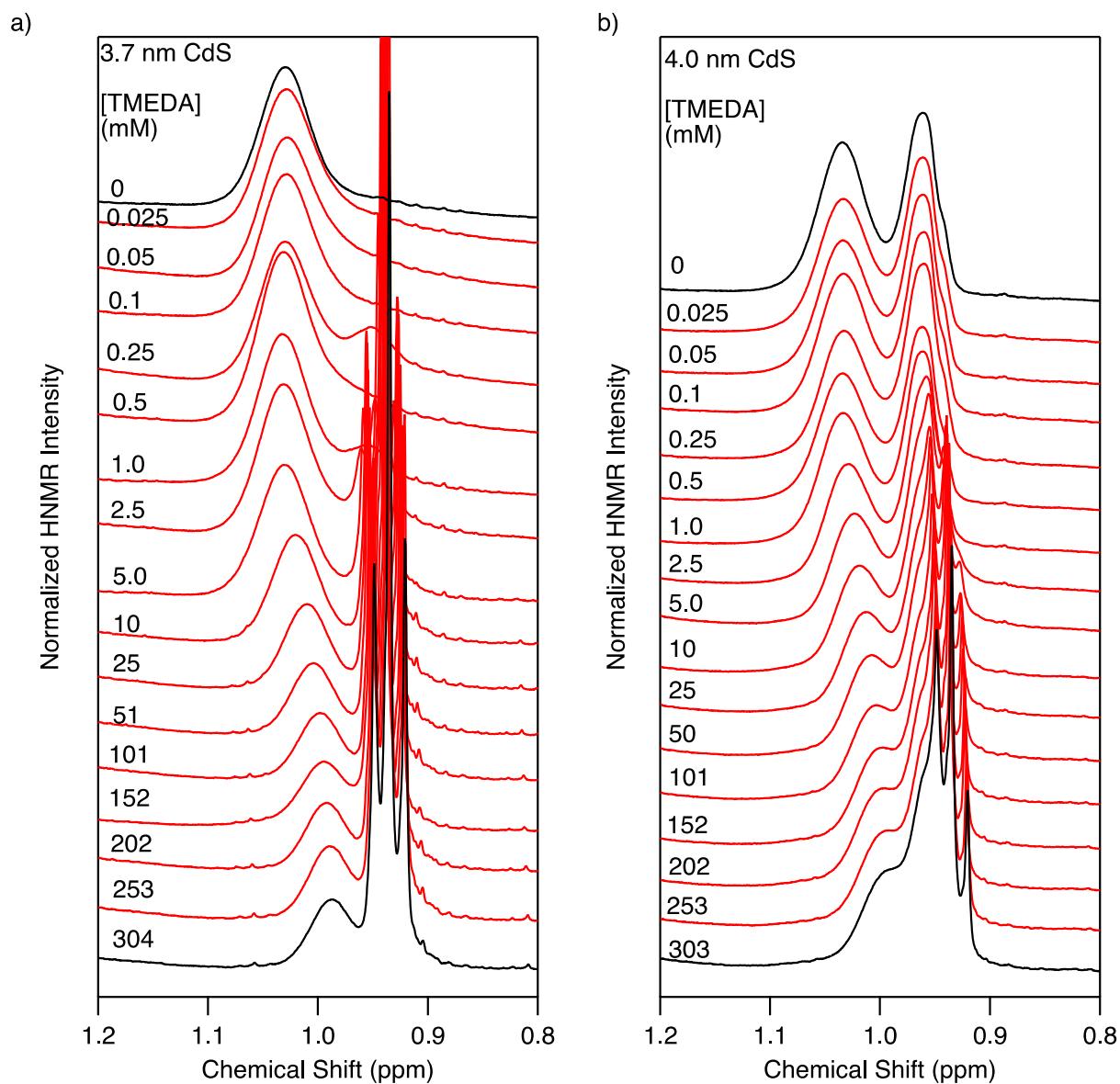


Figure SI 2.11 a) HNMR spectra of 3.7 nm CdS NCs (71 μ M) with various amounts of TMEDA added. b) HNMR spectra of 4.0 nm CdS NCs (70 μ M) with various amounts of TMEDA added.

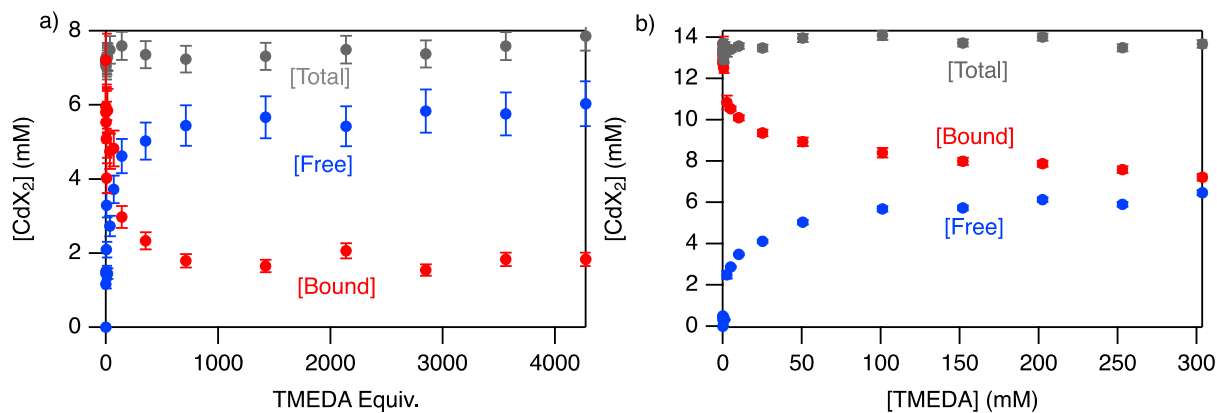


Figure SI 2.12 Total, free, and bound CdX₂ groups as a function of added TMEDA for a 3.7 nm (a) and 4.0 nm (b) CdS sample (71 μM).

SI 2.8.2 Analysis of TMEDA Addition on Other Sizes

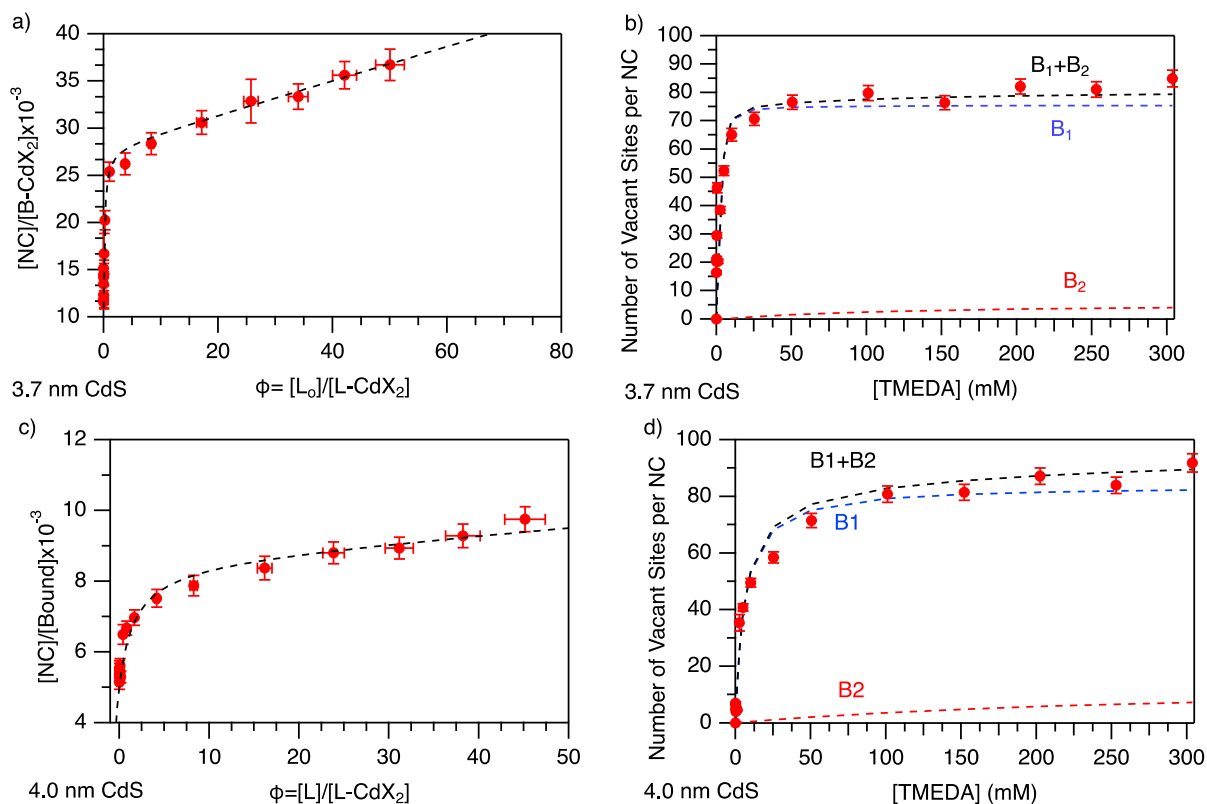


Figure SI 2.13 a&c) TMEDA titration of 3.7 and 4.0 nm CdS NCs (respectively) modeled with eq. 2.12. b&d) Calculated number of B1 (blue), B2 (red), and total (black) vacant sites on the surface of 3.7 and 4.0 nm CdS samples, respectively. The calculated number of sites is equivalent to the number of CdX₂ removed from the surface of CdS (shown in red circles).

Table SI 2.2 CdS Surface-Related Data from TMEDA Titration experiments for different sizes CdS samples.

Size (nm)	N ₁	N ₂	K ₁	K ₂	N _{tot}
3.7	75 ± 4	36 ± 5	0.1 ± 0.2	154 ± 100	111 ± 6
4	84 ± 12	116 ± 13	0.1 ± 0.1	419 ± 128	200 ± 18

Trial	[NC] (μM)	[CdX ₂] (mM)	Surface Coverage (CdX ₂ /nm ²)
3.7	71 ± 2	7.4 ± 0.3	1.8 ± 0.3
4	70 ± 2	13.6 ± 0.3	3.7 ± 0.3

SI 2.8.3. Temperature Dependent ¹H NMR Measurements

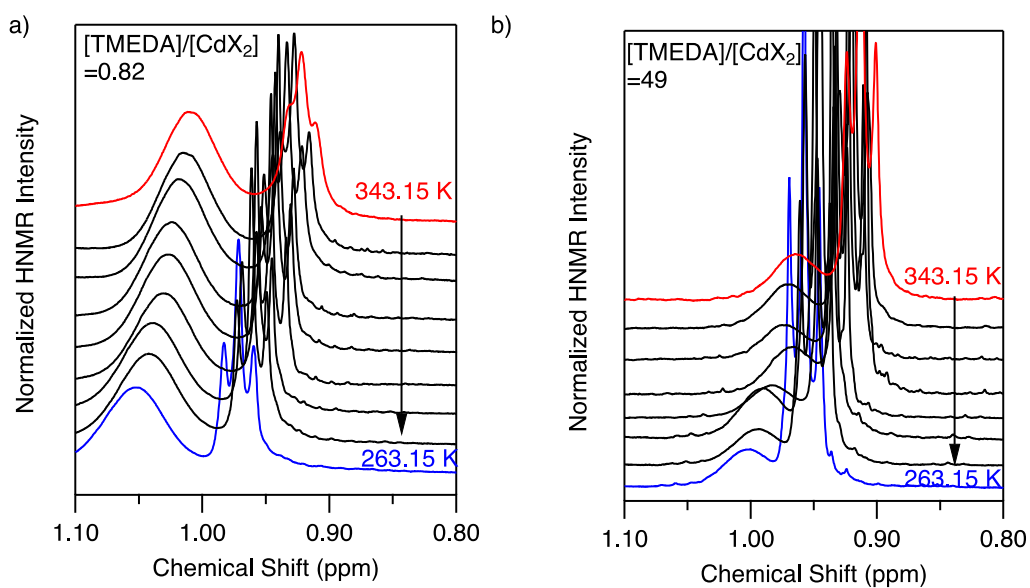


Figure SI 2.14 Temperature dependent HNMR of 3.7 nm CdS with a) 5 mM TMEDA and b) 304 mM TMEDA.

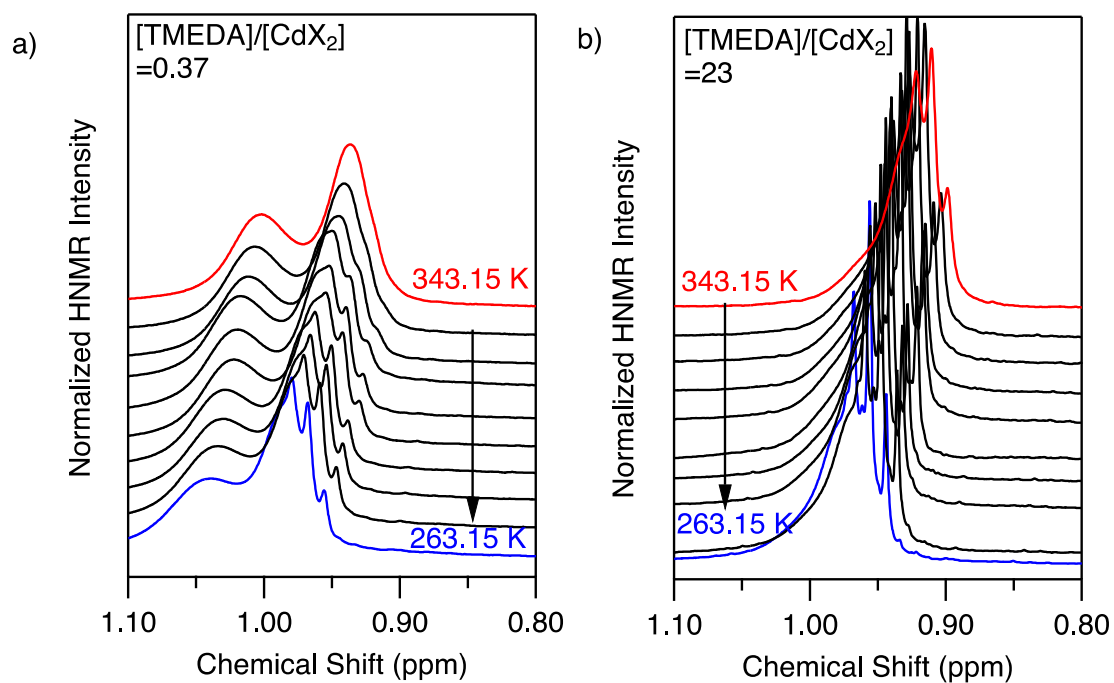


Figure SI 2.15 Temperature dependent HNMR of 4.0 nm CdS with a) 5 mM TMEDA and c) 304 mM TMEDA. Figures b and d show the change in concentration of free and bound CdX_2 at different temperatures.

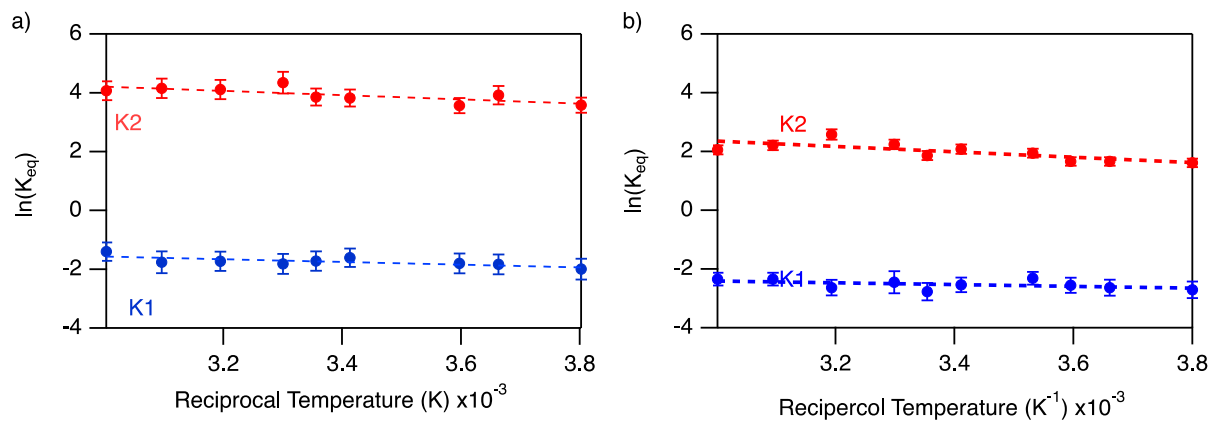


Figure SI 2.16 Temperature dependence of K_1 and K_2 for 3.7 nm (a) and 4.0 nm (b) CdS NCs. Red circles: $[\text{TMEDA}] = 304 \text{ mM}$, Blue circles: $[\text{TMEDA}] = 5 \text{ mM}$.

Table SI 2.3. Thermodynamic parameters for CdX₂ Exchange with TMEDA of CdS NCs

Size (nm)	ΔH_1 (kJ/mol)	ΔH_2 (kJ/mol)	ΔS_1 (J/K mol)	ΔS_2 (J/K mol)	ΔG_1 (kJ/mol)	ΔG_2 (kJ/mol)
3.7	3 ± 2	6 ± 2	-8 ± 1	62 ± 5	6 ± 2	-12 ± 4
4	3 ± 2	-13 ± 2	5 ± 3	70 ± 5	-10 ± 2	-13 ± 2

Size (nm)	$\Delta\Delta H_{2-1}$ (kJ/mol)	$\Delta\Delta S_{2-1}$ (J/K mol)	$\Delta\Delta G_{2-1}$ (kJ/mol)
3.7	3 ± 2	60 ± 5	-18 ± 2
4	-16 ± 2	65 ± 2	-3 ± 2

SI 2.9 Transmission Electron Microscopy (TEM)

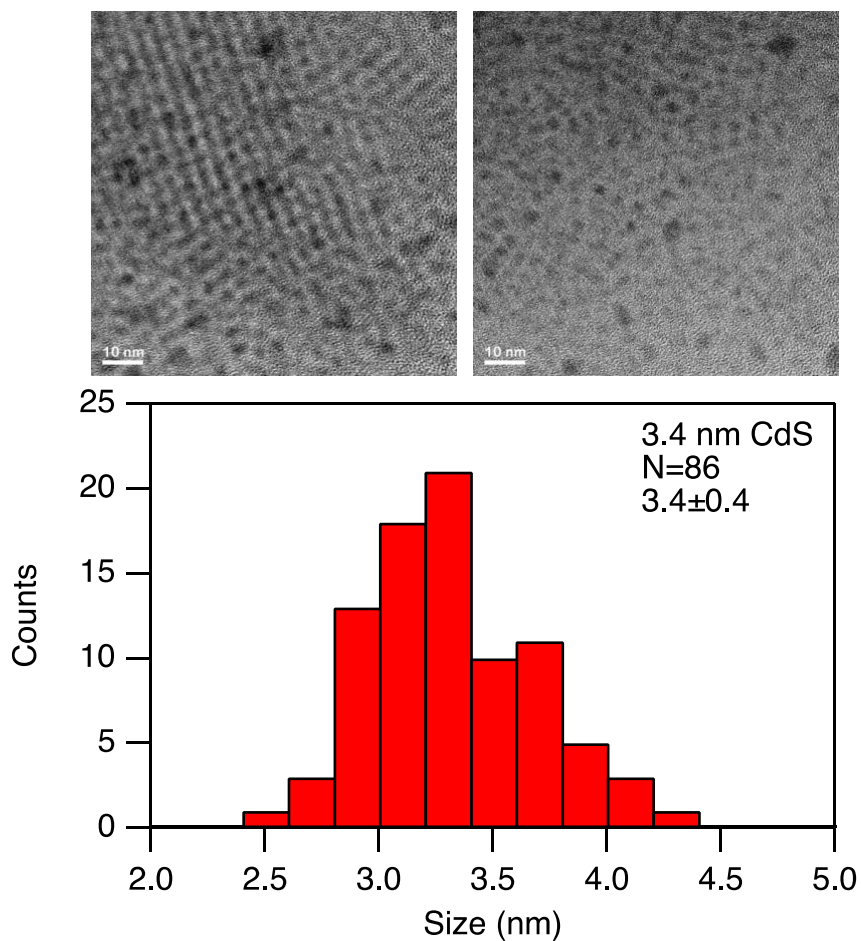


Figure SI 2.17 TEM images and histogram of 3.4 nm CdS NCs.

SI 2.10 Powder X-ray Diffraction

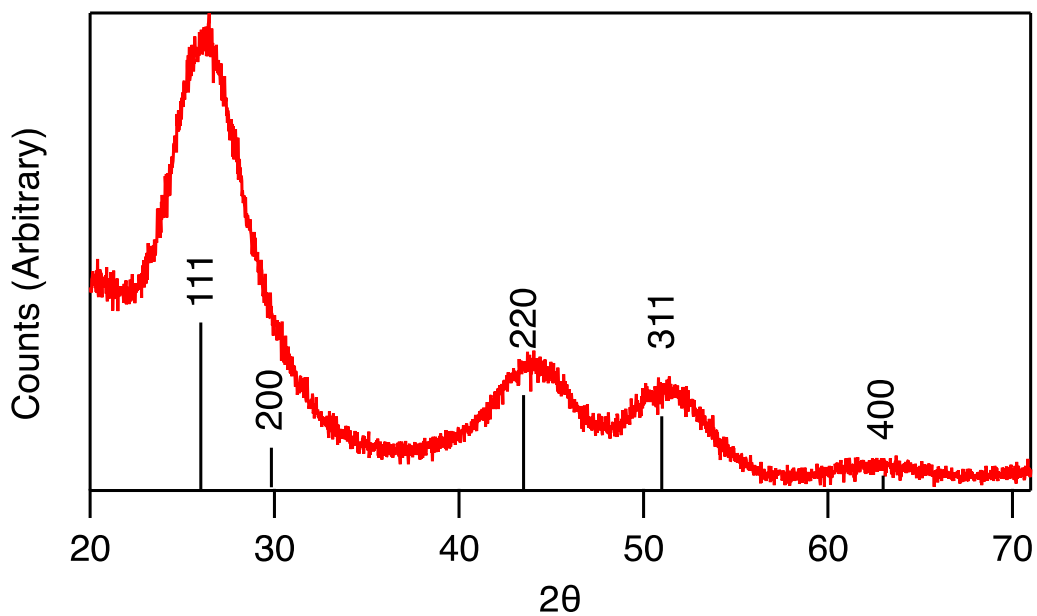


Figure SI 2.18 XRD of 3.4 nm CdS. Reference diffraction angles for bulk zinc-blende CdS are given as black line.

SI 2.11. Kinetics of ^1H NMR CdS

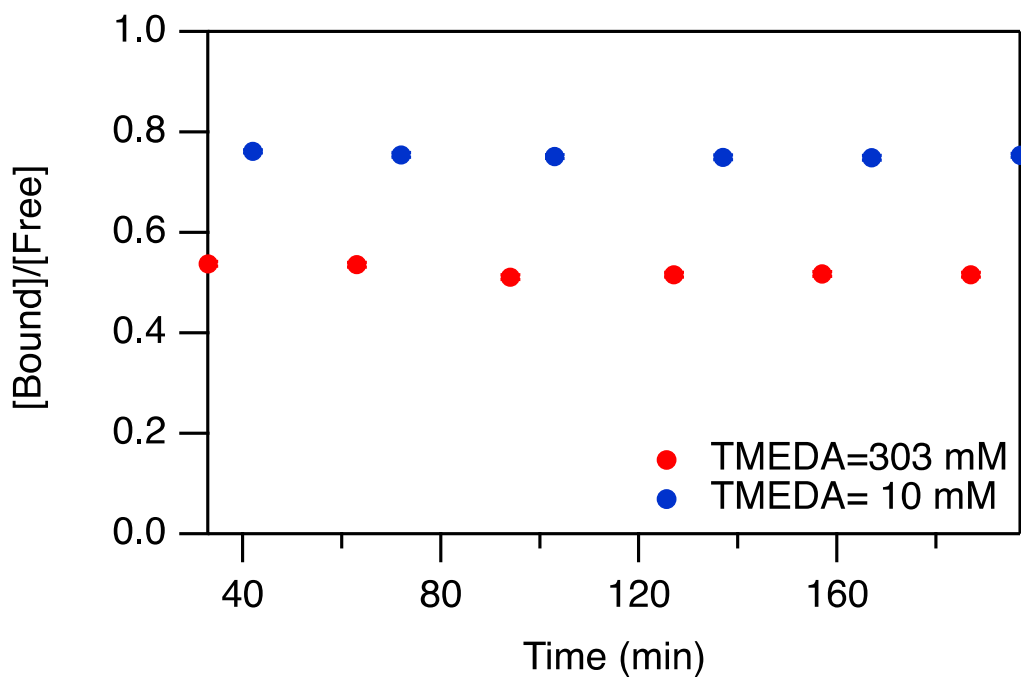


Figure SI 2.19 Kinetic study of ^1H NMR studies to ensure enough time is given for the system to reach equilibrium.

