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by

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**Altering Quantum Confinement in Semiconductor Nanocrystals Using
Strongly Interacting Exciton-Delocalizing Ligands**

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Strongly Interacting Exciton-Delocalizing Ligands**

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Michael Steven Azzaro

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Dedication

To Mom and Dad,

*For your unwavering love and support, without which this work would not have been
possible*

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“The pride and winning tradition of The University of Texas will not be entrusted to the weak nor the timid”

Almost exactly 6 years ago I made the decision to move to Austin and continue my education at The University of Texas. Despite some initial reservations, my desire to take on a new challenge and experience a new place led me on a journey that I now look back upon as the undoubtedly the best decision I have ever made. I have grown to love this university and I am incredibly proud to be a part of its history and tradition. I consider it a great honor to be a Texas Longhorn and will proudly represent the University of Texas for the rest of my life.

While at times it was incredibly difficult, graduate school has taught me a tremendous amount about myself, and what I am capable of accomplishing. Overall, my time in Austin has been an absolute pleasure, and I will look back on this period of my life with great fondness thanks, in no small part, to the many wonderful people I have met during my career here.

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him a friend. I was fortunate enough to be there for the beginning of his career, and I look forward to seeing the tremendous accomplishments he will achieve going forward