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Chapter 3: Correlating the Creation of Surface Defects to Changes in Light Absorption

3.1 Introduction

UV-Vis spectroscopy is a commonly used tool to study the impact of the surface electronic structure on the core exciton of the NC. Typically, UV-Vis spectroscopy characterizes NCs after ligand exchange, surface charging, surface oxidation, or chemical additives.¹⁻⁹ The advantage of UV-Vis spectroscopy is it is a non-destructive characterization method that monitors blue or red shifts, change in light absorption efficiency, or appearances of new features based on alterations made to the NC. In previous studies of surface effects on CdSe NCs, there was no change in the absorption profile of the NC.^{10,11} However, in our studies presented here on CdS, there are noticeable changes to absorption as TMEDA is added. In Chapter 2, we distinguished two different types of surface defects on CdS NCs. These surface defects were correlated to a specific surface type, and we were able to model the creation of each defect with the addition of TMEDA. In this Chapter, we associate each defect creation with its impact on the NCs light absorption. We show that exposure of sulfur on the CdS surface impacts the absorption profile and surface dipole of the NC.

3.2 Experimental Section

For details about the synthesis and optical spectroscopy characterization of CdS NCs, please see Chapter 2, Section 2.

3.3 Impact of Surface Defects on Light Absorption

The absorption and PL spectra of a clean suspension of CdS NCs before the addition of TMEDA are shown in Figure 3.1

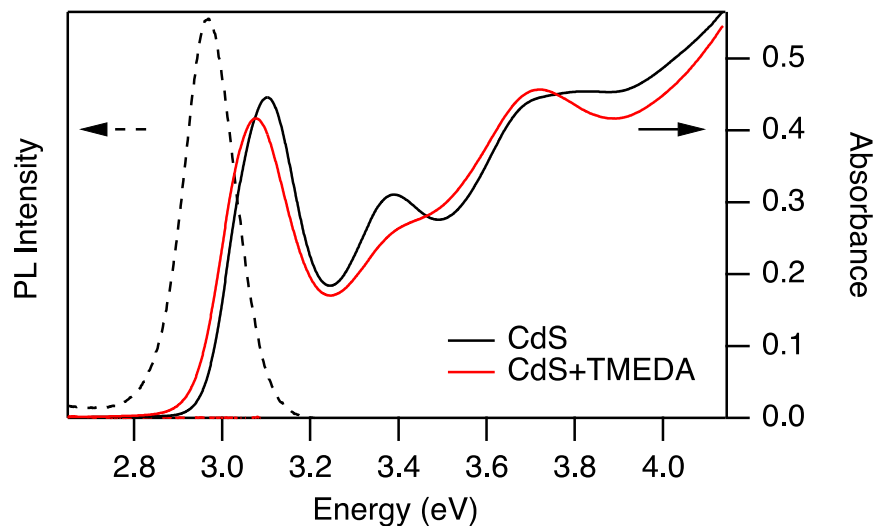


Figure 3.1 Absorption (solid) and photoluminescence (dashed) of 3.4 nm CdS NC (2.0 μM) before (black) and after (red) addition of TMEDA (5 mM).

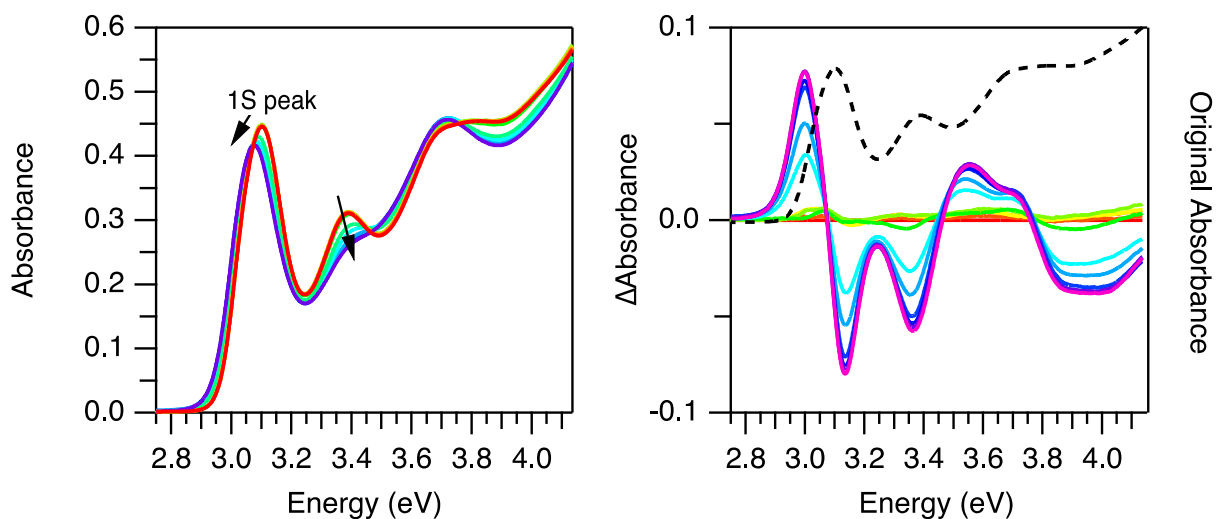


Figure 3.2 (a) Absorption spectra of 3.4 nm CdS (2.0 μM) with varying amounts of TMEDA (0-5 mM) (b) Difference in absorbance after TMEDA has been added.

Upon adding 4500 equivalents of TMEDA per NC, there is a change in the absorption of CdS in two primary forms: (1) a red shift of the excitonic absorption and (2) a broadening of the 2nd absorption peak. We focus on discussing the red shift seen of the excitonic 1S absorption peak to begin our discussion.

3.3.1 Impact of Surface Defects on Excitonic Absorption

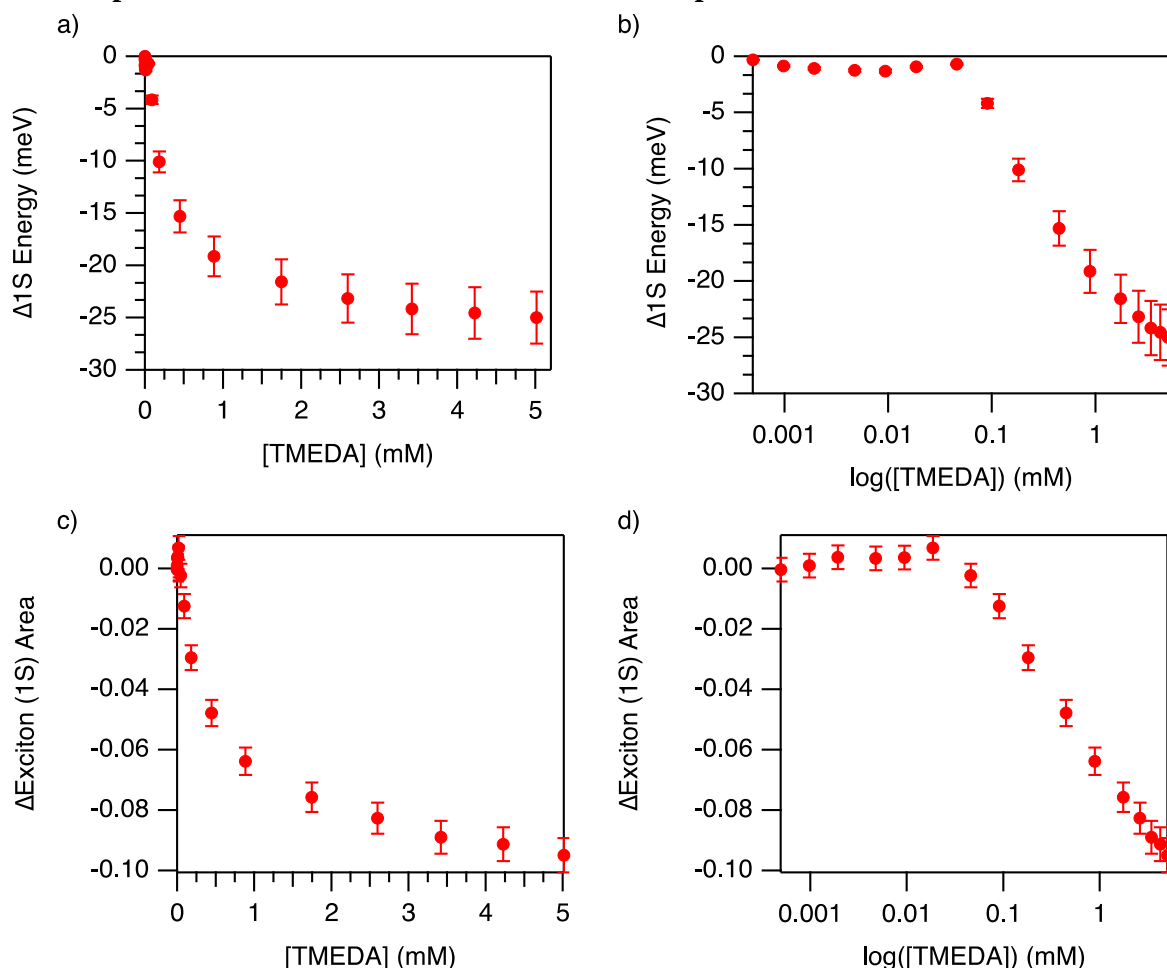


Figure 3.3 (a) The shift of the exciton absorption energy (~ 3.1 eV) of 3.4 nm CdS ($2 \mu\text{M}$) during TMEDA titration. (b) The same graph as (a) but with the x-axis in a log scale to better show the initial energy change. (c) The change in the exciton area during TMEDA titration. (d) The same graph as (d) but with the x-axis in a log scale to better show the initial area change.

As shown in Figure 3.3 (a) and (b), upon the addition of small amounts of TMEDA, there is little change in the energy of the excitonic absorption. Once the ratio of TMEDA to CdS NC is 45:1, we start to see the red shift of the exciton absorption happen. We see the same behavior with the change in the excitonic absorption area: the difference becomes significant at the same ratio. It could be expected that upon stripping the surface of CdX_2 that the size of the NC would decrease and would result in a blue shift of the excitonic peak due to quantum confinement effects. Smaller

NCs have a larger band-gap, which would correlate to a blue-shift in the excitonic absorption.^{3,12,13} However, in our system, as presented in Figure 3.3, this is not the case, and a red shift is prevalent. Further inspection in Figure 3.4 reveals that this red shift is also directly correlated with decreased area under the 1S peak.

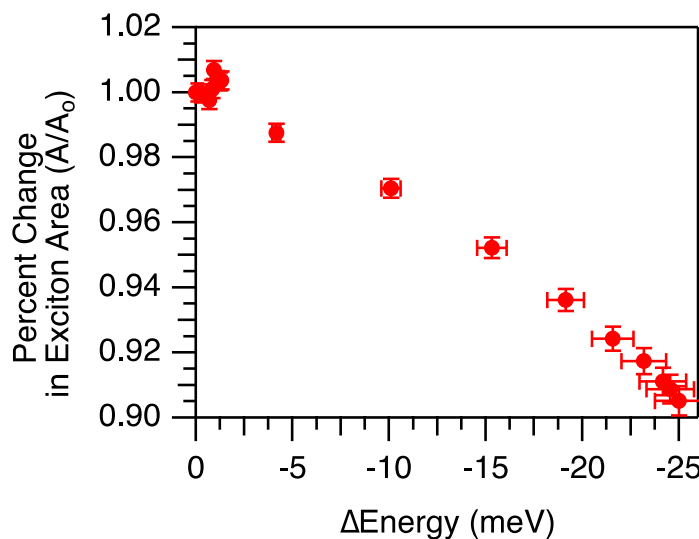


Figure 3.4 Correlation between the shift in exciton energy (~ 3.1 eV) with the change in the exciton area.

To gain further insight into the cause of this shift, ^1H NMR data collected in Chapter 2 can be used to elucidate the origin of these optical changes, as shown in Figure 3.5.

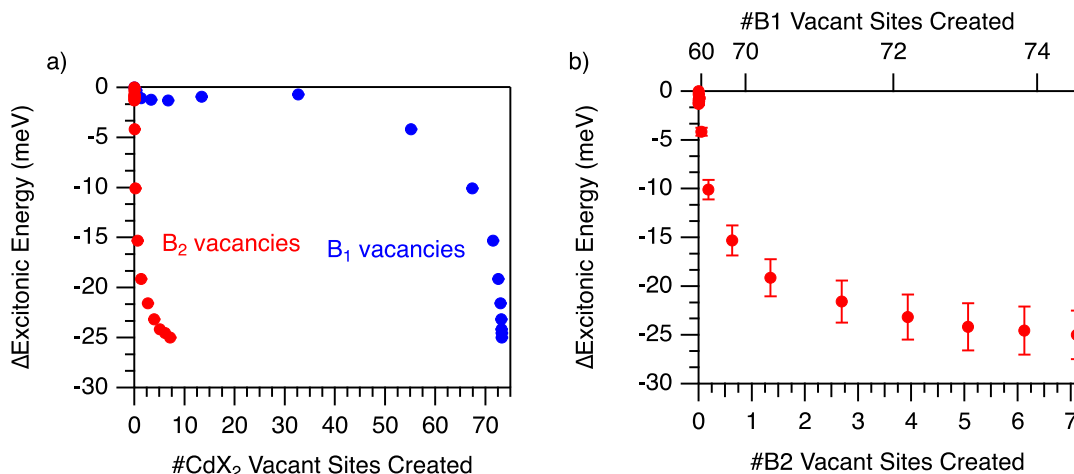
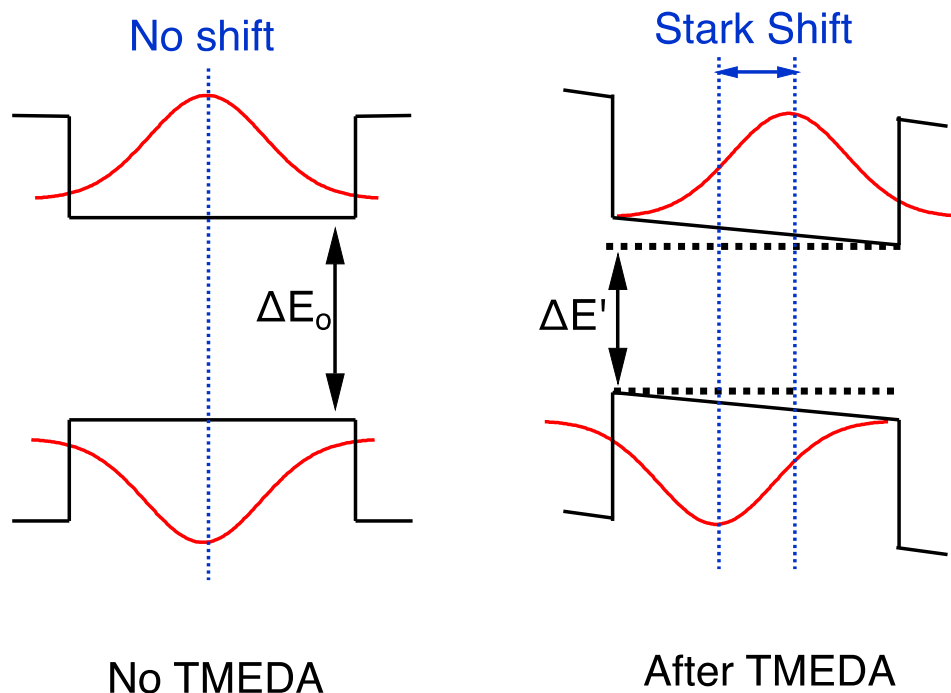


Figure 3.5 (a) Correlation of the creation of B_1 and B_2 vacancies with the shift in exciton absorption energy (~ 3.1 eV) during TMEDA titration. (b) Correlation of the creation of B_1 and B_2 vacancies with a shift in excitonic absorption. The top x-axis (B_1 vacant sites) is correlated to the bottom x-axis (B_2 vacant sites) to show the impact of creating a B_2 vacancy.

Figure 3.5 strongly correlates the creation of B_2 vacancies with this red shift, whereas the creation of B_1 sites seemingly does not start to affect the absorption energy until half of the B_1 sites are created. Red shifts observed in other NC systems have been previously attributed to a quantum-confinement Stark effect.^{14–17} In the presence of a constant external electric field, a red shift of the optical transition is induced.^{14,18,19} In our CdS system studied in this thesis, the red shift observed could be due to having a more ionic surface, leading to a Stark effect once the surface dipole is perturbed through removal of CdX_2 . As CdX_2 is removed from the surface, bare sulfur sites are exposed, polarizing the surface. This polarization of the surface can create a Stark shift where an electron can be stabilized at the surface, and this will lower the energy of the transition. Since the surface is polarized, it will also reduce the probability of a transition occurring, decreasing the absorption intensity. This Stark effect can be better visualized by utilizing the particle-in-a-box model, as shown in Scheme 3.1.



Scheme 3.1 Changes in the potential well after addition of TMEDA to the surface of CdS NCs.

As shown in Scheme 3.1, before the addition of TMEDA and without a surface dipole, the potential energies are flat (flat-bottom wells), and the maximum (center) of each wavefunction is aligned with each other. This perfect alignment of the wells defines the probability of absorption, as an excitation overlaps the two wavefunctions together. As a surface dipole is created (upon addition of TMEDA and creation of surface defects), an internal electric field is created inside the well, adding a linear potential energy term (i.e., Stark effect). Because of this internal electric field, the potential wells now have a slope, which will bring the electron to one side of the well (where the potential energy is lower) and the hole to the other side (where the potential energy is higher). This internal electric field separates the two wavefunctions and decreases their overlap, which is why the absorption cross-section decreases, and we see a red shift in the absorption energy.

3.3.2 Impact of Surface Defects on the 2nd Absorption Peak

The lowest energy absorption is altered with the removal of CdX₂ from the surface. However, we see an even more significant impact on the 2nd absorption peak. The 2nd absorption peak blue shifts and broadens as more CdX₂ is removed from the surface, as shown in Figure 3.1.

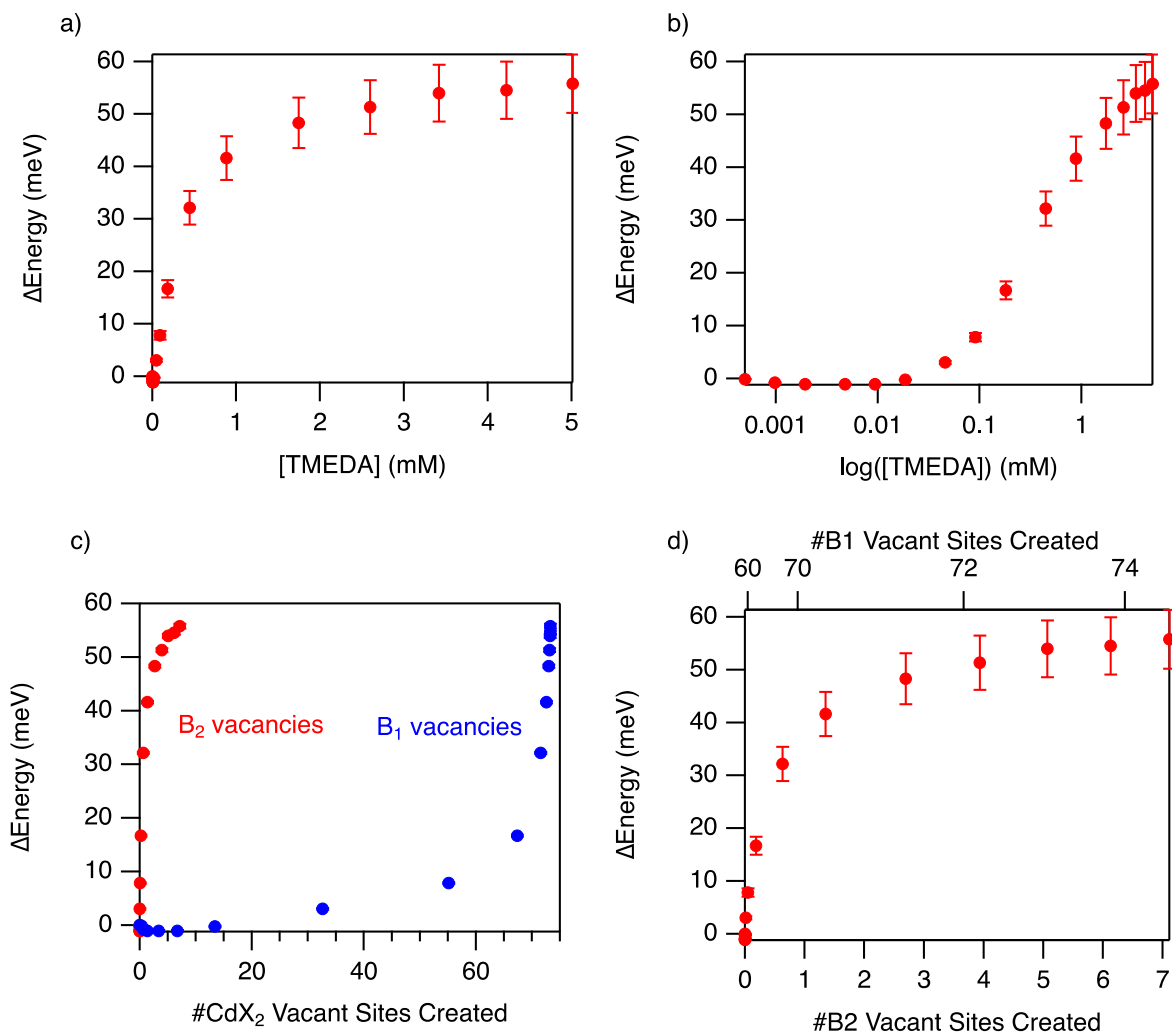


Figure 3.6 (a) The shift of the 2nd absorption energy (~ 3.4 eV) of 3.4 nm CdS (2 μM) during TMEDA titration. (b) The same figure as (a) but with a log scale for the x-axis. (c) Correlation of the creation of B₁ and B₂ vacancies with the shift in 2nd absorption energy during TMEDA titration. (d) Correlation of the creation of B₁ and B₂ vacancies with a shift in 2nd excitonic absorption. The top x-axis (B₁ vacant sites) is correlated to the bottom x-axis (B₂ vacant sites) to show the impact of creating a B₂ vacancy.

Figure 3.6 (a) quantifies the change in the 2nd absorption energy with each addition of TMEDA. Much like what was seen in the excitonic absorption energy change, there is no change in the 2nd absorption energy with small amounts of TMEDA added. However, once 45:1 TMEDA to CdS NCs is added, we start to see the blue shift of the peak occur. Figure 3.6 (c) and (d) show that this change is correlated to creating B₂ vacant sites and seems directly associated with the changes in the excitonic absorption peak, as shown in Figure 3.7. This shows the direct impact that the creation of defect sites has on the photophysical properties of CdS. Any 1 B₂ vacancy can significantly alter how NCs interact with light.

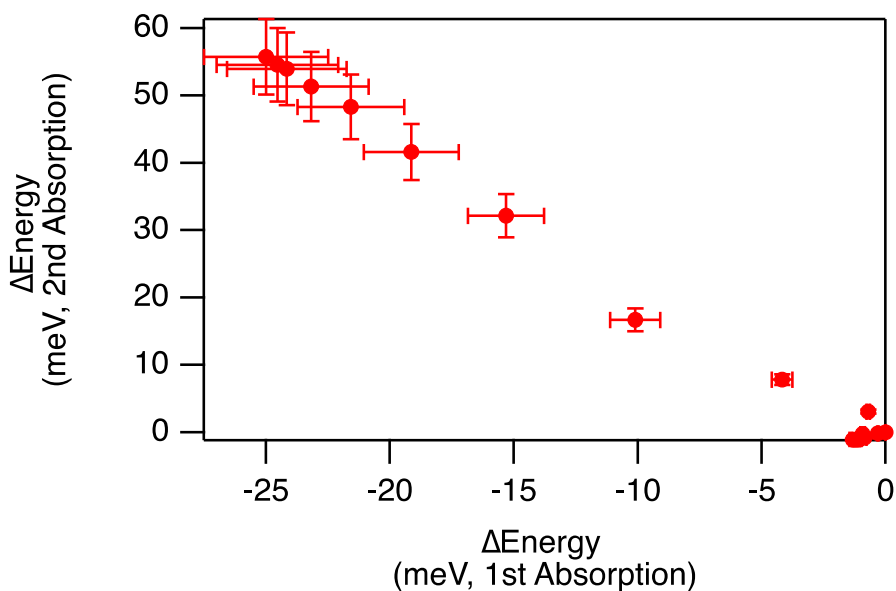


Figure 3.7 Correlation between the shift in the 2nd absorption energy (~3.4 eV) and the excitonic absorption shift (~3.1 eV).

The change of the 2nd absorption peak has been previously reported for CdSe nanocrystals due to the exchange of surface ligands from oleate to oleylamine capped NCs.³ In this study, the absorption change of the NC was monitored as the ligand exchange occurred, and it was shown that upon completed ligand exchange, the 2nd absorption peak decreased in intensity and red-

shifted in energy. The exact change was also seen in CdTe and CdS NCs. All the NCs studied within this paper are cadmium-rich NCs, meaning a thin layer of excess Cd^{2+} exists on the surface. This thin layer of Cd^{2+} on the surface creates a type II shell with its valence and conduction band lower than the core. Upon removing this type II shell, the $1\text{S}_e\text{-}2\text{S}_{3/2h}$ absorption is reduced by broadening, and the energy difference between the exciton and 2^{nd} absorption peak narrows. Other studies have shown that upon altering this Cd^{2+} shell on the surface, the 2^{nd} absorption is impacted; however, the origin of these changes remains unclear.^{3,20,21} In our studies here, we see the opposite occurring. The energy difference between the excitonic absorption and 2^{nd} absorption broadens as more CdX_2 is removed and is related to removing CdX_2 from the surface. Further investigation is required to understand the nature of these changes thoroughly; however, we can see that the change in both the excitonic and 2^{nd} absorption peaks is due to the creation of B_2 sites on the surface of CdS. Much like CdSe, the creation of B_2 sites significantly affects how CdS interacts with light.

3.4 Conclusions

Throughout this Chapter, we have demonstrated a direct correlation between the specific surface defects and changes within the absorption profile of CdS NCs. We show that the B_2 vacancies are correlated with a red shift in excitonic absorption and a blue shift and broadening of the $1\text{S}_e\text{-}2\text{S}_{3/2h}$ absorption. Our results support the proposal that any change to the Cd^{2+} layer on the surface can lead to drastic changes in the optical properties of the NC. The red shift seen in the excitonic absorption can be due to surface polarization upon removal of CdX_2 , stabilizing the electronic transition due to a Stark effect on the NCs. However, the direct cause of the broadening and blue shift of the 2^{nd} absorption peak needs to be investigated further. The result from this work further highlights the importance of the surface on optoelectronic properties. Any change in the surface, leads to drastic changes in how CdS interacts with light. Controlling and understanding the surface

is vital to prevent undesirable reduction in light absorption. To further fine tune CdS NC for specific applications (such as CdS as a light harvesting material), the surface and B₂ vacancies on the surface need to be controlled and well understood.

APPENDIX

SI 3.1 Effect of TMEDA addition to UV/Vis Spectra on 3.4 nm CdS Samples

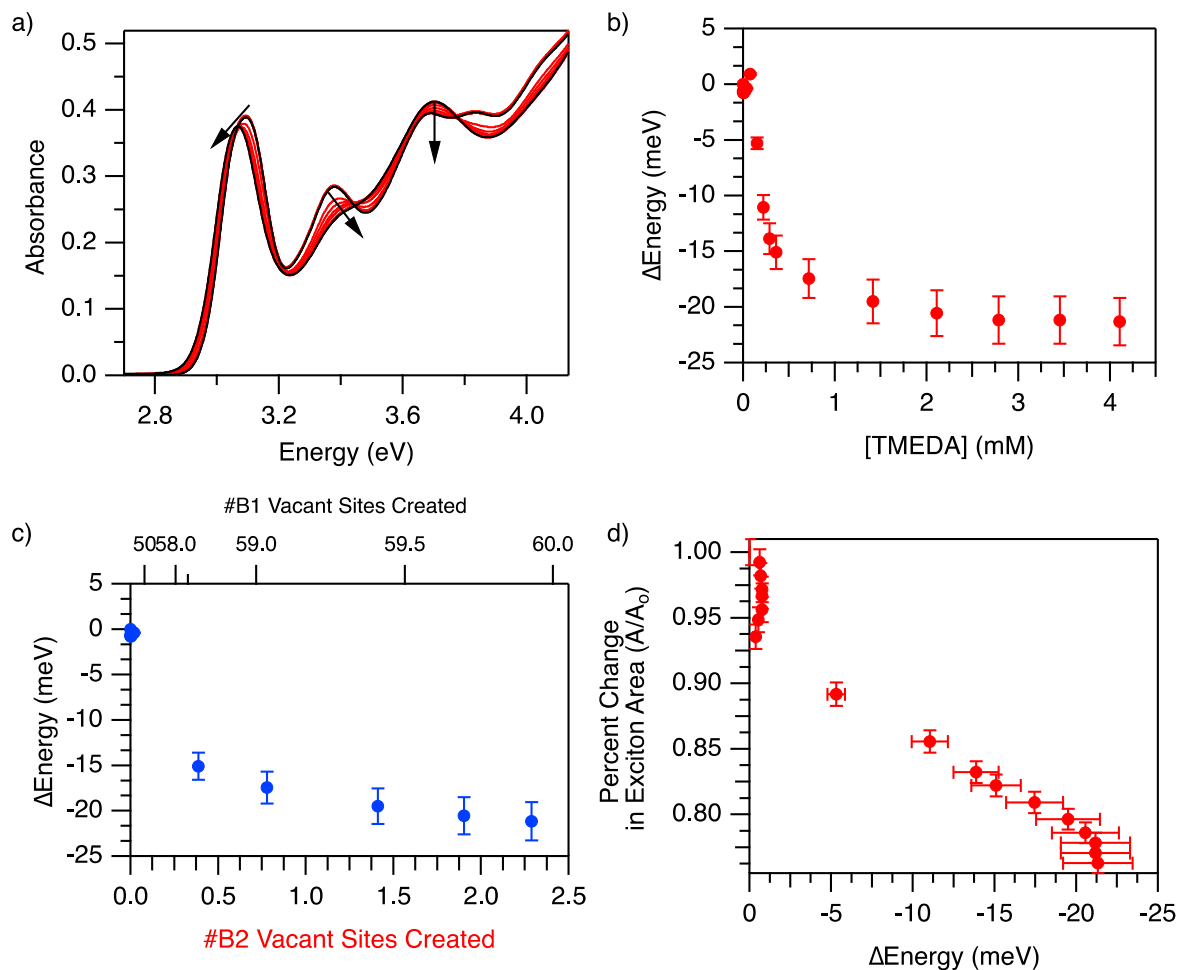


Figure SI 3.1 a) Absorption spectra of 3.4 nm CdS (trial 1,1 μM) with varying amounts of TMEDA. (b) The shift of the exciton absorption energy of 3.4 nm CdS during TMEDA titration. (c) Correlation of the creation of B1 and B2 vacancies with the shift in exciton absorption energy during TMEDA titration. (d) correlation between the shift in exciton energy with the change in the area of the exciton.

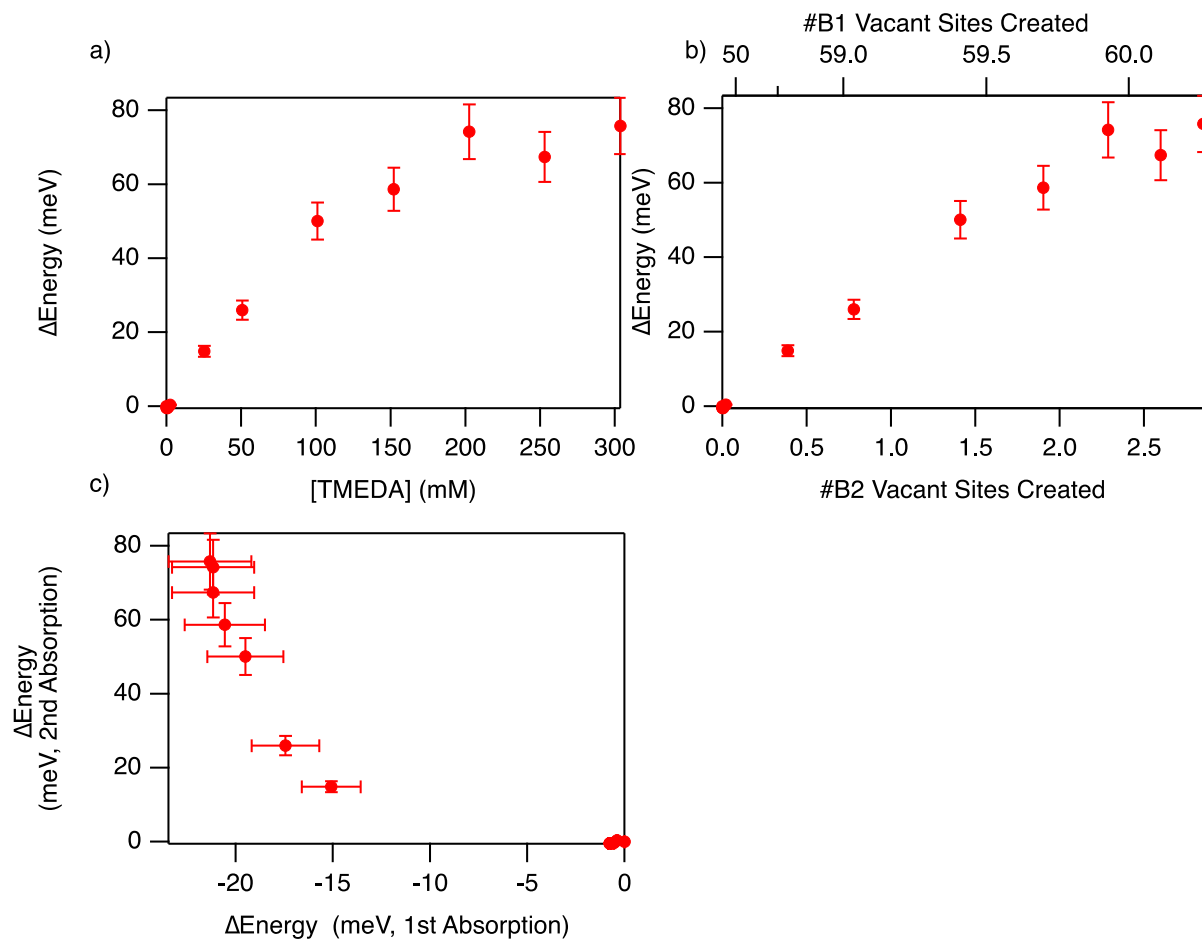


Figure SI 3.2 (a) The shift of the 2nd absorption energy of 3.4 nm CdS during TMEDA titration. (b) Correlation of the creation of B1 and B2 vacancies with the shift in 2nd absorption energy during TMEDA titration. (c) Correlation between the shift in 2nd absorption energy with the shift in the excitonic absorption.

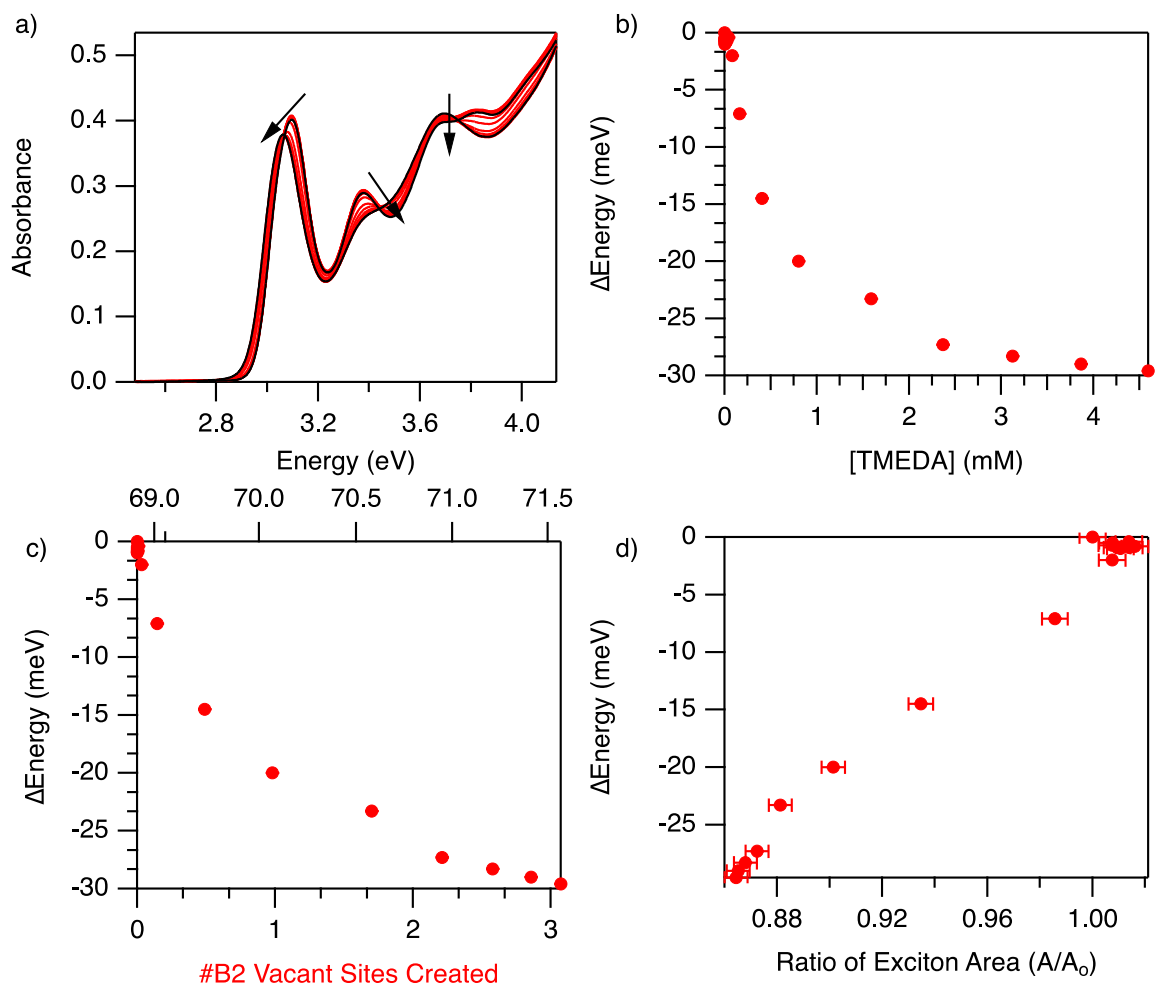


Figure SI 3.3 a) Absorption spectra of 3.4 nm CdS (trial 2,1 μM) with varying amounts of TMEDA. (b) The shift of the exciton absorption energy of 3.4 nm CdS during TMEDA titration. (c) Correlation of the creation of B1 and B2 vacancies with the shift in exciton absorption energy during TMEDA titration. (d) correlation between the shift in exciton energy with the change in the area of the exciton.

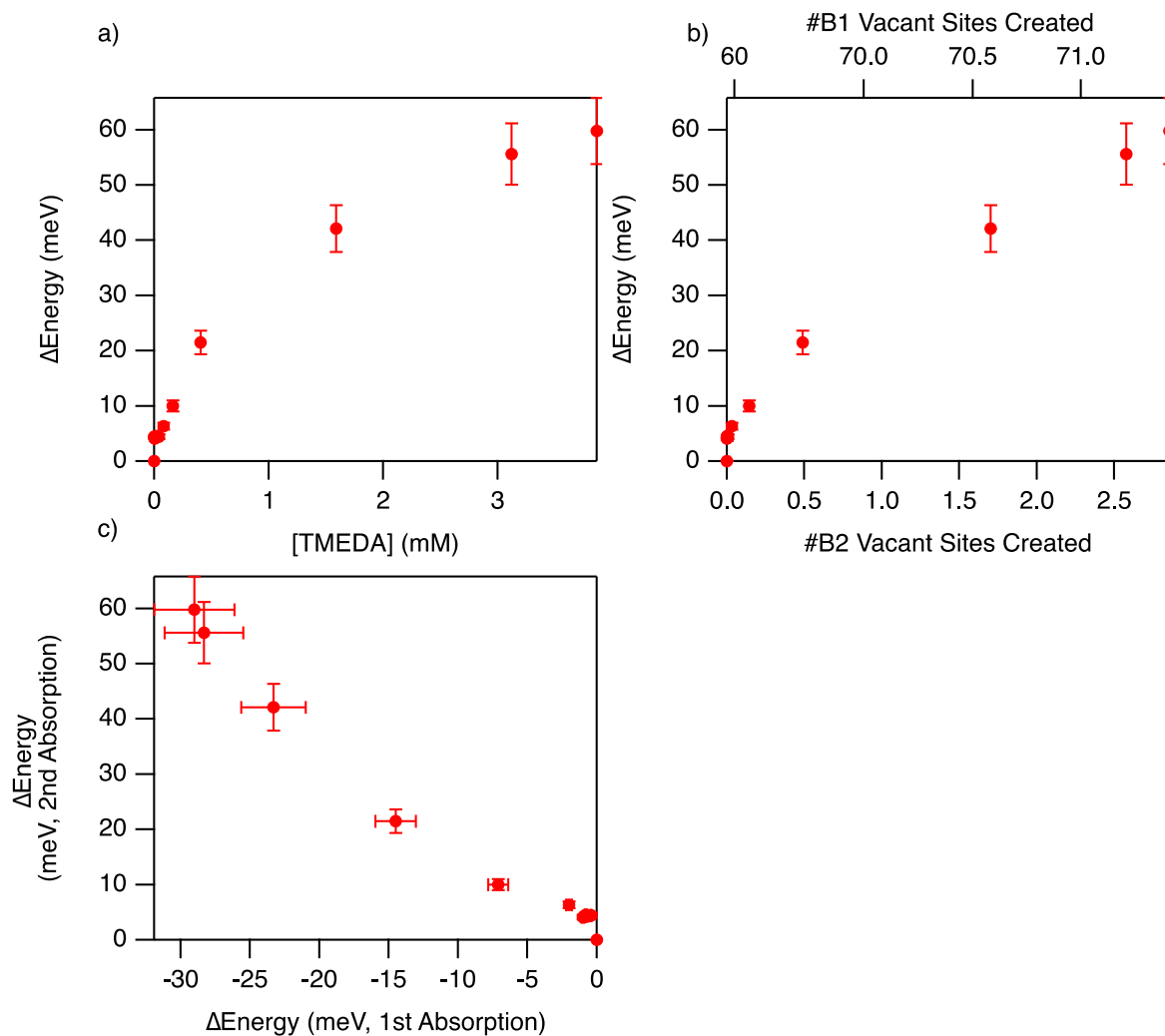


Figure SI 3.4 (a) The shift of the 2nd absorption energy of 3.4 nm CdS (trial 2,1 μ M) during TMEDA titration. (b) Correlation of the creation of B1 and B2 vacancies with the shift in 2nd absorption energy during TMEDA titration. (c) correlation between the shift in 2nd absorption energy with the shift in the excitonic absorption.

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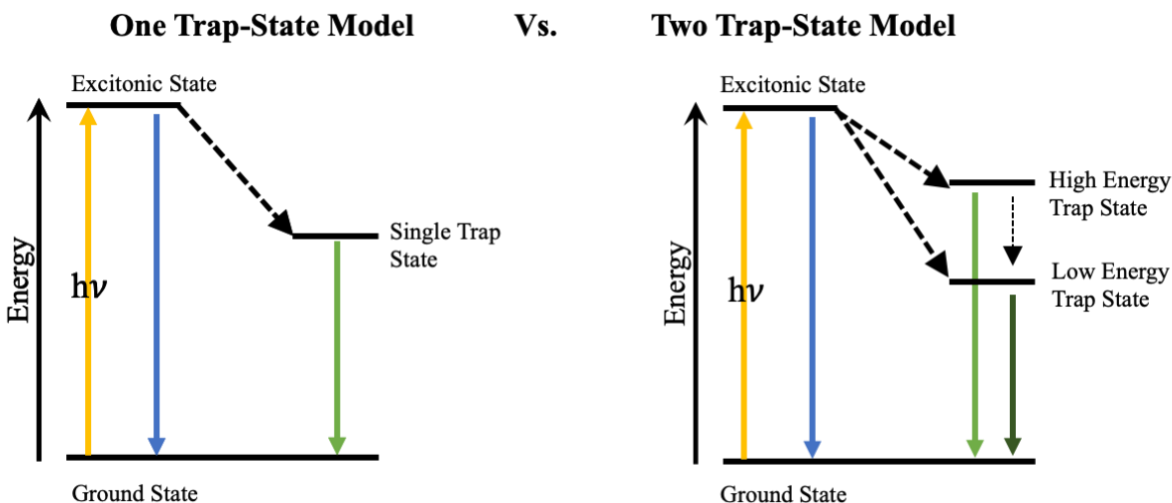
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Chapter 4: Correlating the Impacts of Surface Defects on Photoluminescence Efficiency

4.1 Introduction

The surface chemistry of NCs plays a central role in controlling optoelectronic properties for different applications.^{1–3} One of the primary tools to determine the impact of surface sites is photoluminescence (PL) spectroscopy. Steady-state PL spectroscopy can reveal information about the existence of mid-gap trap states at the NC surface. These mid-gap states can be either radiative or non-radiative. A decrease of intensity in band-edge PL can signal the formation of such mid-gap trap states due to surface defects. Many groups have used PL spectroscopy to investigate the impact of ligands on optical properties.^{1,4–8} Previous studies on CdSe NCs have correlated the creation of surface defects with the impacts on radiative recombination. These studies showed that Cd vacancies on (100) centers are efficient trapping centers and provided insights into the complexity of the surface of CdSe NCs.^{3,9} However, direct information on the trap states could not be obtained from these studies because the trap states were non-radiative for these CdSe NCs. CdS NCs differ because their trap states have efficient radiative recombination and fall in the visible region.^{9,10} Trap emission can be monitored to track any changes in the trap states caused by changes in the surface chemistry. Past studies on CdS NCs have focused on characterizing trap PL states using low-temperature PL and PL lifetime measurements.^{2,7,10–15} From these studies, it was determined that trap PL is due to trapping either an electron or a hole and its following recombination.^{7,10,16–18} The Kambhampati group further studied the surface chemistry of CdS through low-temperature measurements on the emission of trap states. However, the role of ligands was not considered.^{19–22}



Scheme 4.1 Comparison of the one trap-state model vs. the two trap-state models. The blue arrow depicts excitonic emission, where the green-colored arrows represent trap state emission.

There are two different models of trap states that need to be discussed to gain a more insightful picture of CdS NC trap states: 1) single-state model and 2) two-state model as shown in Scheme 4.1. There has been emerging research in the last decade to support the existence of each model. In NCs, the broad, low-energy PL from the surface has traditionally been understood as coming from a distribution of midgap defect states at the surface.^{12,17,23,24} By employing capping ligands unto the surface of the NC, the surface emissions are eliminated.²⁵ However, low-temperature PL experiments revealed that the surface PL increases in intensity at low-temperature with a form distinct from band-edge core excitonic PL, suggesting thermal population exchange between surface states and band-edge core exciton.²⁶ However, the surface PL was redshifted from the core more than what would be expected for the scenario just described, contradicting the idea that there is a distribution of deep trap states, but instead coming from a single surface state that is coupled to the excitonic state.^{18–22} However, this model does not consider different surface stoichiometries, the density of trap states, or the impact of ligands (and different types of defects) into account.²¹

The two-state model was utilized upon disturbing the surface by changing the ratio of sulfur to cadmium on the surface. These studies presented by Li et al. have shown that the trap emission of CdS NCs can be divided into two different emission bands centered around 540 nm and 650 nm.²⁷ The intensity of these bands can be modulated through change the ratio of sulfur and cadmium: the lower energy band (650 nm) is not as sensitive to the ratio of sulfur to cadmium, whereas the higher energy band (540 nm) is surface feature dependent and becomes more intense with lower sulfur to cadmium ratio on the surface.²⁷ More studies have shown that the low energy trap state is correlated to sulfur vacancies and is due to the recombination of holes in the balance band and electrons trapped at S^{2-} sites.^{2,27-29} Whereas the high energy trap states are typically attributed to shallow traps caused by surface states and depend greatly on particle size and surface composition.^{26,27,30,31}

In Chapter 2, we distinguished two different types of surface defects on CdS NCs. These surface defects were correlated to a specific surface type, and we were able to model the creation of each defect with the addition of TMEDA. In this Chapter, we associate each defect with its impact on the NCs light emission. We show that creating each type of defect, B₁ or B₂, impacts the PL excitonic and trap emission in a specific manner and model our trap emission with the two-state model described above.

4.2 Experimental Details

For details about the synthesis and optical spectroscopy characterization of CdS NCs, please see Chapter 2, Section 2.

4.2.1 Sample Preparation for Photoluminescence Spectroscopy

Samples for photoluminescence spectra measurements were prepared by diluting 30 μ L samples of 133 μ M CdS NCs to 2 mL with toluene ($[CdS]=2.0 \mu M$). TMEDA was added to each CdS

sample to ensure that the same number of TMEDA to NC equivalents was added compared to the ^1H NMR experiments in Chapter 2. This was done to ensure that any changes in PL could be correlated to specific numbers of B_1 or B_2 sites created. Each sample was given 30 minutes to reach equilibrium, and samples were stirred during collection.

4.3 Impact of Surface Defects on Exciton Photoluminescence Efficiency

From Chapter 2, we determined the existence of two different sites on the surface of CdS NCs, and each site has its energetics of CdX_2 binding. With this information now, it is possible to correlate the creation of these defects to their impact on the PL of CdS NCs. Compared to CdSe NCs, CdS NCs have radiative emission of both their excitonic and trap states allowing us to correlate the impact of surface defects on both the exciton and trap states. As shown in Figure 4.1, the addition of TMEDA to CdS NC suspensions does indeed affect both excitonic PL (~ 2.9 eV) and trap PL (centered around 1.8-2.1 eV).

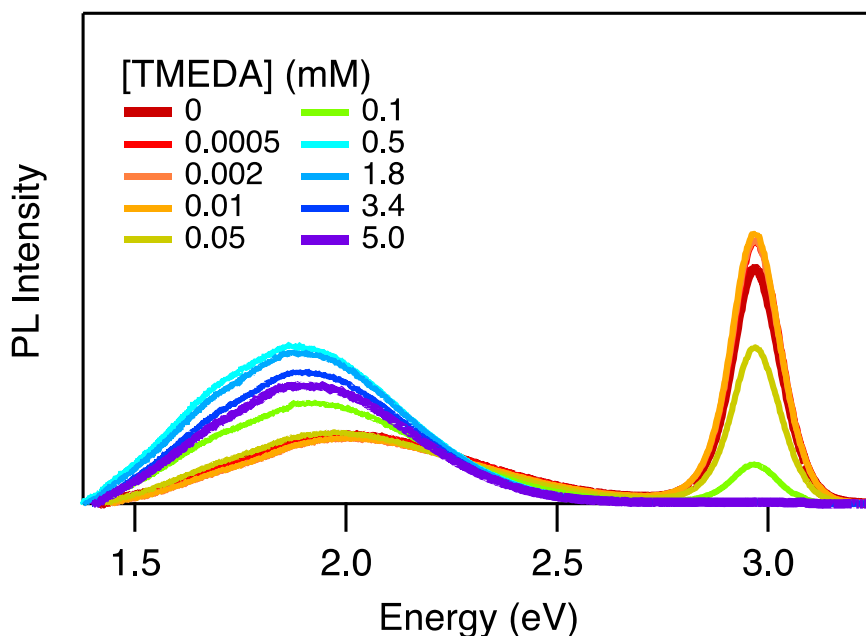


Figure 4.1 PL spectra ($\lambda_{\text{exc}}=3.3$ eV) of 3.4 nm CdS NCs (2 μM in toluene), with varying amounts of TMEDA (0-5 mM).

This section focuses on the change in the excitonic PL as TMEDA is added to the system. Figure 4.1 shows that the addition of TMEDA to CdS NCs affects both excitonic and trap state PL emission. To start, we will focus on the impact of surface defects on the excitonic PL emission.

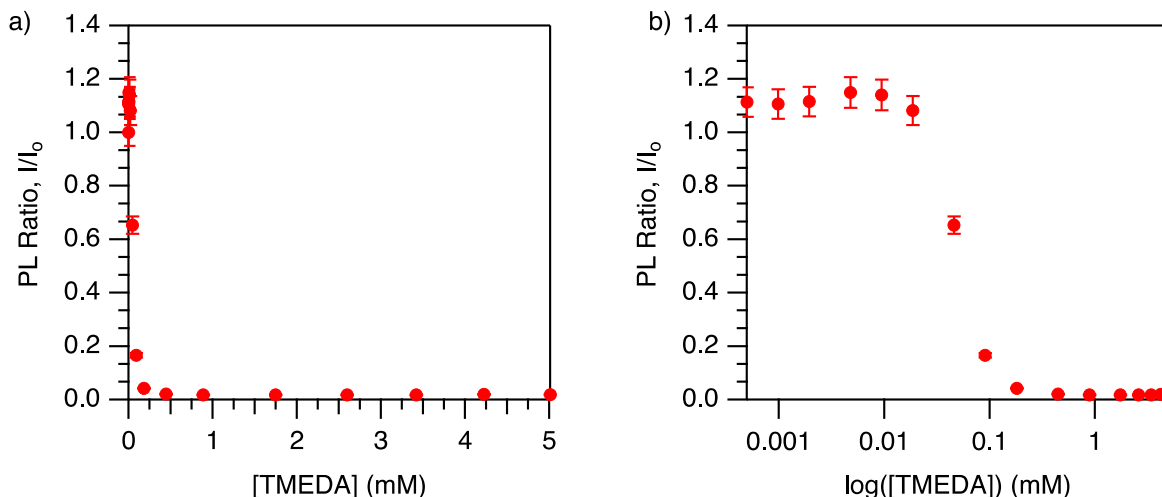


Figure 4.2 (a) PL ratio of 3.4 nm CdS (2 μM) with varying amounts of TMEDA added (0 – 5 mM). (b) Same figure as (a), but with [TMEDA] in a log scale to better show the initial changes in the PL ratio with small amounts of TMEDA added.

Figure 4.2 shows that the addition of TMEDA to CdS NCs initially increases the excitonic PL intensity. However, when 25:1 TMEDA to NC is added, the PL intensity is dramatically quenched, suggesting that trap states are created. This initial increase of the excitonic PL intensity could be due to the changes in existing trap states, which could increase the PL of the excitonic state. However, based on several trials on other 3.4 nm CdS NCs (as shown in the SI), it seems that the magnitude of this initial increase is sensitive to sample preparation and synthesis. More studies would be required to correlate the direct cause of this initial increase, and we instead focus our attention on the quenching of the exciton upon adding TMEDA to the solution.

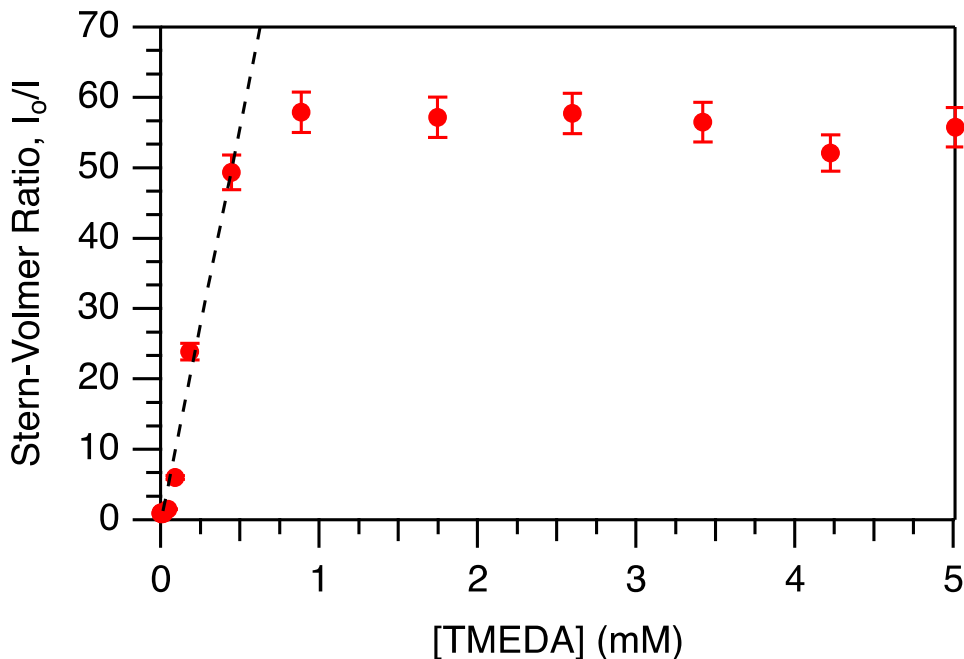


Figure 4.3 Quantification of CdS quenching using TMEDA reported as the Stern-Volmer ratio. The dashed line represents the efficiency of PL quenching, $K_{SV}=112 \pm 5 \text{ mM}^{-1}$.

To better quantify the PL quenching efficiency, the Stern-Volmer formalism is used, whereby the reciprocal of the PL intensities is normalized to the PL intensity in the absence of the quencher (I_0), as shown in Figure 4.3:

$$\frac{I_0}{I} = 1 + K_{SV}[Q] \quad \text{eq. 4.1}$$

where $[Q]$ is the concentration of the quencher species (TMEDA), and K_{SV} is a constant that characterizes the efficiency of PL quenching, $K_{SV}=112 \pm 5 \text{ mM}^{-1}$ for the data in Figure 4.3. It is important to note here that TMEDA is not the direct quencher itself but rather acts indirectly by creating CdX_2 vacancies on the surface that are trap centers.^{3,32,33} Since the direct impact of TMEDA on the displacement of CdX_2 has been fully characterized in Chapter 2, a direct connection between the PL efficiency and the surface composition can be made and is given in Figure 4.4.

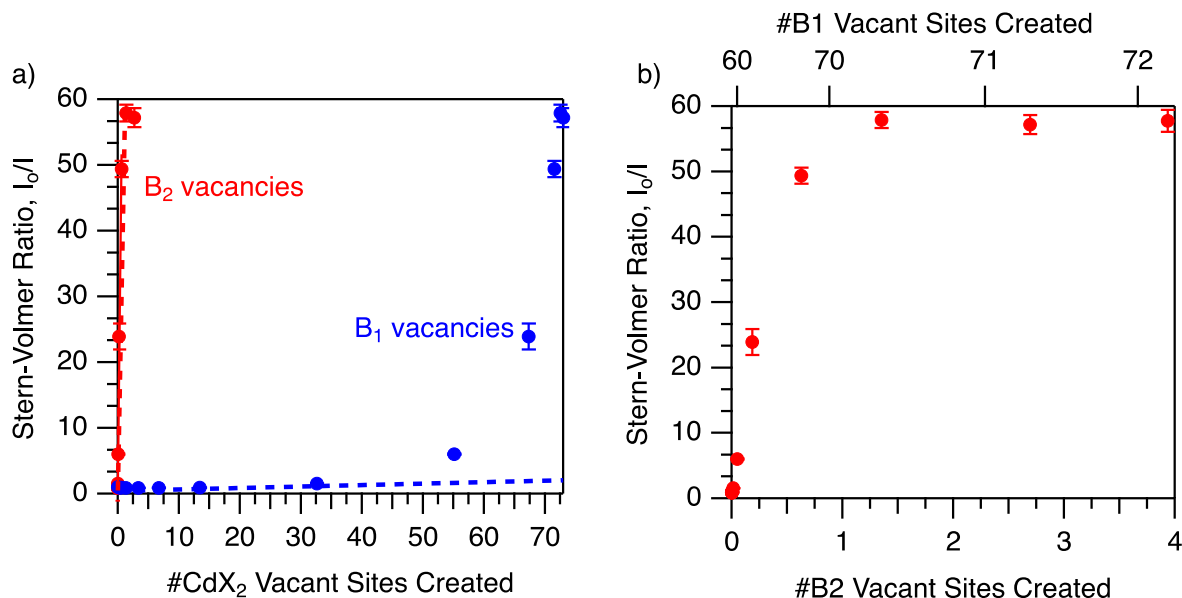


Figure 4.4 (a) CdS NC PL quenching efficiencies of each type of vacancy. (b) Correlation of the creation of B_1 and B_2 vacancies with quenching of exciton photoluminescence during TMEDA titration. The top x-axis (B_1 vacant sites) is correlated to the bottom x-axis (B_2 vacant sites) to show the impact of creating a B_2 vacancy. PL quenching seems to be controlled by the creation of B_2 vacant sites. The same quenching effect for the creation of B_2 sites is not seen until at least 60 B_1 vacant sites have been created.

Similar to what was seen in CdSe NCs, there is a strong correlation with efficient quenching when B_2 sites are created ($K_{\text{SV},\text{B}_2} = 79 \pm 5 / \text{B}_2 \text{ vacancy}$) compared to when B_1 sites are created ($K_{\text{SV},\text{B}_1} = 0.02 \pm 0.003 / \text{B}_1 \text{ vacancy}$).^{3,9} The significant quenching seen with large displacement at B_1 sites is actually due to the creation of B_2 sites that is happening at the same time. The efficiency of a B_2 vacancy is nearly 4000 times larger than that of a B_1 vacancy. This stark contrast between each vacancy highlights that not all surface defects are equivalent, even though both defects are from removing a CdX_2 species. Even though it is harder to create B_2 vacancies on the surface (as explained in Chapter 2), creating a B_2 vacancy leads to a more significant impact on the PL quenching. The excitonic recombination efficiency is extremely sensitive to the creation of B_2 vacancies, and if these vacancies were to persist after synthesis, the PLQY of the exciton would be diminished. Without the strong thermodynamic stability of CdX_2 bound to these sites, the use

of Cd-based Z-type ligands to passivate undercoordinated sulfur sites would become unsuccessful in controlling non-radiative recombination processes from defect sites.

4.4 Impact of Surface Defects on Trap Photoluminescence Efficiency

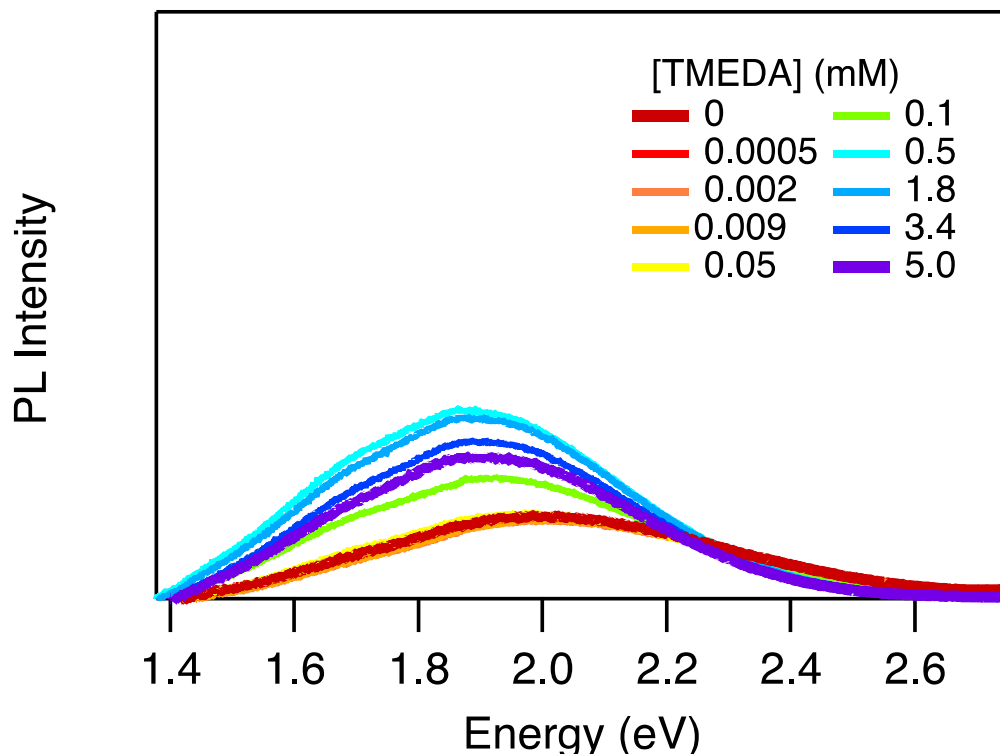


Figure 4.5 PL spectra of the trap states of 3.4 nm CdS (2 μ M), with varying amounts of TMEDA.

Upon addition of TMEDA to suspension of CdS NCs, the trap state emission is changed in two significant ways: 1) increase of PL efficiency of the trap state and 2) a red shift of trap state emission as shown in Figure 4.5. The cause of these changes could be due to a change in a singular surface trap state distribution or could be a combined change in the emission of two (or more) transitions where the energy of these transitions does not change, but the intensities vary with TMEDA. The following analysis in this Chapter attempts to determine the source of these changes.

4.4.1 Single-Trap State Model

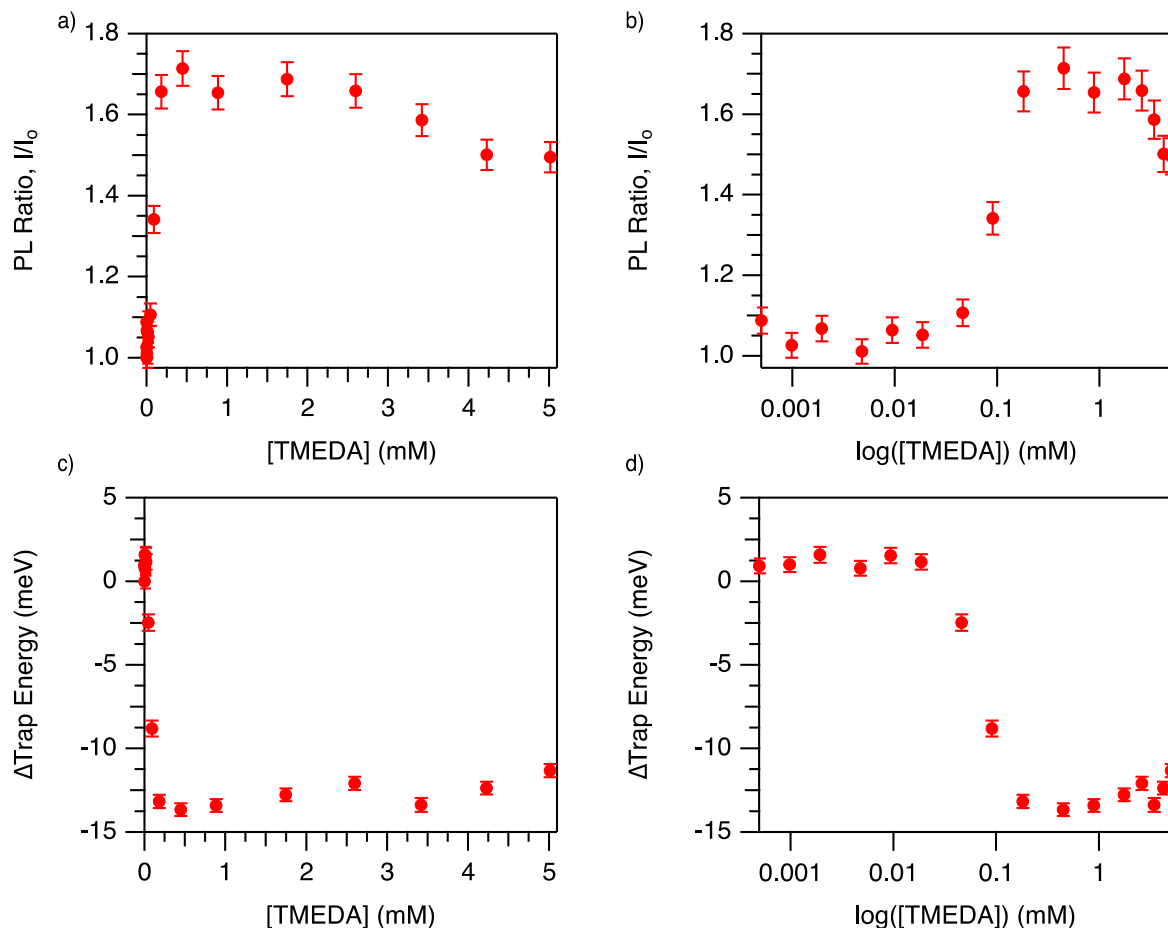


Figure 4.6 (a) Quantification of CdS ($2\ \mu\text{M}$) trap-state quenching using TMEDA, reported as the PL ratio. (b) Same figure as (a), but with [TMEDA] in a log scale to better show the initial changes in the PL ratio with small amounts of TMEDA added. (c) Quantification of CdS trap-state energy shift throughout titration with TMEDA. (d) The same figure as (c), but with [TMEDA] in a log scale to better show the initial changes in energy with small amounts of TMEDA added.

Figure 4.6 summarizes all the changes that happen to the trap-state emission throughout the titration with TMEDA if treated as a singular trap-state changing throughout. As shown in Figure 4.6 (a), upon the addition of TMEDA to the suspension, we see an overall increase in the PL efficiency of the trap-states. Upon closer inspection in Figure 4.6 (b), we see that a small amount of TMEDA virtually does not affect the PL intensity. However, after 90:1 TMEDA to NC is added, the PL intensity increases with each addition of TMEDA. This rapid increase stops once the

TMEDA: NC ratio reaches 250:1. In terms of the change in energy, we see very similar behavior at first; small amounts of TMEDA have no effect on the energy of trap-state emission, however, once 90:1 TMEDA has been added, we start to see the red shift start to happen. Since we've already built a detailed picture about the specific defect sites created upon the addition of TMEDA, we can now start to correlate these changes in the PL emission intensity and energy to the surface composition as shown in Figure 4.7 and Figure 4.8, respectively.

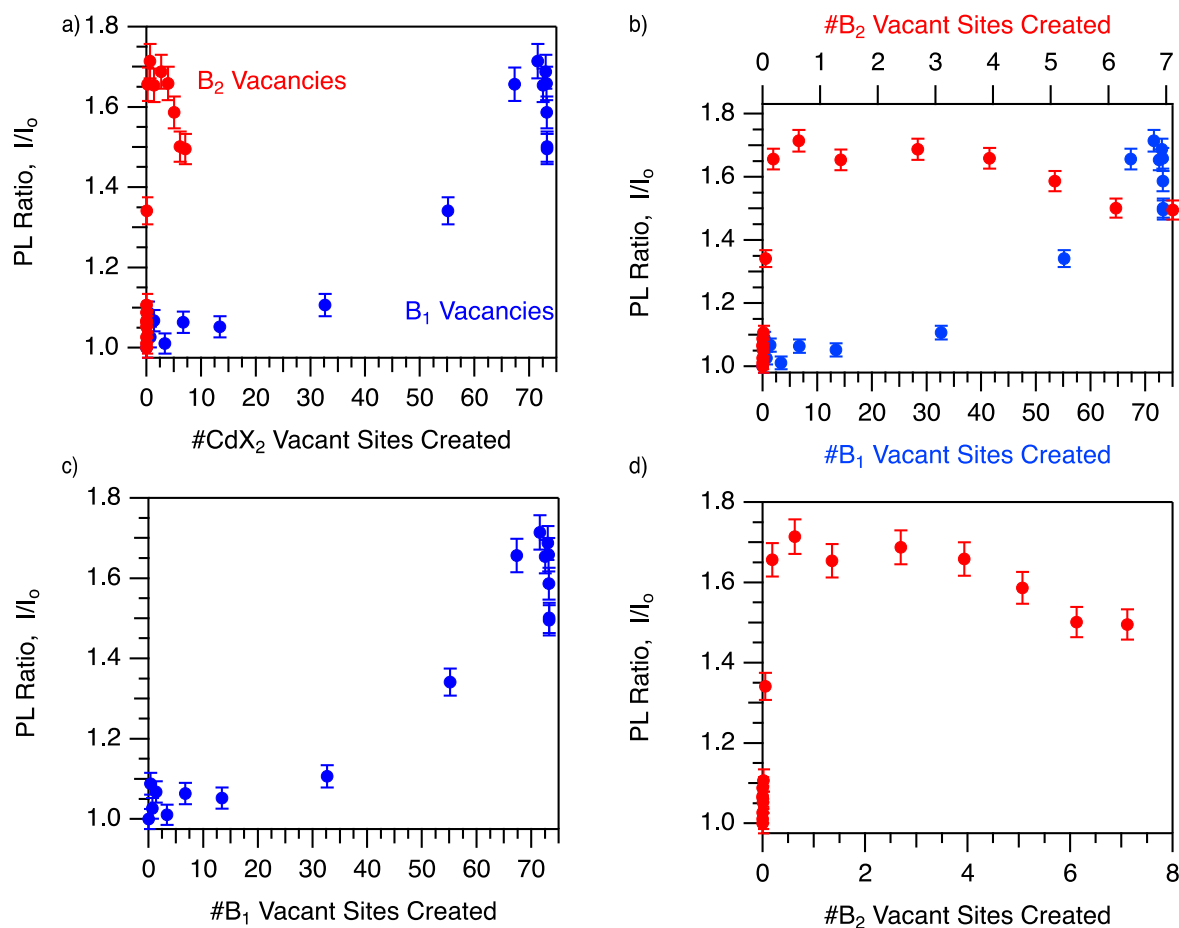


Figure 4.7 (a) Correlation of the creation of B_1 and B_2 vacancies with the change in the PL Ratio of trap state PL during TMEDA titration. (b) Correlation of creation of specific defect types with the change in the PL ratio. The top x-axis represents the creation of B_2 vacant sites, and the bottom x-axis represents the creation of B_1 vacant sites. (c) Correlation of the creation of B_1 vacant sites to the change in the PL ratio. (d) Correlation of the creation of B_2 vacant sites to the change in the PL ratio.

At the beginning of the titration, as B₁ vacant sites are being created, we can see a slight increase in the PL emission, as shown by Figure 4.7(c). However, most of the increase of the PL emission is due to the creation of B₂ vacancies on the surface. Figures 4.7 (a) and (d) support this idea due to the rapid increase in PL emission as soon as B₂ vacancies are started to be created. Once many vacant sites are created, regardless of if they are a B₁ or B₂ vacant site, the total PL emission starts to decrease, as shown by Figure 4.7 (c) and (d).

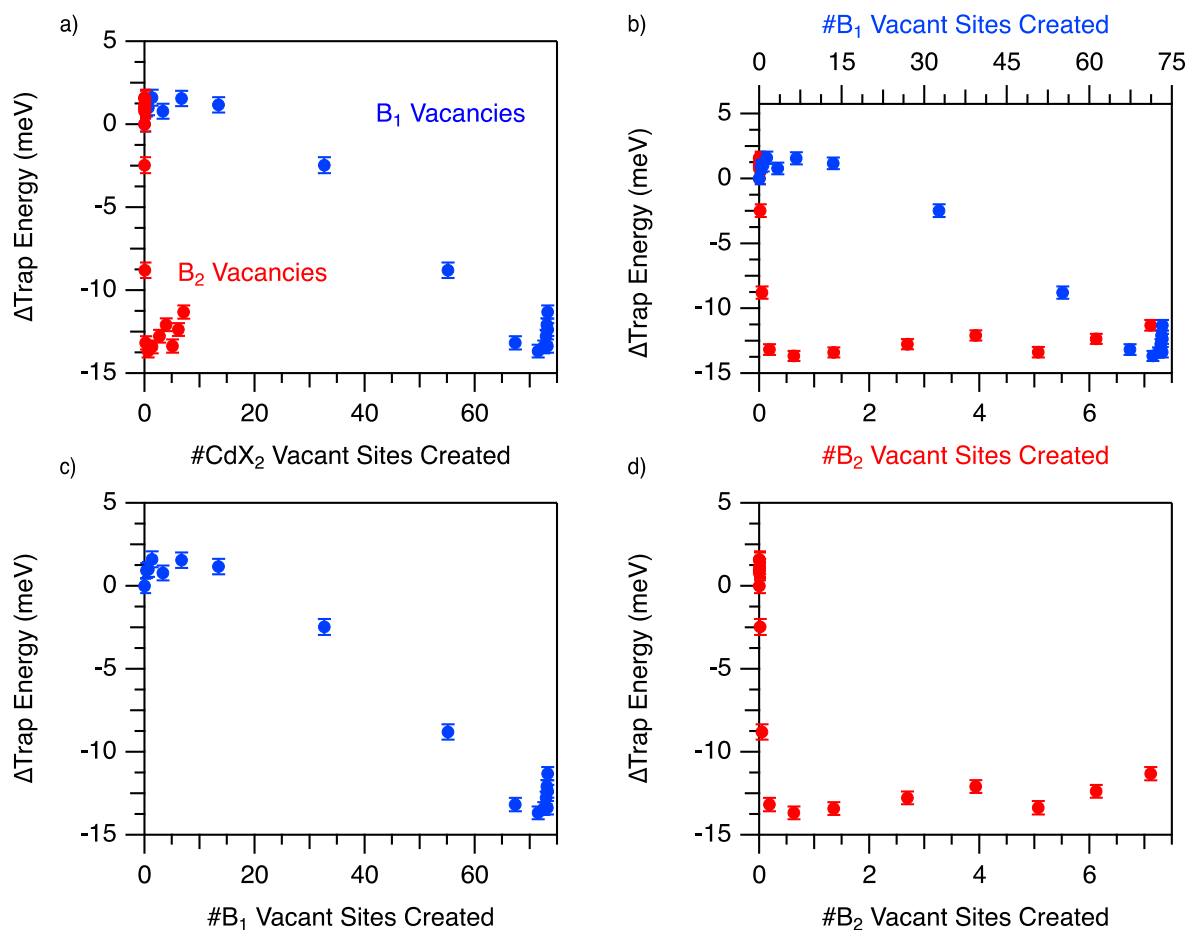
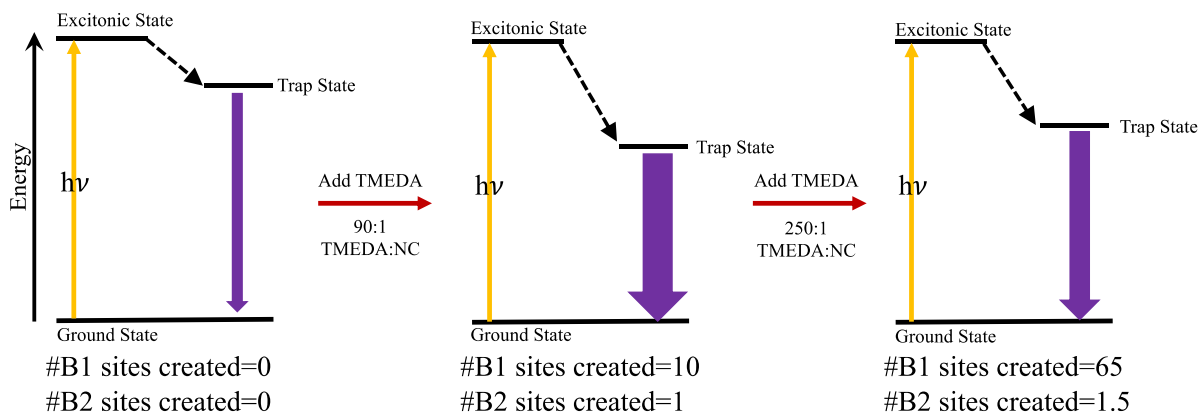


Figure 4.8 (a) Correlation of the creation of B₁ and B₂ vacancies with the change in the energy of trap state PL during TMEDA titration. (b) Correlation of creation of specific defect types with the change in the energy of trap state PL. The top x-axis represents the creation of B₂ vacant sites, and the bottom x-axis represents the creation of B₁ vacant sites. (c) Correlation of the creation of B₁ vacant sites to the change in the energy of trap state PL. (d) Correlation of the creation of B₂ vacant sites to the change in the energy of trap state PL.

The red shift that is seen throughout the titration can also be correlated to the creation of specific defect sites, as shown in Figure 4.8. As shown in Figure 4.8 (a) and (b), we see that the red shift is at first caused to the creation of B₂ vacant sites. The creation of B₁ vacant sites has no initial impact on the emission energy. As shown by Figure 4.8 (c), there is no initial change in the energy with the creation of ~15 B₁ vacant sites. However, Figure 4.8 (d) shows that 1 B₂ vacant site creation causes the immediate red shift. Once more than 60 B₁ vacant sites are created, the emission energy starts to slightly blue shift, however, the magnitude of the blue-shift is small (the magnitude of the blue shift is around 1 meV, much smaller than the overall red shift in the emission which is 13 meV).

With the analysis above in hand, we can now build a picture to help capture the changes in trap-state PL with each addition of TMEDA, as shown in Scheme 4.2.



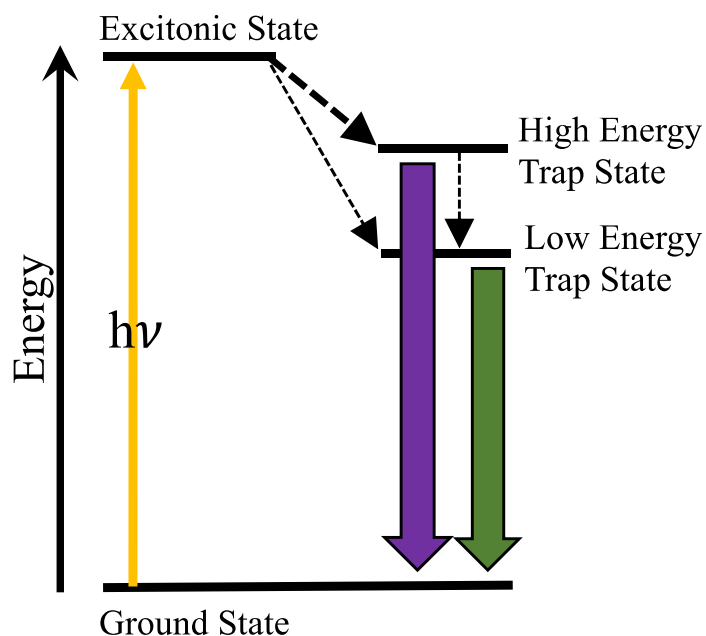
Scheme 4.2 Summary of the effects of TMEDA addition to a suspension of CdS NCs in a single trap-state model.

Upon creating just 1 B₂ vacant site, we see the red shift of the trap emission and an increase in the PL emission. The impact of just one B₂ vacant site cannot be understated as it has great impacts on the trap-state PL emission and must be controlled to tailor CdS NCs for specific applications. However, just as important is that upon creating 65 B₁ vacant sites, we start to slightly blue shift,

and the trap state becomes slightly less emissive. Overall, the impact of the above results dictates how important it is to control the surface composition of NCs. To better validate this is an accurate model to describe the trap state emission of CdS NCs, temperature-dependent PL would be required, and these studies were not done for this work.

4.4.2 Two-Trap State Model

As stated earlier in this Chapter, there are two prevalent models of describing the trap state PL emission in CdS NCs. The previous section treated the trap states as a singular type of emissive defect that changes upon modification of the surface. However, during the titration of TMEDA to the surface, we are displacing CdX_2 moieties from the surface, effectively changing the cadmium to sulfur ratio on the surface. With this in mind, we attempt to model the changes in the PL ratio and energy (as shown in Figure 4.6) in this section as two distinct sites, each with its energy that does not change throughout the titration but rather changes in intensity, as shown by Scheme 4.3.



Scheme 4.3 Summary of the two-state model.

To elucidate the energy of each trap state within the overall trap PL emission, a double gaussian global fit was done for all titration samples. The equation used to fit each graph was as follows:

$$f(x) = Y_{\text{off}} + a_1 \times \exp\left(\left(-\frac{x-X_{01}}{W_1}\right)^2\right) + a_2 \times \exp\left(\left(-\frac{x-X_{02}}{W_2}\right)^2\right) \quad \text{eq. 4.2}$$

Y_{off} is a constant baseline, X_{01} and X_{02} are the energies of each trap state, W_1 and W_2 are the widths of each gaussian for each trap state, and a_1 and a_2 are the amplitudes of each gaussian. For each fit, the energies, widths, and offset were linked together so that the only change in each gaussian was the amplitude of each gaussian. The resulting parameters (shown in Table 4.1) of each fit were used to model each gaussian on each graph.

Table 4.1 Parameters used in fit from eq. 4.2.

Parameter	Value
X_{01}	1.87 eV
X_{02}	2.15 eV
W_1	0.33 eV
W_2	0.48 eV

There are two distinct trap states with their energies that compose the overall trap emission. Trap state 1 is the lower energy trap state, and trap state 2 is the higher energy trap state. To avoid confusion between B_1 and B_2 and trap states 1 and 2, each trap state will be called either high energy or low energy trap. Figure 4.9 shows some of the results from the fitting procedure done.

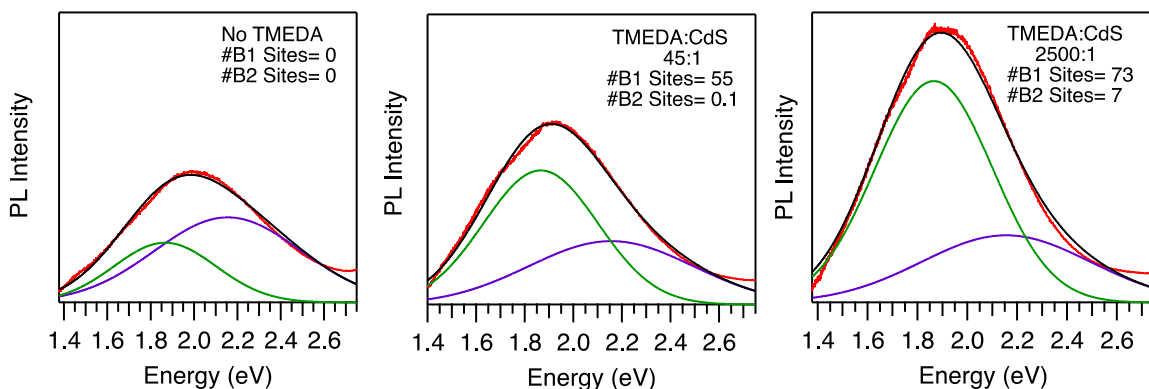


Figure 4.9 Modeling of each trap state gaussian under that trap emission of 3.4 nm CdS NCs (2 μ M). The red line is the original trap state emission. The green and the purple gaussian represent the low and high energy trap states, respectively. The black line models the double gaussian fit.

As can be seen from Figure 4.9, throughout the titration, as more CdX_2 is displaced from the surface, the amplitude of each gaussian changes. The fraction of the total PL ratio change in terms of the high and low energy trap states is shown in Figure 4.10.

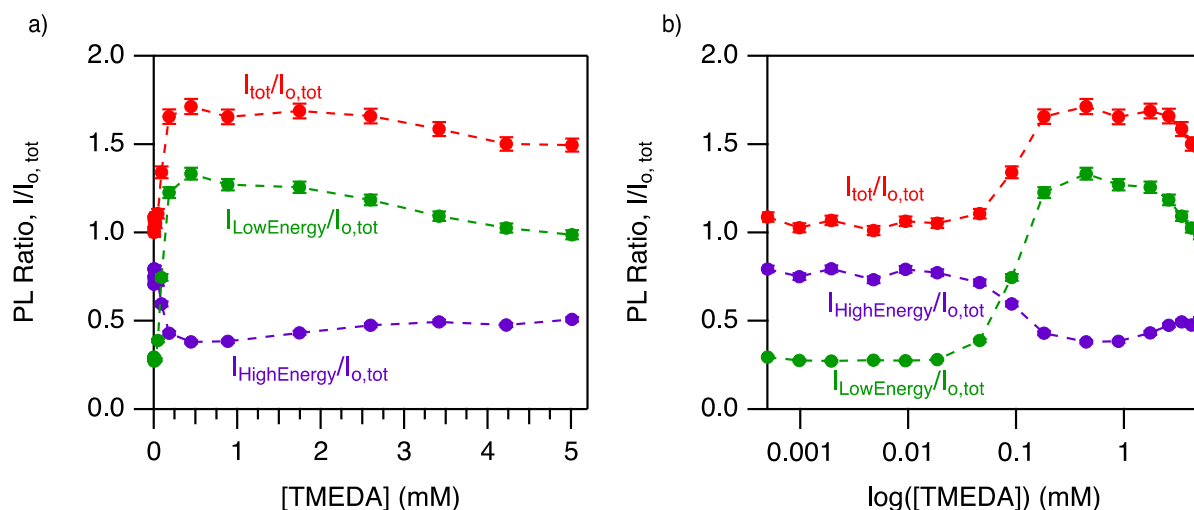


Figure 4.10 (a) The change in PL trap emission for the total, high energy, and low energy trap states normalized to the total initial PL trap emission for CdS NCs (2 μ M). (b) Same figure as (a), but with [TMEDA] in a log scale to better show the initial changes in the PL ratio with small amounts of TMEDA added.

Before any TMEDA has been added into the sample at the beginning of the titration, the high energy trap state slightly dominates the overall trap state emission. As more TMEDA is added and

some defect sites are created, the low energy trap state quickly becomes brighter and dominates the trap state emission, as shown in Figure 4.10. With the sense of how the total trap PL emission is changed with each trap state, we can now investigate how each trap state is affected throughout the titration.

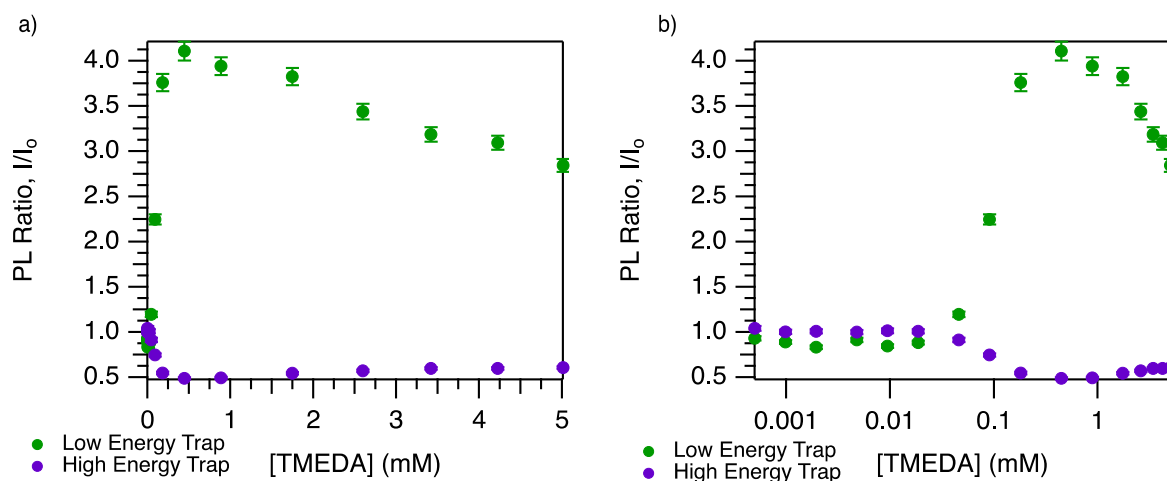


Figure 4.11 (a) The PL ratio of each trap state throughout titration with TMEDA. (b) Same figure as (a), but with [TMEDA] in a log scale to better show the initial changes in the PL ratio with small amounts of TMEDA added.

With small amounts of TMEDA added, there are no changes in either the high or low energy trap states, which is expected because, as explained earlier, no change in the PL intensity is reported for low TMEDA amounts. However, once we reach 45:1 TMEDA to CdS ratio, we start to see the changes in each trap state occur, as shown in Figure 4.11 (b). At this point, we see the low energy trap increase in intensity more than the high energy trap decreases in intensity. This alludes to the fact that the changes caused by creating defects do not impact each trap state equally, and this needs to be considered, as shown in Figure 4.12.

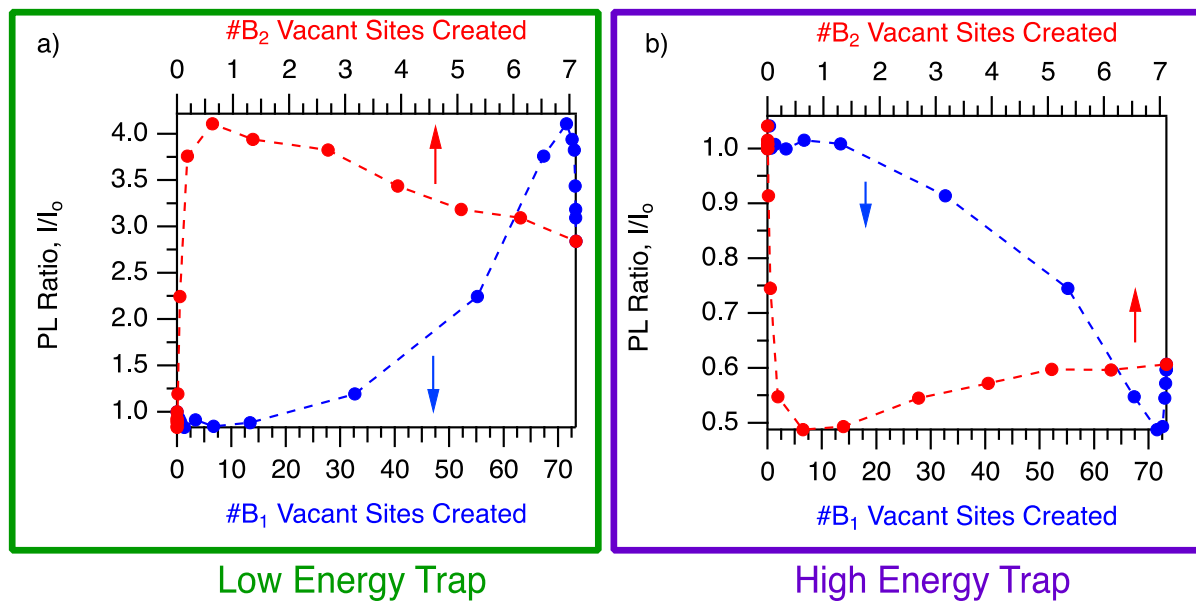
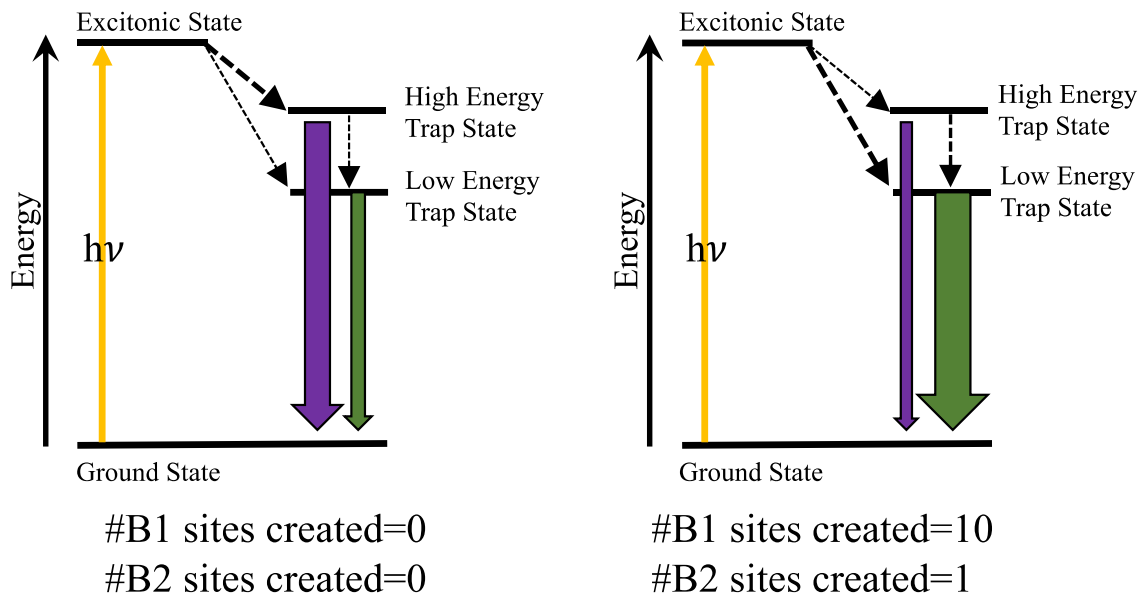


Figure 4.12 (a) Correlating the change in the PL ratio of low energy trap with the number of B₁ and B₂ vacant sites created. The top x-axis represents the number of B₂ vacant sites created and the bottom x-axis represents the number of B₁ vacant sites. (b) Correlating the change in the PL ratio of the high energy trap state with the number of B₁ and B₂ vacant sites created. The top x-axis represents the number of B₂ vacant sites created and the bottom x-axis represents the number of B₁ vacant sites.

During the titration, the trap state emission is greatly affected by the creation of B₂ sites. From Figure 4.12, the creation of one B₂ site changes both the high and low energy trap PL efficiency. As one B₂ site is created, the PL efficiency of the low energy is increased, and the high energy trap state is quenched, as shown in Figure 4.12 (a) and (b). It seems that B₂ sites quench trap emission from the high energy trap state as they are created. Defects at any B₂ site could be correlated to a low energy trap state, and as more sites are created, it could be more probable for energy transfer to occur from the high energy to the low energy trap state. This would decrease the emission from the high energy trap state while the low energy trap state becomes brighter, as summarized by Scheme 4.4.



Scheme 4.4 Summary of the effects of the creation of defect sites on trap emission.

Li et al. have shown that changing the S/Cd ratio impacts each trap state emission.²⁷ In this study, small increases in the S/Cd ratio greatly quenches the high energy trap state, whereas the low energy trap state is not quenched until the ratio of S/Cd becomes much greater. In our studies presented here, the immediate quenching of the high energy trap state could be due to the increase in the S/Cd ratio due to the removal of CdX₂ from the surface. We also start to see quenching of the low energy trap state once enough defects have been created, and this could also be attributed to the increase in the S/Cd ratio. This could then be used to help correlate B₂ surface sites to deep S²⁻ traps, and B₁ sites are correlated to shallow surface states. However, more studies would need to be done to confirm the direct correlation of the S/Cd ratio changing to PL emission. The two trap-state model better captures the behavior of the trap state throughout the titration and creates a more detailed picture about the photophysics of each defect site.

4.5 Conclusions

This Chapter has shown a direct correlation between the creation of specific surface defects and the radiative recombination process of both the exciton and trap states of cadmium-rich zinc-blende CdS NCs. The two types of sites, B₁ and B₂, have strikingly different effects on the PL emission of CdS. B₂ vacant sites are shown here to be immensely effective exciton quenchers and influence the trap emission. The trap emission was demonstrated to be composed of two different trap states that can be changed through changing the Cd/S ratio through creation of defect sites. To further confirm that changing the ratio of Cd/S truly affects the trap state emission, XPS measurements need to be taken as each vacant site is created and correlated to any changes seen in the trap state emission with changes in the Cd/S ratio. The creation of B₂ sites enhances the emission of low energy traps and quenches the emission of high energy traps. These results give direct insight into the complexity of the surface and its effects on optoelectronic properties. It further supports the idea that to tailor CdS NCs for specific applications, careful control over the surface and specific defect types is necessary. It further emphasizes the large impact that the creation of B₂ vacant sites has on the optoelectronic properties of the NC. Any B₂ vacant site left vacant will quench excitonic PL and change the energy of trap state PL.

APPENDIX

SI 4.1 Effect of TMEDA addition on PL Spectra on 3.4 nm CdS Samples

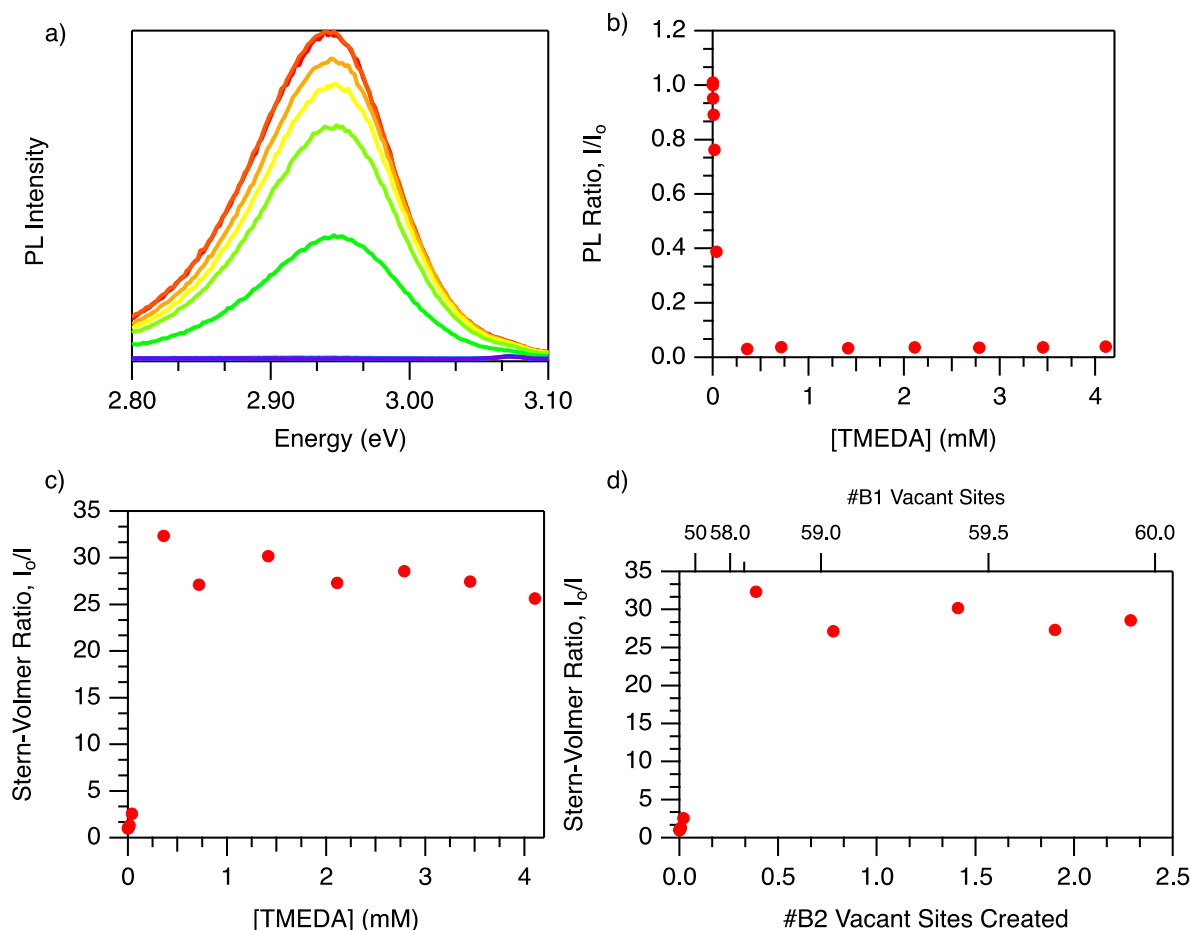


Figure SI 4.1 (a) PL spectra of the excitonic emission after addition of TMEDA to trial 1 3.4 nm sample of CdS (1 μ M). (b) PL intensity of the exciton of 3.4 nm CdS (1 μ M), with varying amounts of TMEDA. (c) Quantification of CdS quenching using TMEDA, reported as the Stern-Volmer ratio. (d) Correlation of the creation of B₁ and B₂ vacancies with quenching of exciton photoluminescence during TMEDA titration.

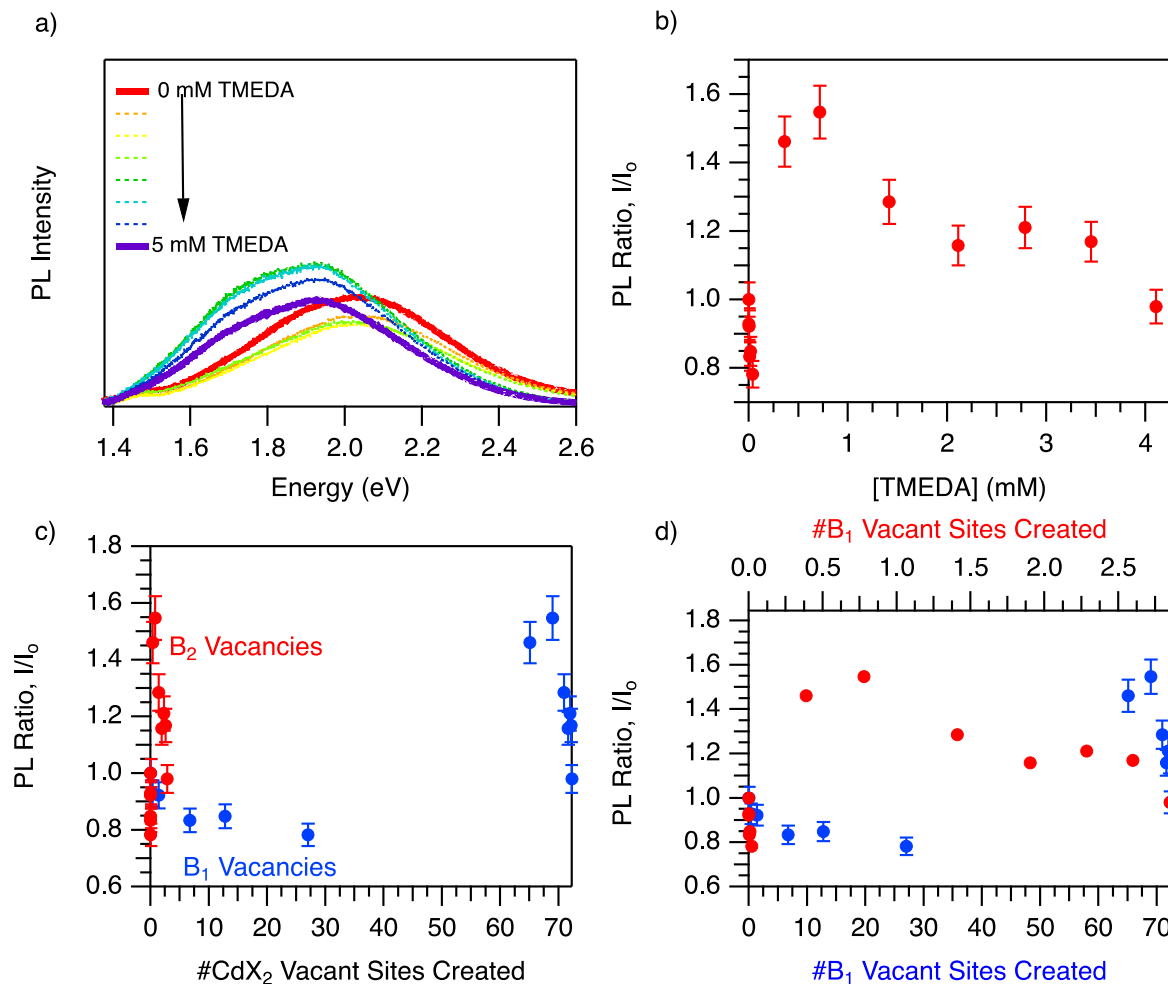


Figure SI 4.2 (a) PL spectra of the trap emission after addition of TMEDA to trial 1 3.4 nm sample of CdS. (b) PL ratio of trap state of 3.4 nm CdS (1 μ M), with varying amounts of TMEDA. (c) Correlation of CdS PL ratio after addition of TMEDA to B₁ and B₂ vacant sites. (d) Correlation of the creation of B₁ and B₂ vacancies with the PL ratio during TMEDA titration. The top x-axis represents the number of B₂ vacant sites created and the bottom x-axis represents the number of B₁ vacant sites.

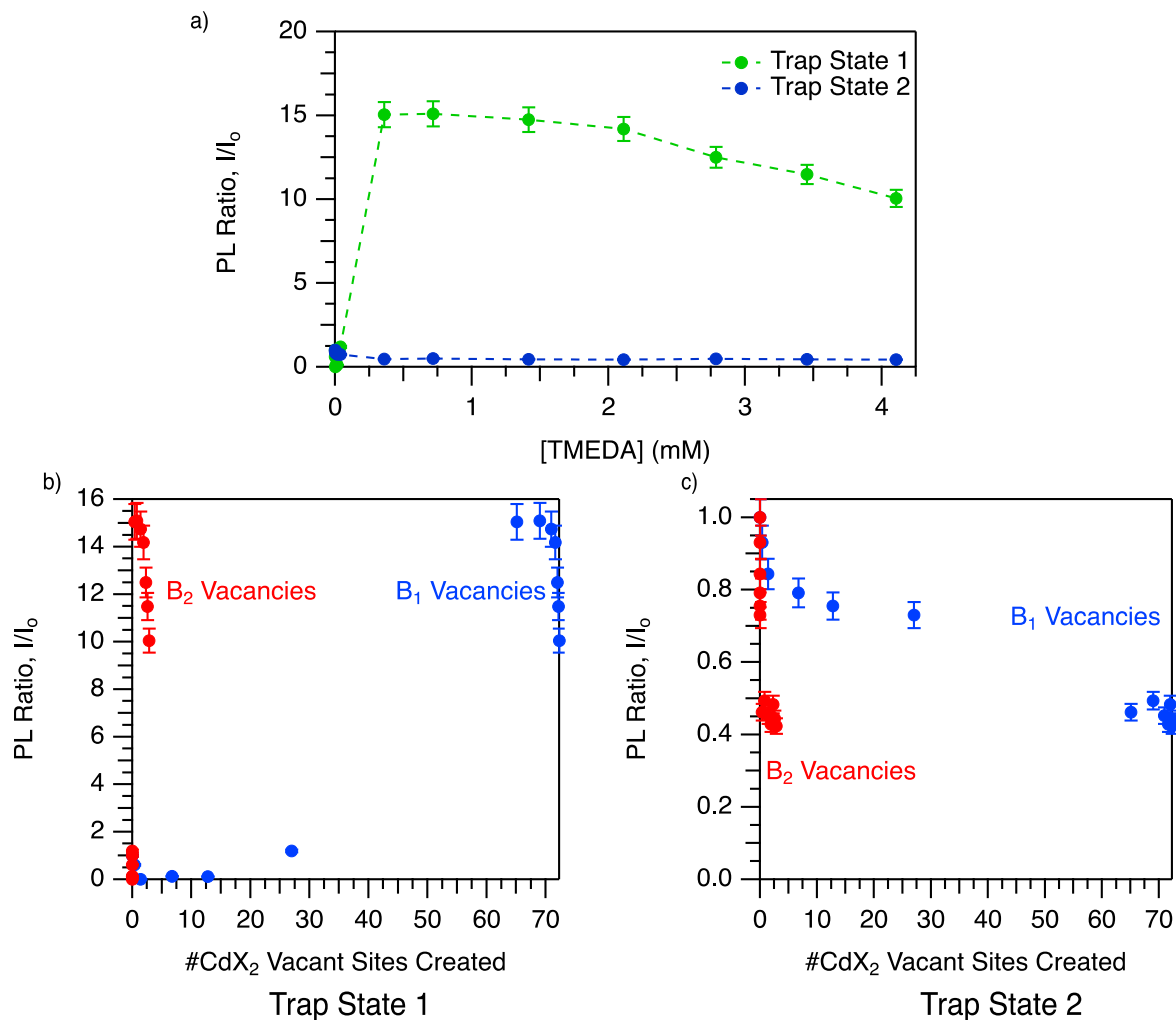


Figure SI 4.3 (a) The PL ratio of each trap state throughout titration with TMEDA for trial 1 of 3.4 nm CdS. (b) Correlating the change in the PL ratio of the low energy trap state with the number of CdX₂ sites created. (c) Correlating the change in the PL ratio of the high energy trap state with the number of CdX₂ sites created.

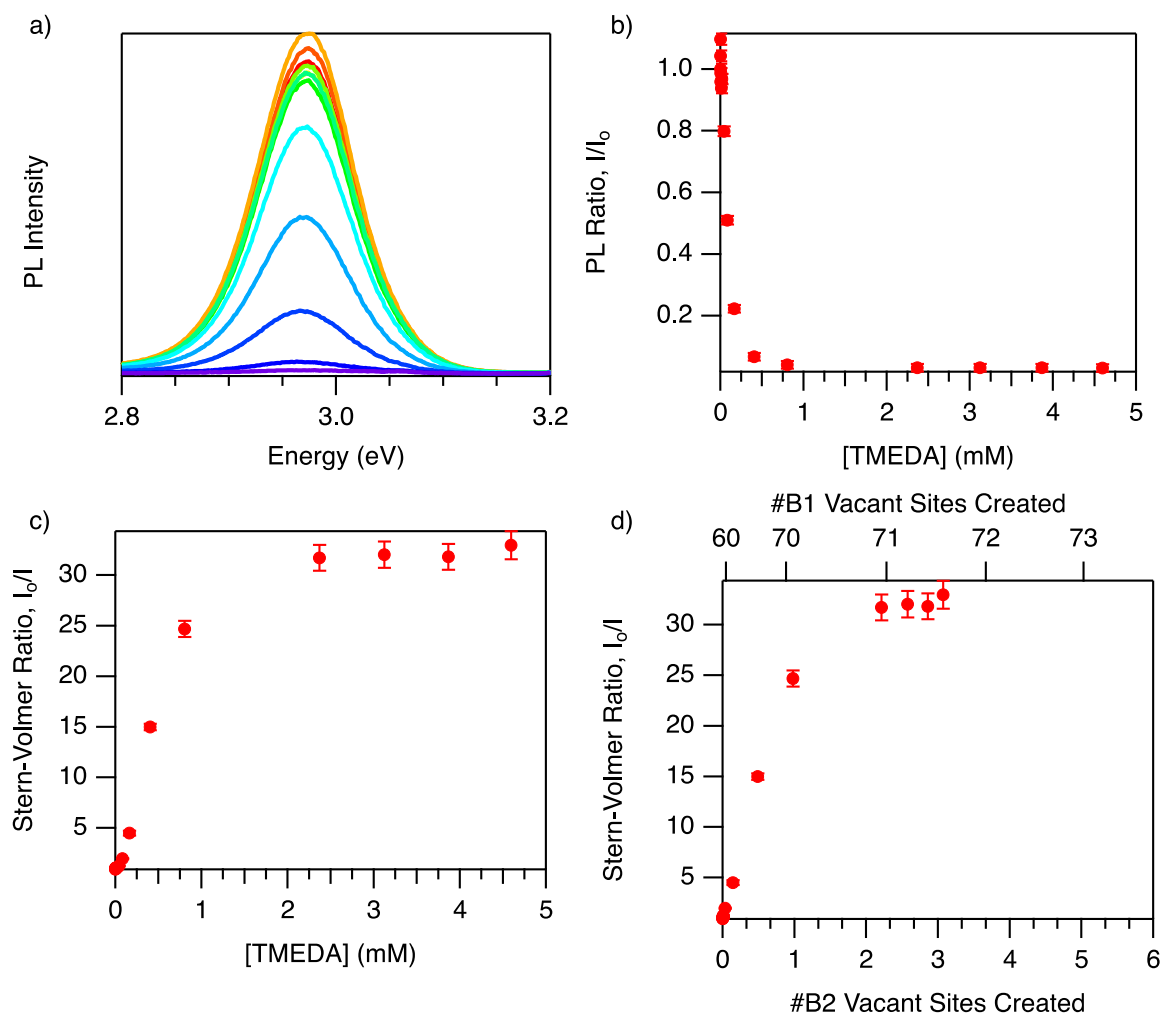


Figure SI 4.4. (a) PL spectra of the excitonic emission after addition of TMEDA to trial 2 3.4 nm sample of CdS (b) PL intensity of the exciton of 3.4 nm CdS (1 μM), with varying amounts of TMEDA. (c) Quantification of CdS quenching using TMEDA, reported as the Stern-Volmer ratio. (d) Correlation of the creation of B₁ and B₂ vacancies with quenching of exciton photoluminescence during TMEDA titration.

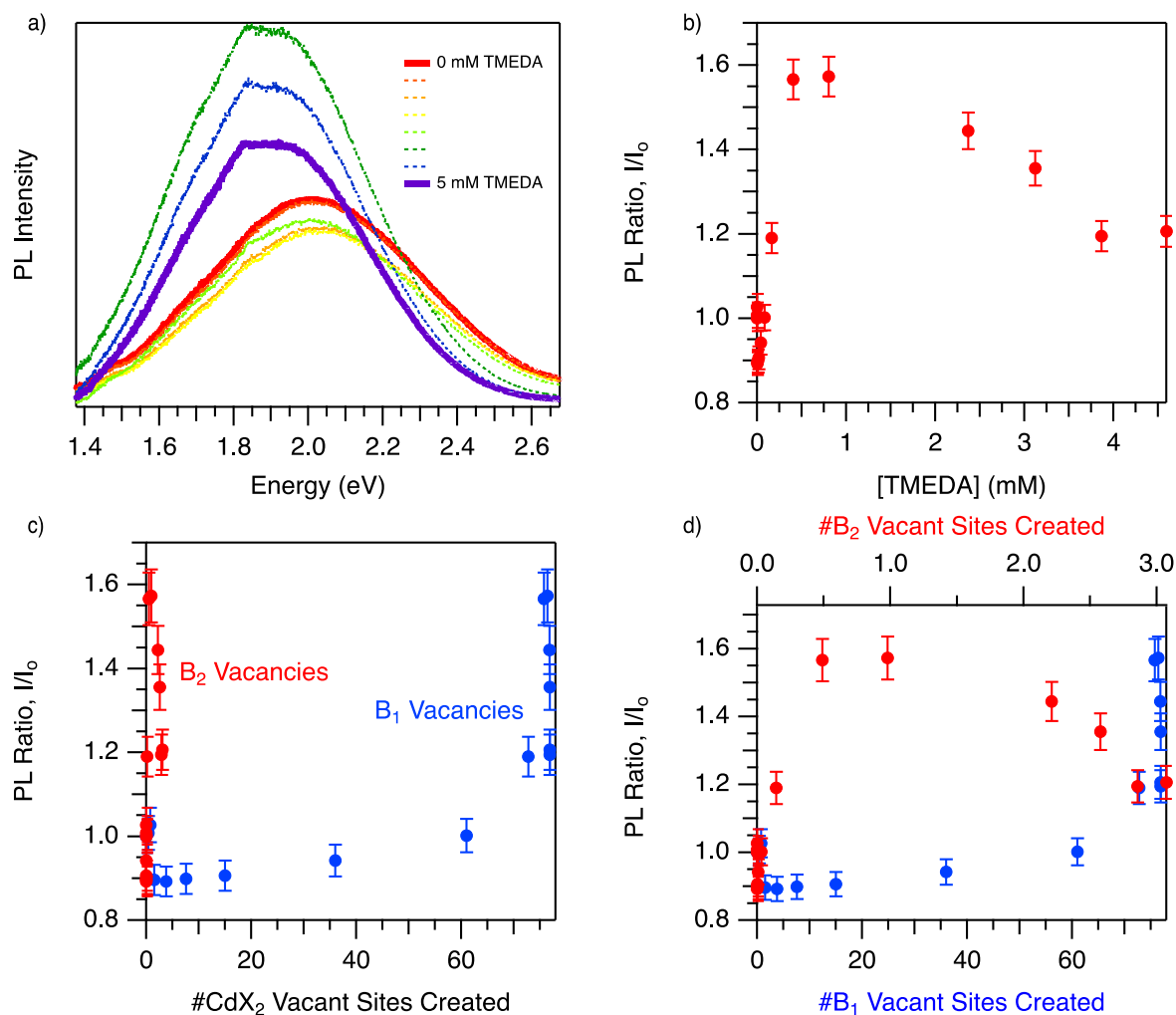


Figure SI 4.5. (a) PL spectra of the trap emission after addition of TMEDA to trial 2 3.4 nm sample of CdS. (b) PL ratio of trap state of 3.4 nm CdS (1 μ M), with varying amounts of TMEDA. (c) Correlation of CdS PL ratio after addition of TMEDA to B₁ and B₂ vacant sites. (d) Correlation of the creation of B₁ and B₂ vacancies with the PL ratio during TMEDA titration. The top x-axis represents the number of B₂ vacant sites created and the bottom x-axis represents the number of B₁ vacant sites.

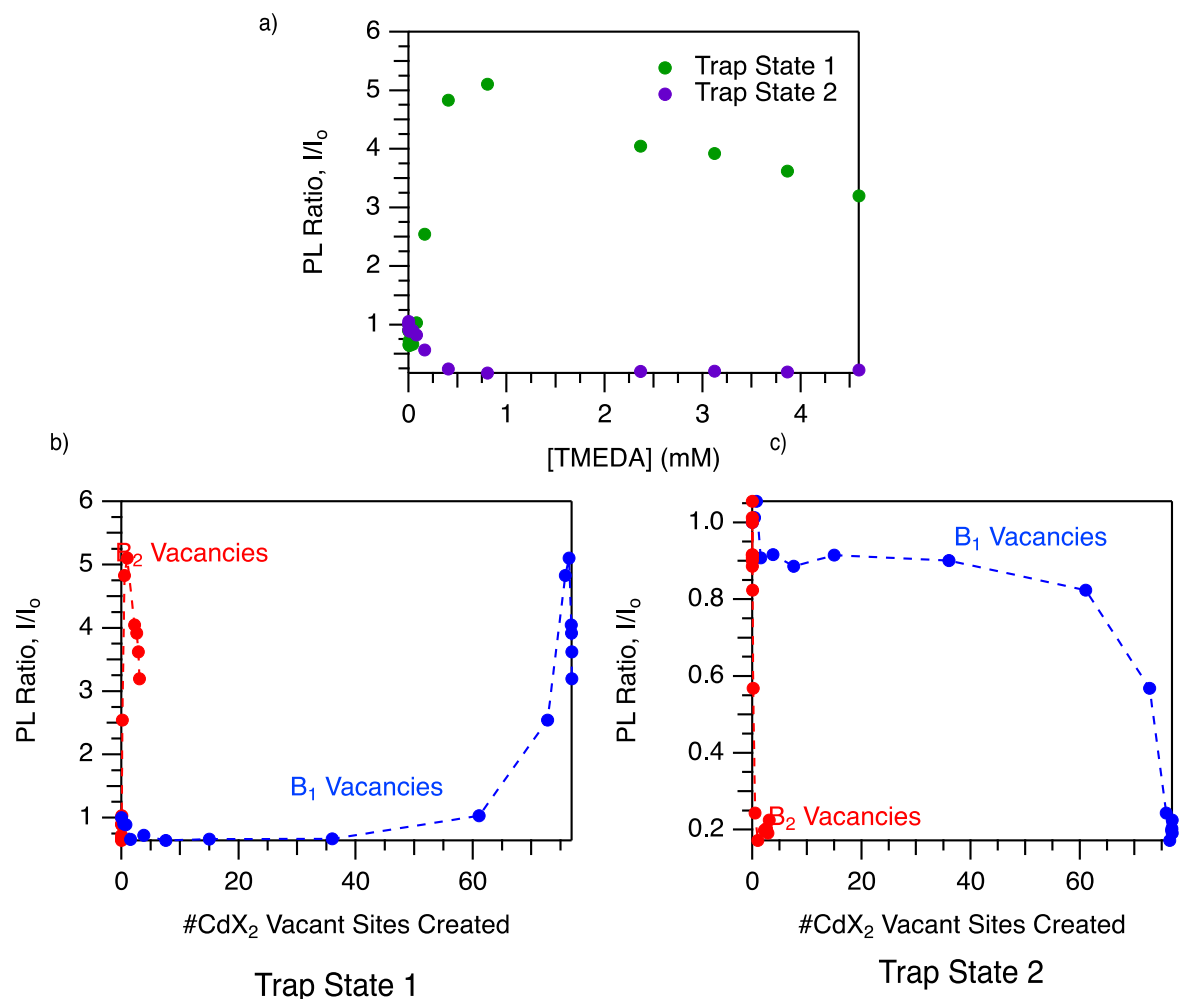


Figure SI 4.6 (a) The PL ratio of each trap state throughout titration with TMEDA for trial 2 of 3.4 nm CdS. (b) Correlating the change in the PL ratio of the low energy trap state with the number of CdX₂ sites created. (c) Correlating the change in the PL ratio of the high energy trap state with the number of CdX₂ sites created. Lines are just guide for the eyes.

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**Chapter 5: Analysis of Multi-Exponential Excited-State Dynamics of Colloidal CdS
Nanocrystals**

5.1 Introduction

To better control their optoelectronic properties, the surface chemistry of SC NCs needs to be well understood. For example, the accurate implementation into solar energy devices requires an understanding of relaxation pathways of photoexcited NCs and of their charge-separated states.^{1–}

⁶ Typically, surface defects are associated with trap states that reduce the efficiency of excitonic recombination through non-radiative energy transfer. Typically, to mitigate such effects NCs are coated with organic ligands or inorganic shells to remove unwanted energy losses. Due to their ease of synthesis, metal chalcogenide NCs, such as CdSe and CdS NCs, have led to many studies investigating their steady-state and time-resolved excited state spectroscopy. Many studies have been done to characterize the excited state dynamics of CdS NCs and many groups have used PL spectroscopy to investigate the impact of ligands on optical properties.^{4,7–16} However, many of these studies have only focused on steady-state PL and ignore the role of the surface.^{17–22} Much has been learned and characterized about exciton PL, but the chemical origin of trap state emission remains poorly understood, and the related dynamics are not well understood either. Trap states in CdS NCs have been characterized using low-temperature PL lifetime measurements, but studies explicitly done to understand the impact of the surface on the emission of trap states have largely ignored the direct role of ligands.^{7,8,10–13,21,23} While, many studies have tried to analyze the impact of surface structure and NC size on the emission and dynamics of trap states, few have explicitly focused on characterizing the energetics of specific defects and their impacts on emission.^{13,24–29} In Chapter 2, two different types of surface defects on CdS NCs were identified. Furthermore, in Chapter 4 it was found that there are two different emitting trap states that are uniquely changed upon modification of the surface. With this knowledge in hand, this Chapter further associates

each defect creation with its impact on the NCs time-dependent PL. We show that each type of defect leads to specific effects on the time-resolved PL emission.

5.2 Experimental Details

For details about the synthesis and optical spectroscopy characterization of CdS NCs, please see Chapter 2, Section 2.

5.2.1 Optical Spectroscopy

The preparation for optical spectroscopy is described in Chapter 2, Section 2.2.4. For these experiments, time-dependent PL spectra were measured with a T900 time-correlated single-photon counting (TCSPC) setup with a PMT detector (Hamamatsu H7422-40). The pulsed excitation light source was a 405 nm diode laser from Picoquant (LDH-D-C-405M, CW-80 MHz). The steady-state excitation beam for these experiments was obtained from a tungsten bulb filtered through a 0.3 nm monochromator at 405 nm. The laser pulse frequency was 125 kHz, to allow the excited NCs to relax while generating a high enough photon count. The laser intensity was adjusted so that the photon emission rate was smaller than 3% of the start frequency. The time window for photon counting was 5 μ s, divided evenly into 4096 channels.

5.2.2 Sample Preparation for Steady-State and Time-Resolved Photoluminescence.

Samples for photoluminescence spectra measurements were prepared by diluting 30 μ L samples of 133 μ M CdS NCs to 2 mL with toluene. TMEDA was added to each CdS sample to ensure that the same ratio of TMEDA to NC equivalents was added, compared to the ^1H NMR experiments described in Chapter 2. This was done to ensure that any changes in PL could be correlated to specific numbers of B₁ or B₂ sites created. Each sample was given 30 minutes to reach equilibrium, and samples were stirred during collection.

5.3 Impact of Surface Defects on Exciton Time-Resolved Photoluminescence

As described in Chapter 4, CdS NCs have both excitonic and trap state radiative emission. In that Chapter, we correlated the change in both excitonic and trap states with the creation of specific defect sites. As shown in Figure 5.1, the addition of TMEDA to CdS NCs affects both excitonic PL and trap PL. Further details of the change were given in Chapter 4.

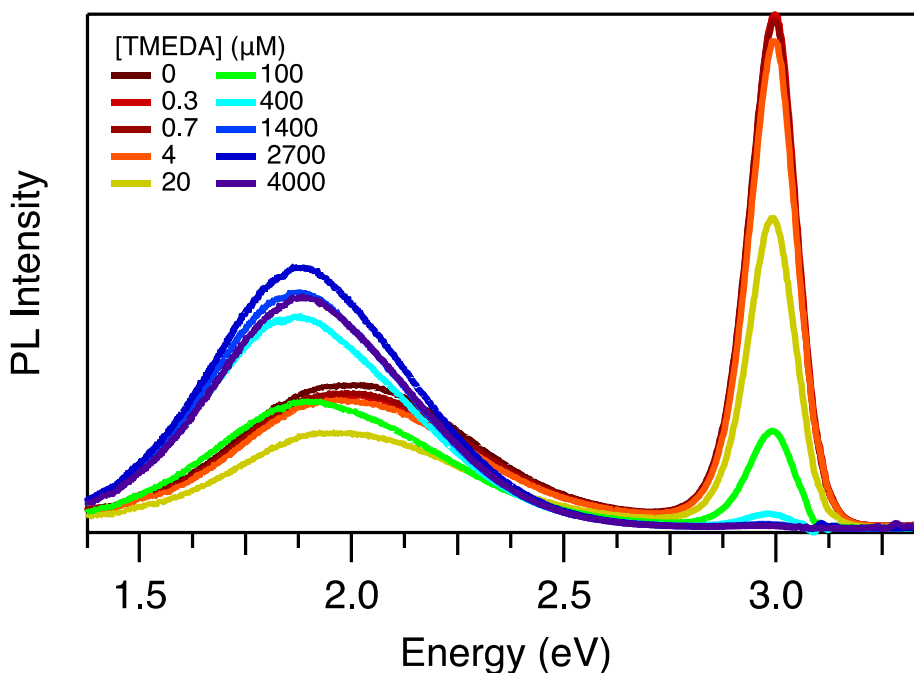


Figure 5.1 PL spectra of 3.4 nm CdS NCs ($\sim 2 \mu\text{M}$ in toluene), with varying amounts of TMEDA (0-4 mM).

Upon addition of TMEDA to the CdS NC suspension, the overall excitonic PL intensity decreases, as shown in Figure 5.1 and 5.2 (a), and the quenching from the creation of each site was characterized in Chapter 4. This PL quenching effect can also be quantified in the time domain. As shown in Figure 5.2 (b), the excitonic recombination deviates from a single-exponential decay dynamic that is typically associated with a simple first-order relaxation process.^{3,30-34} This is typically observed for both CdSe and CdS NCs and is due to inhomogeneities within the NC ensemble, leading to distributed excitonic recombination rate constants.^{3,30-34} The quenching of

the PL can also be quantified by integrating the entire time-dependent PL decay over the time domain:

$$I_{tot} = \int_0^{\infty} I(t)dt \quad \text{eq 5.1}$$

The comparison of the steady-state and time-dependent Stern-Volmer ratios, as shown in Figure 5.2 (c), indicates that any ultra-fast (shorter than 1 ns here) or ultra-long processes (longer than 5 μ s here) do not partake in the observed PL quenching seen in the steady-state and time dependent data.

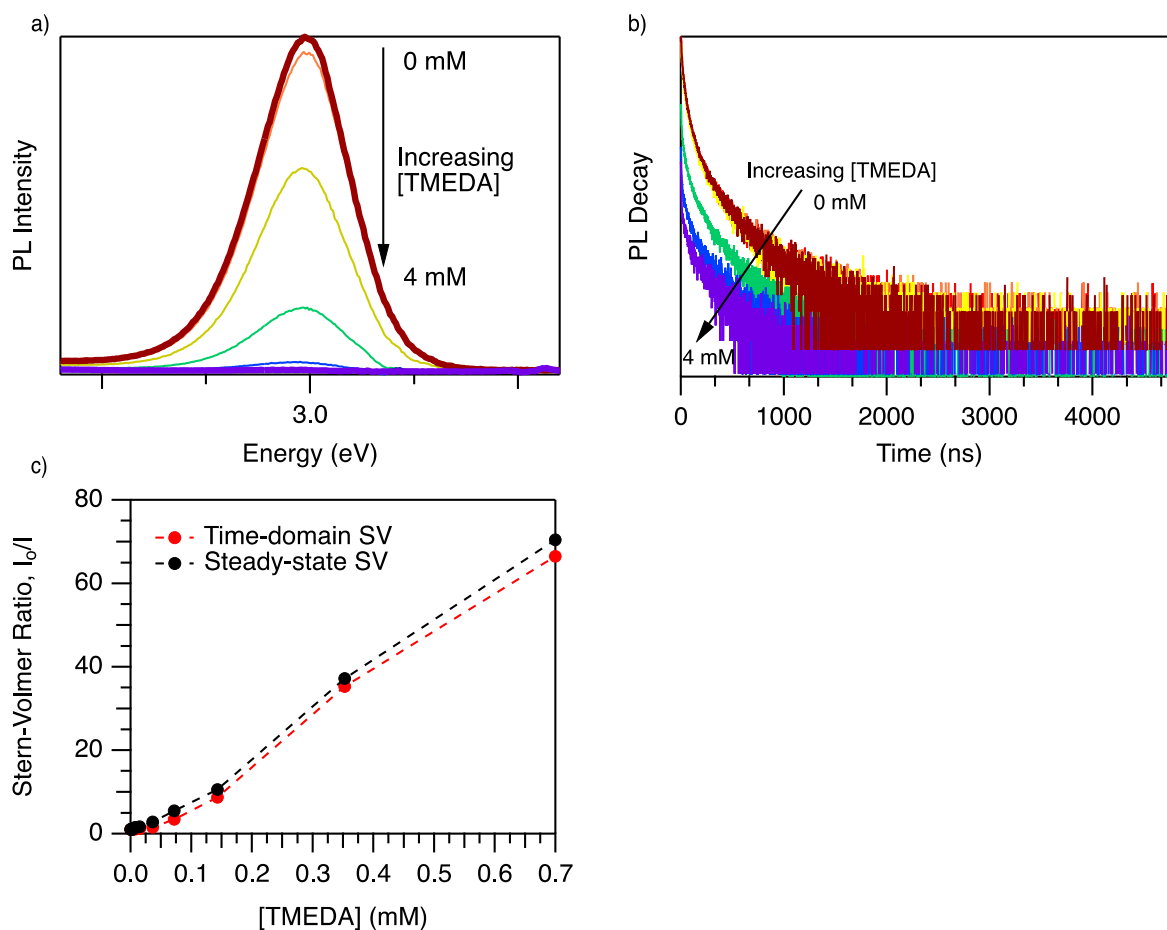


Figure 5.2 (a) PL intensity of the exciton of 3.4 nm CdS (1 μ M), with varying amounts of TMEDA, added. (b) PL decay dynamics of the spectra shown in (a). (c). Comparison of quenching quantified from the steady-state spectra (red) and the time-dependent spectra (black). Dashed lines are a guide to the eyes.

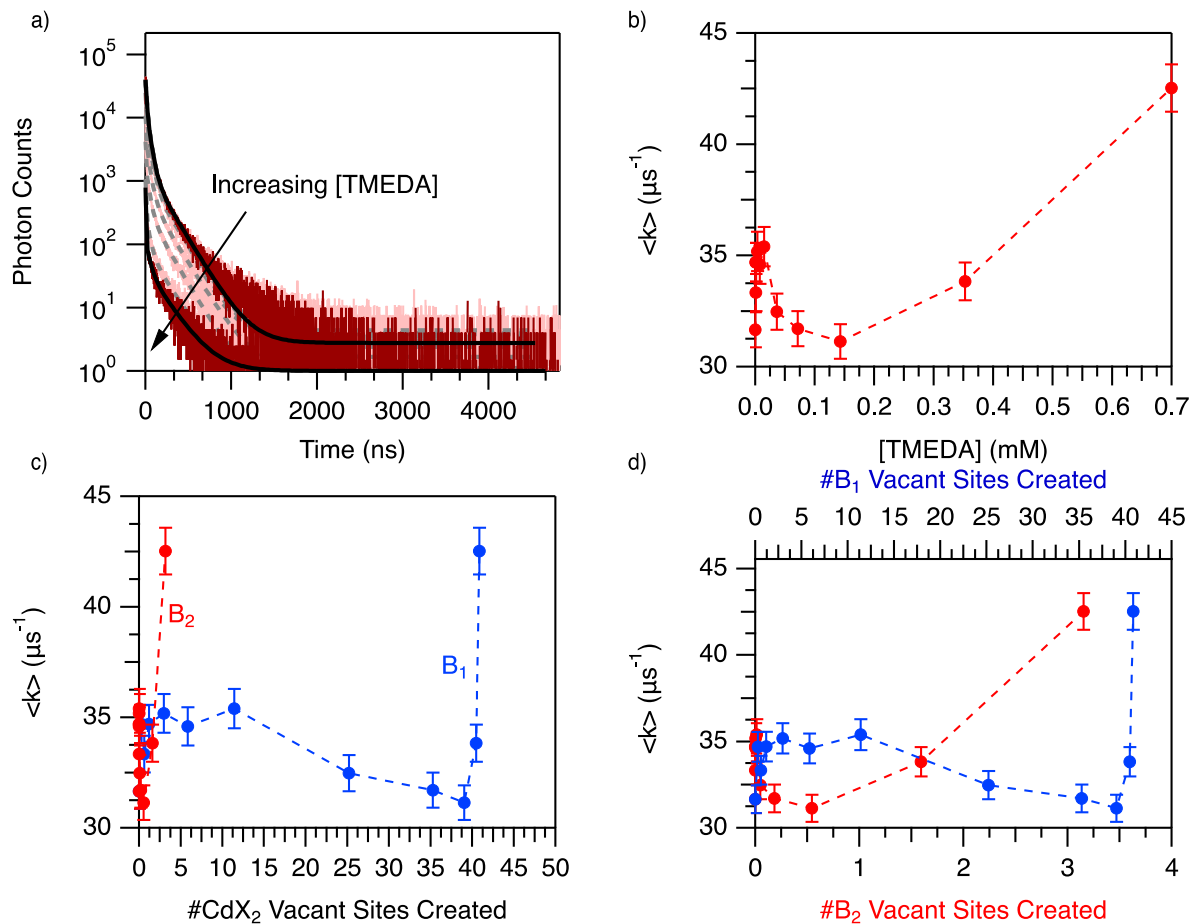


Figure 5.3 (a) Time-dependent PL analysis of exciton with TMEDA added (0 – 1 mM). Experimental PL decay curves and least-square triple-exponential fits (black lines). (b) Average (harmonic mean) rate constant of each triple-exponential fit from (a). (c) Change in average (harmonic mean) rate constant correlated to the creation of each site. (d) Correlating the change in the average rate constant with the number of B_1 and B_2 vacant sites created. The top x-axis represents the number of B_1 vacant sites created and the bottom x-axis represents the number of B_2 vacant sites.

To better characterize the change in each PL decay, the PL decay was fitted with a triple-exponential fit. The analysis of the time-dependent PL quenching data in Figure 5.3 (a) is complicated by inhomogeneities of the NC recombination rates (as shown by the multiexponential nature of the decay). To find the average rate constant ($\langle k \rangle$) of the quenching process, the distribution of rate constants responsible for the behavior of the ensemble needs to be quantified. The PL decays shown in Figure 5.3 (a) can be represented by a triple-exponential decay function:

$$I(t) = A_1 \times \exp(-k_1 t) + A_2 \times \exp(-k_2 t) + A_3 \times \exp(-k_3 t) \quad \text{eq. 5.2}$$

The result of this fitting is shown in Figure 5.3 (a) and adequately captures the PL decay. There is no fundamental reason to use a triple exponential fit (a 4,5, or 1000-exponential fit could have been used to model data), however this was the simplest way to best fit the data. It is important to note that such a phenomenological model cannot be expected to represent the complex photophysics of the ensemble but can be used to find an adequate average rate constant through the harmonic mean of k_1 , k_2 , and k_3 :

$$\langle k \rangle = \frac{A_1 k_1^{-1} + A_2 k_2^{-1} + A_3 k_3^{-1}}{A_1 + A_2 + A_3} \quad \text{eq. 5.3}$$

Previous studies have shown that this over simplified model can adequately describe the average rate constant of the ensemble, however it is important to remember that this model cannot be used to completely capture the complex photophysics of the ensemble.³⁴ The fitting parameters from eq 5.2 (k_1 , k_2 , and k_3) have no physical meaning and only the average $\langle k \rangle$ is physically meaningful. Previous studies have associated the shorter lifetime components to the intrinsic recombination of initially populated core states, and the longer lifetime components to the recombination of electrons and holes of the NC surface.^{13,25,35–37} Figure 5.3 (b) shows the change of the average rate constant throughout the addition of TMEDA. The average rate constant behaves erratically at the beginning of the titration but then increases as more TMEDA is added. The initial erratic behavior could be related to the increase in the PL intensity of the exciton state upon the addition of small amounts of TMEDA. However, the cause of this increase has not been investigated here. Much like what was seen in Chapter 4, creating any B₂ vacant sites on the NC surface significantly impacts the average rate constant of the exciton. Studies have shown that carriers trapped on the surface have an increased radiative lifetime due to the poor overlap of carrier wave functions.³⁸ This further supports the idea that creating B₂ vacancies on the surface leads to decreased exciton PL due to trapping from trap states on those sites.

5.4 Impact of Surface Defects on Trap Time-Resolved Photoluminescence

In Chapter 4 we determined that the creation of surface sites on CdS NCs impacts that trap PL in two significant ways: 1) increase in overall PL efficiency and 2) a red shift of trap state emission as shown in Figure 5.4 (a).

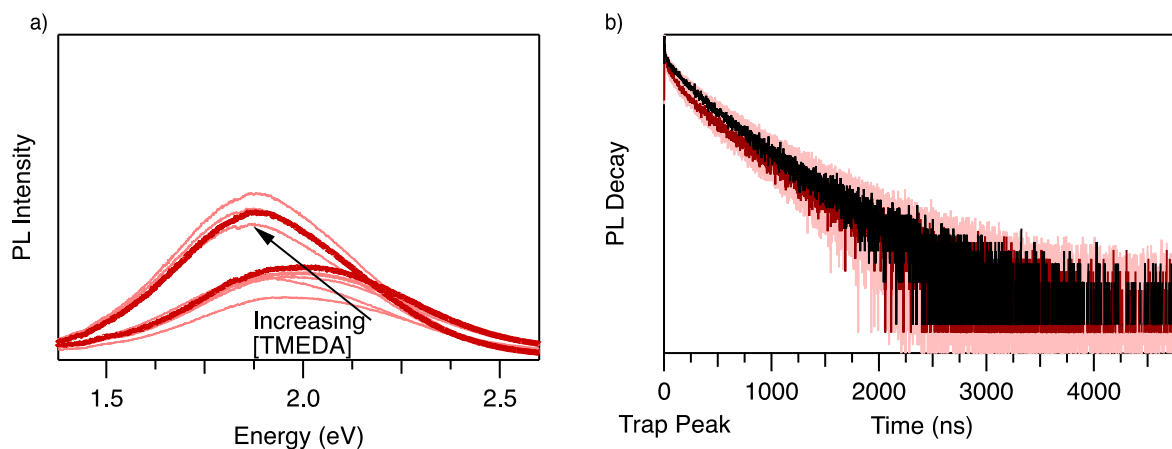


Figure 5.4 (a) PL intensity of the trap states of 3.4 nm CdS (1 μ M), with varying amounts of TMEDA added (0 – 5 mM). (b) PL decay dynamics of the spectra shown in (a) measured at the energy correlating to the maximum of the PL curve at the beginning (black) and end (dark red) of TMEDA titration.

We correlated the trap state PL changes due to the presence of two emissive trap states that are impacted differently upon creating B_2 vacancies throughout the addition of TMEDA, as shown in Figure 5.5. We were interested in seeing the change in time-dependent PL spectra upon creating these surface states, as shown in Figure 5.4 (b), we note here that the PL decays were measured at the energy corresponding to the maximum PL emission (λ_{trap}).

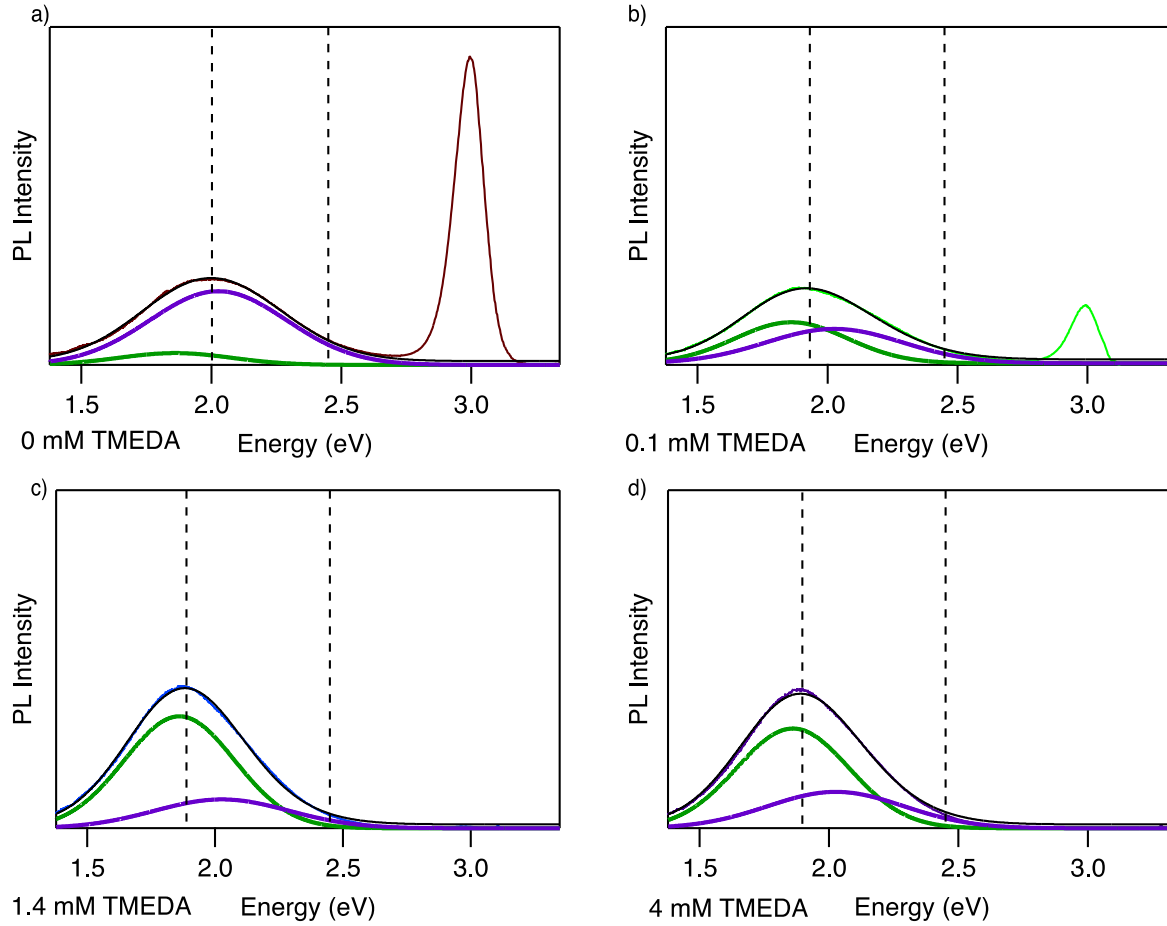


Figure 5.5 (a)-(d) Modeling of each trap state gaussian under that trap emission of 3.4 nm CdS NCs. The green and the purple gaussian represent the low and high energy trap states, respectively. The black line models the double gaussian fit. Each vertical line correlates to the energy that lifetime measurements were recorded at in Figure 5.4 (b) and Figure 5.6.

At first glance, the time-dependent PL spectra show very little change across all TMEDA titrations. However, it is important to note that the energy at which the time-dependent PL decay was taken is under the influence of the high energy and low energy trap states, as shown in Figure 5.5. Assuming there are two PL transitions at λ_{trap} , as seen in Figure 5.5:

$$I_{tot}(t, \lambda_{trap}) = I_{cw}(\lambda_{trap})[P_1(\lambda_{trap}) \times I_1(t) + P_2(\lambda_{trap}) \times I_2(t)] \quad \text{eq. 5.4}$$

Where $I_{cw}(\lambda_{trap})$ is the total PL intensity, steady-state conditions measured at λ_{trap} (the maximum of the steady-state trap PL curve). $I_{tot}(t, \lambda_{trap})$ is the total decay curve, measured at

λ_{trap} . This is the actual measured time-dependent decay of the trap states at the maximum of the PL trap curve (~ 2.0 eV). $P_1(\lambda_{trap})$ and $P_2(\lambda_{trap})$ is the weight of each trap state (high energy and low energy trap state) at the lifetime energy probed for the measurement. This was found by looking at the PL steady-state curve and finding the ratio of the high energy and low energy trap states at the measured energy of the PL decay.

Then by default:

$$\int_0^{\infty} I_{tot}(t, \lambda_{trap}) \times dt = I_{cw}(\lambda_{trap}) \quad \text{eq. 5.5}$$

To fulfill eq 5.5 above, the area underneath the PL decay curve is set to be equal to the intensity of the trap at that wavelength (as described above). To deconvolve the two trap states from Figure 5.4 (b), we start from eq. 5.4.

At this point, we have two unknown variables, $I_1(t)$ and $I_2(t)$, which correspond to the PL decay of each trap state. The energy where the PL decay is measured in figure 5.4 (b) influences the ratio of the high energy and low energy trap state. Another PL decay at different energy was taken to deconvolve each trap state PL decay at different energy levels, as shown in Figure 5.6 at 2.45 eV.

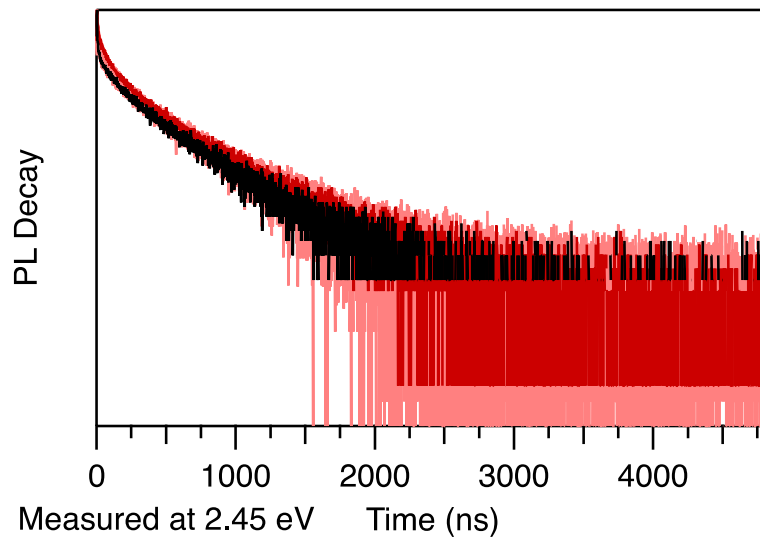


Figure 5.6. PL decay dynamics of the spectra shown in figure 5.4 (a) measured at 2.45 eV.

By using this PL decay measured at 2.45 eV, we can solve for one of the trap states PL decay. Even at this energy, both trap states still influence the PL, so this needs to be considered as shown in eq. 5.6 below:

$$I_{tot}(t, \lambda_{HE}) = I_{cw}(\lambda_{HE}) \times (P_1(\lambda_{HE}) \times I_1(t) + P_2(\lambda_{HE}) \times I_2(t)) \quad \text{eq. 5.6 (a)}$$

$$I_2(t) = \frac{\frac{I_{tot}(t, \lambda_{HE})}{I_{cw}(\lambda_{HE})} - (P_1(\lambda_{HE}) \times I_1(t))}{P_2(\lambda_{HE})} \quad \text{eq. 5.6 (b)}$$

Now that we have an equation representing an isolated high energy trap state lifetime ($I_2(t)$) with respect to the low energy trap state and the PL decay at 2.45 eV, we can use that to find an equation representing the low energy trap state lifetime ($I_1(t)$) at the original trap energy in Figure 5.4 (b):

$$I_1(t) = \frac{\frac{I_{tot}(t, \lambda_{trap})}{I_{cw}(\lambda_{trap})} - \frac{P_2(\lambda_{trap}) \times I_{tot}(t, \lambda_{HE})}{I_{cw}(\lambda_{HE}) \times P_2(\lambda_{HE})}}{\frac{P_1(\lambda_{trap})}{P_2(\lambda_{HE})} - \frac{P_2(\lambda_{trap}) \times P_1(\lambda_{HE})}{P_2(\lambda_{HE})}} \quad \text{eq. 5.7}$$

Once the low energy trap state lifetime is found, the high energy trap state PL decay can be found from rearranging eq 5.4.

$$I_2(t) = \frac{\left(\frac{I_{tot}(t, \lambda_{trap})}{I_{cw}(\lambda_{trap})} - P_1(\lambda_{trap}) \times I_1(t) \right)}{P_2(\lambda_{trap})} \quad \text{eq. 5.8}$$

This process of manipulating the PL decays at different energies provides information on the PL decays of each trap state, regardless of what energy the PL decay is measured at. Figure 5.7 shows the individual PL decays of the low and high energy trap states throughout the TMEDA titration. Each PL decay was fitted to determine the average rate constant. The low energy trap state PL decay is best fitted with a mono-exponential equation, whereas the high energy trap state is best modeled with a triple-exponential fit. For the high energy trap state, the average (harmonic mean) of the rate constant was found. It should be noted that the necessity for a triple-exponential fit to

adequately model the high energy trap state further confirms the complex nature behind surface defects.

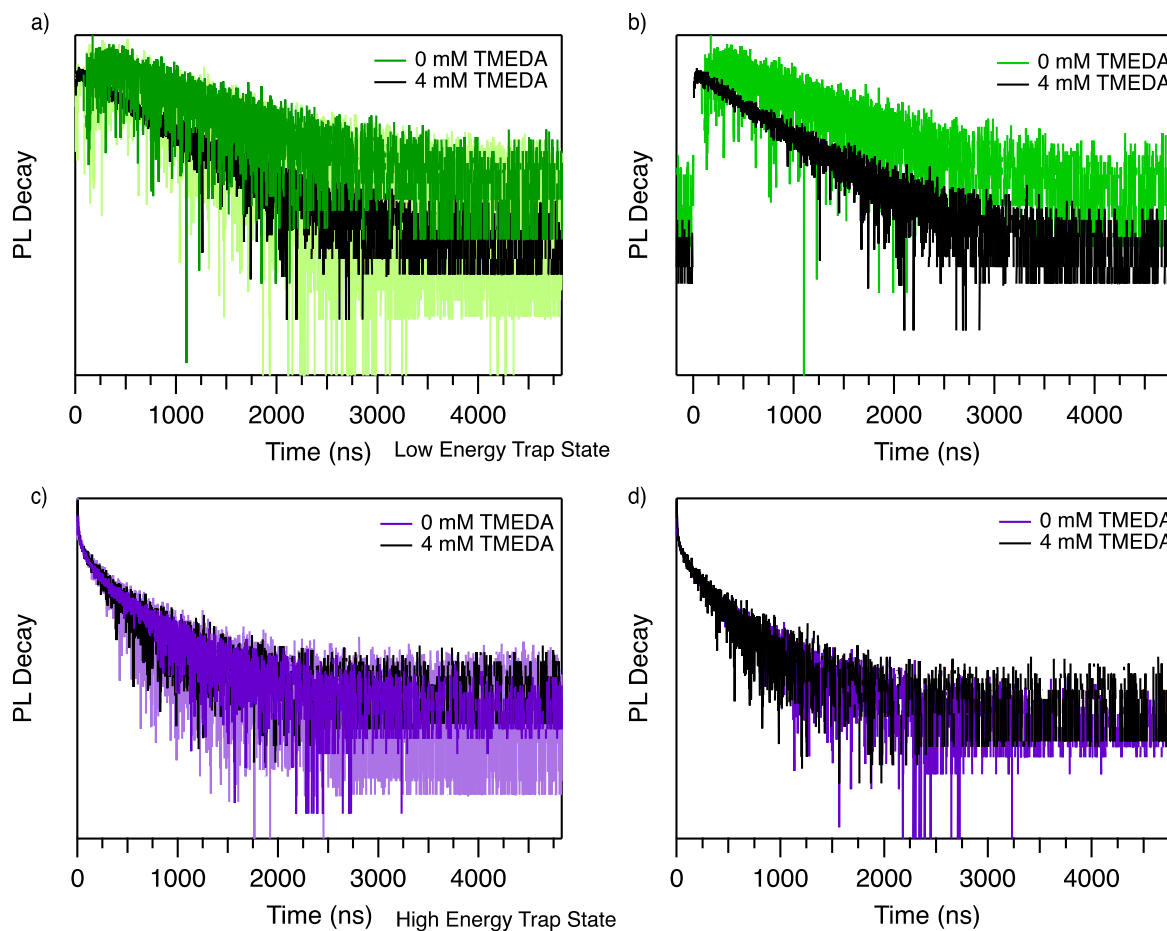


Figure 5.7 (a) PL decay dynamics of the low energy trap state with varying amounts of TMEDA added. The light green spectra represent points in between the start and end of the titration. (b) PL decay dynamics of the low energy trap state at the beginning and end of the titration. (c) PL decay dynamics of the high energy trap state with varying amounts of TMEDA added. The light purple spectra represent points in between the start and end of the titration. (d) PL decay dynamics of the high energy trap state at the beginning and end of the titration.

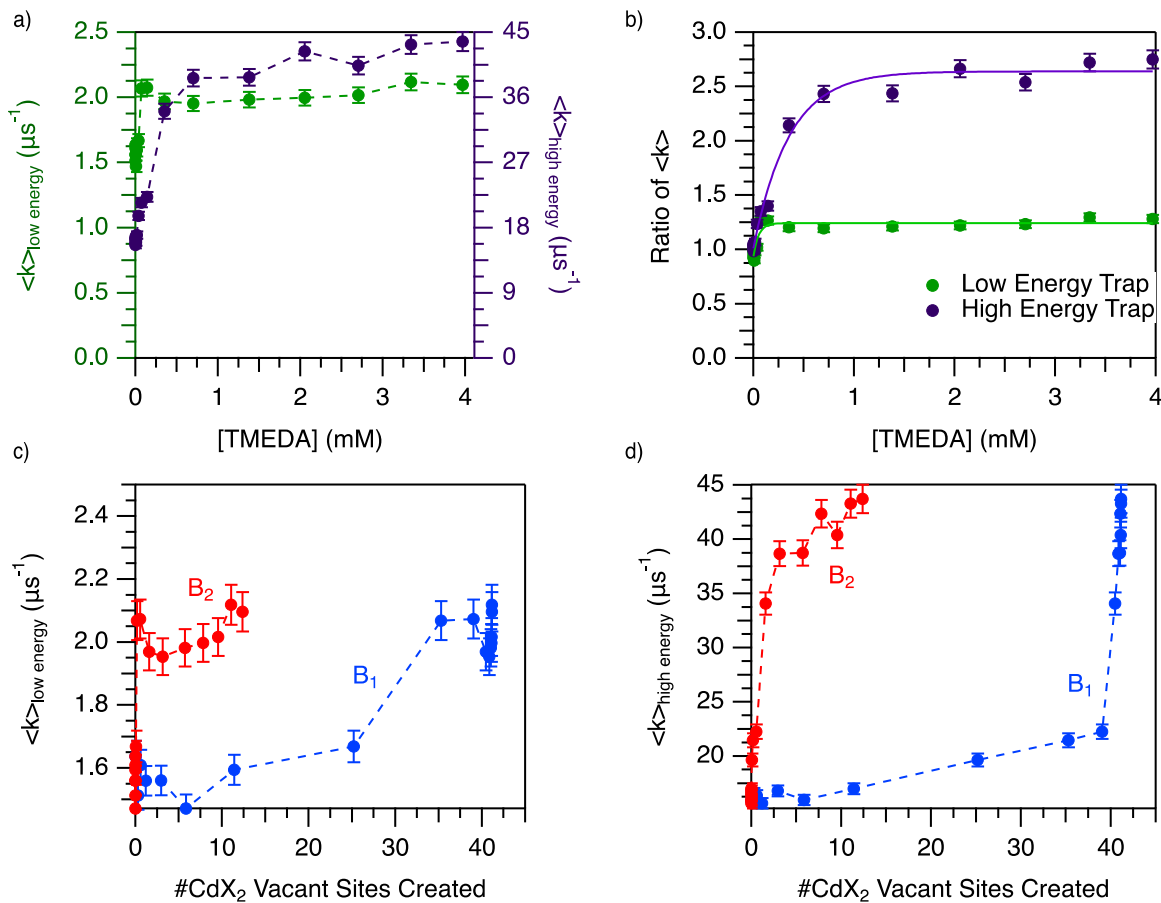


Figure 5.8 (a) Average (harmonic mean) rate constant of each mono-exponential and triple-exponential fit from Figure 5.7 for the low and high energy trap states, respectively. The low energy trap state (green circles) lifetimes were fit with a mono-exponential fit, and high energy trap state (purple circles) lifetimes were fit with a triple-exponential fit. (b) Change in the ratio of the average (harmonic mean) rate constant throughout the titration. Green circles represent the low energy trap state, and purple circles represent the high energy trap state. (c) Correlating the change in the average rate constant with the number of B₁ and B₂ vacant sites created for the low energy trap state. (d) Correlating the change in the average rate constant with the number of B₁ and B₂ vacant sites created for the high energy trap state.

The change in the rate constants for the low and high energy trap states are shown in Figures 5.8 (a) and (b). As more TMEDA is added to the system and more surface defects are created, the average rate constants of each trap state increase. The rate constant of the high energy trap state increases by 3x the original amount, and this is correlated to the creation of defects on the surface. This indicates a change in the dynamics of recombination of the high energy trap state. This effect is seemingly correlated to the creation of B₂ vacancies on the surface, as shown in Figures 5.8 (c)

and (d). The low energy trap state is initially susceptible to the creation of one B₂ vacant site. Once B₂ sites are created, further alterations of the surface no longer affect the dynamics of the high energy trap state. These analyses presented here are not sufficient to draw a comprehensive picture as to why each defect impacts the PL dynamics as it does. However, it can be seen here that the creation of any B₂ vacancy significantly alters the photophysical properties of CdS NCs. Any change seen in Figure 5.8 (c) and (d) for the creation of B₁ vacant sites is due to the cocreation of B₂ vacant sites on the surface.

5.5 Conclusions

This Chapter has shown a direct correlation between creating specific surface defects and their impact on PL decay of both the exciton and trap states within CdS NCs. The two types of sites, B₁ and B₂, have strikingly different effects on the PL decay. It was determined that creating any B₂ vacancy on the surface drastically alters both the excitonic and trap PL decay. By creating surface defects, the excitonic PL decay becomes longer due to the creation of surface states that trap electronic carriers. Furthermore, creating B₂ vacancies on the surface leads to longer low and high energy trap state excited-state lifetimes. However, the reasoning as to why this happens was not investigated here. These results give direct insight into the complexity of the surface and its effects on the PL decay of CdS NCs. More studies need to be done on the effect of creating defect sites on the surface and how they impact PL time dependent decay. Temperature dependent lifetime studies need to be done to further elucidate the effects of defect sites on trap states PL time dependent decay. Temperature dependent decay studies will help determine if the high energy trap state is energetically coupled with the low energy trap state.

APPENDIX

SI 5.1 ^1H NMR data to determine the number of B₁/B₂ vacant sites

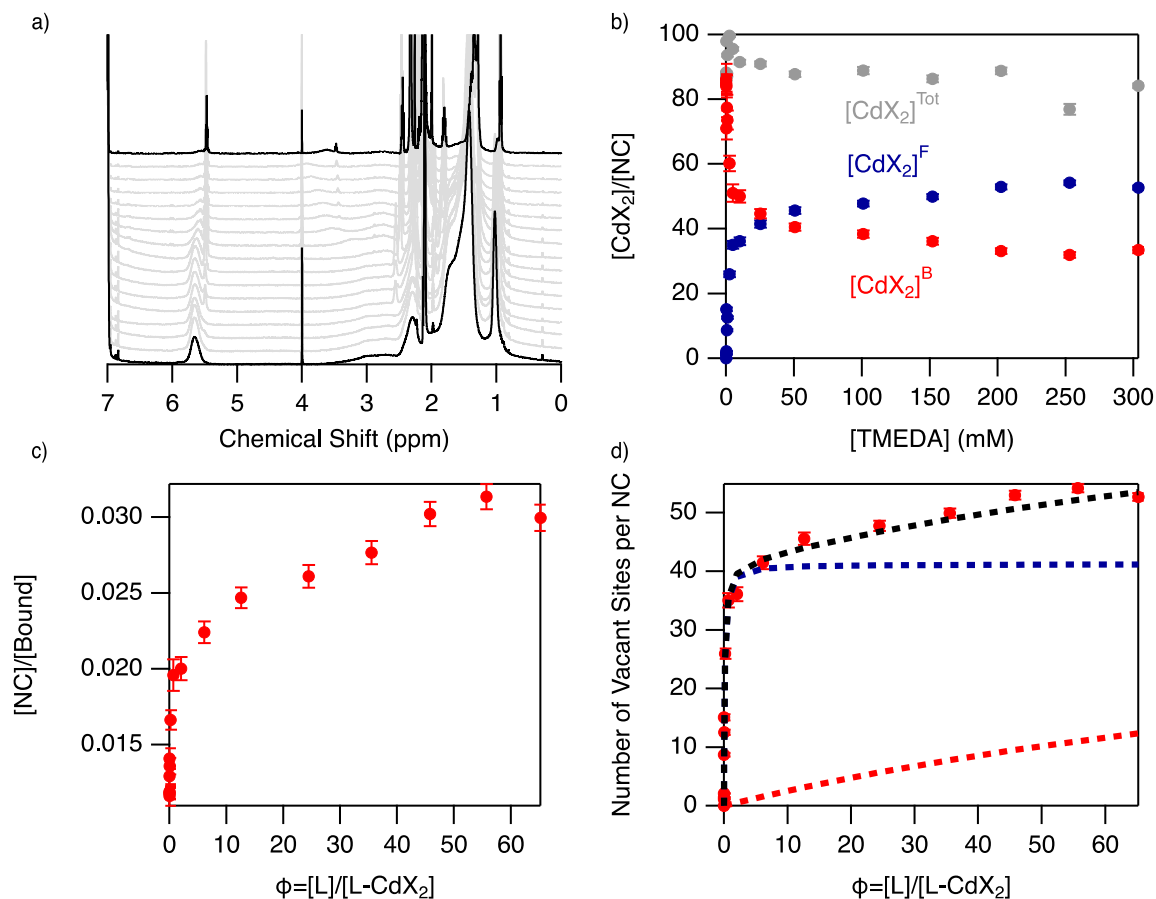


Figure SI 5.1 (a) ^1H NMR spectra of 3.4 nm CdS NCs (67 μM) with various amounts of TMEDA added (0 – 303 mM) (b) Ratio of the total (gray), free (blue), and bound (red) CdX_2 groups as a function of added TMEDA. (c) TMEDA titration of 3.4 nm CdS NCs (67 μM in d-toluene). (d) The calculated number of B₁ (blue), B₂ (red), and total (black) vacant sites on the surface of the 3.4 nm CdS sample. The calculated number of sites is equivalent to the number of CdX_2 removed from the surface of CdS (shown in red circles).

SI 5.2 PL data for each trap state

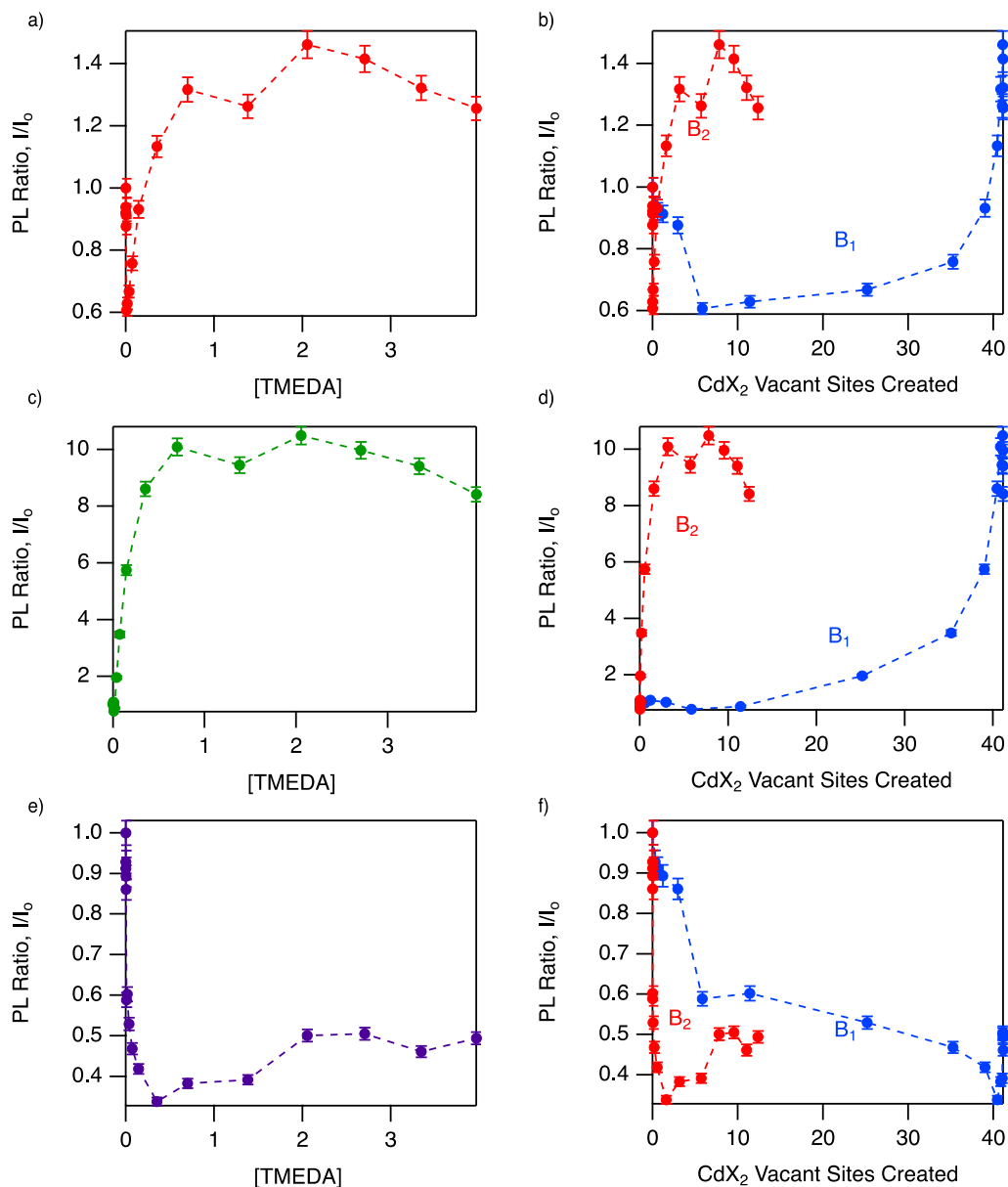


Figure SI 5.2. (a) PL ratio of trap state of 3.4 nm CdS (1 μ M), with varying amounts of TMEDA (0 – 303 mM). (b) Correlation of CdS PL ratio of trap state after addition of TMEDA to B₁ and B₂ vacant sites. (c) The PL ratio of the low energy trap state throughout the titration. (d) Correlation of CdS PL ratio of the low energy trap state to B₁ and B₂ vacant sites. (e) The PL ratio of high energy trap state throughout the titration. (f) Correlation of CdS PL ratio of the high energy trap state to B₁ and B₂ vacant sites.

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Chapter 6: Concluding Remarks

The overall arching goal of this research was to understand the complexity of the surface of CdS NCs and the effects of the surface on the optical properties of CdS NCs. From work presented in this thesis, it can be determined that controlling the surface of CdS NCs is of the utmost importance to tailor its photophysical properties for future applications. Zinc blende CdS NCs capped with carboxylate ligands were prepared to study the surface of CdS NCs. Their surface chemistry was studied using a ligand exchange analyzed through ^1H NMR analysis and optical spectroscopies PL and UV-Vis absorption.

Our first investigation into the surface of CdS was based on the equilibria from Z-type ligand exchange with TMEDA in Chapter 2. These ligand exchange experiments determined that two different binding sites exist on the surface, B₁ and B₂ sites. Each site has its binding affinity to CdX₂ ligands, and a model was used to help quantify the number of each site on the surface. Furthermore, this model was used to help determine the equilibrium constants Z-type ligand binding to each surface site. To further investigate the thermodynamics of binding to each site, temperature-dependent ^1H NMR studies were done coupled with Van't Hoff analysis to help identify that the origin of binding differences is mainly to an entropic effect. It was determined that much like CdSe NCs, B₂ vacant sites exist on the (100) facet due to entropic effects discussed in Chapter 2.

Furthermore, the data collected on CdS was compared to original CdSe studies done, and the difference in enthalpic effects was discussed using Sanderson bond calculations. These calculations determined that the slight difference in the enthalpic effects is due to a slightly stronger Cd-S bond than Cd-Se bond. Further experiments could also quantify the unique thermodynamics of binding to each site through isothermal titration calorimetry. This method would offer a more sensitive and precise way to measure ligand exchange thermodynamics.

Once the composition of the surface was more understood, we moved on to correlating each surface defect site and its impact on the photophysical properties of CdS NCs in Chapters 3,4 and 5. We first focused on the impact of these surface defects on the absorption profile of CdS NCs. Our initial surface studies demonstrated a direct correlation between a red shift of the excitonic peak with the creation of B₂ vacancies. This red shift was further attributed to the creation of a Stark effect on our NC system. Furthermore, the broadening of the 1S_e-2S_{3/2h} absorption is also due to the creation of B₂ vacancies on the surface. We propose that changing the Cd²⁺ layer on the surface leads to drastic changes in surface polarization, altering the absorption profile.

Furthermore, a direct correlation between creating B₂ vacancies and changes in PL emission of CdS was established. Each site has strikingly different effects on PL emission. Much like what was seen previously in CdSe NCs, B₂ vacancies are excellent exciton quenchers and greatly influence trap state emission. It was determined that the trap state emission is composed of two different trap emission states, a low and high energy trap state, respectively. It was determined that the PL efficiency of each state was influenced by the creation of surface defects and changing the S/Cd ratio on the surface.

Furthermore, we were able to directly probe the lifetimes of each trap state and determine the effects of specific surface defects. These results gave direct insight into the complex nature of the surface and how it impacts the photophysical properties of NCs. However, more studies are necessary to capture the subtle complexities of the surface thoroughly. Temperature-dependent PL studies are required to understand further the extent (if any) of energetic coupling between the excitonic state and the trap states. Furthermore, these temperature-dependent studies will also help reveal if a two trap or one trap state model is the most accurate model for our system.

Overall, from our studies presented in this thesis, it can be concluded that the creation of any B₂ vacant sites on the surface has a massive impact on the properties of the CdS NC. To fine-tune the optoelectronic properties for specific applications, B₂ vacant sites would have to be adequately quenched by surface ligands. Furthermore, the interesting behavior seen in the trap state with the creation of B₂ vacancies could potentially be used to help modulate the trap state emission for different applications. The work from the studies significantly highlights the uniqueness of the surface and that not every surface defect is equal.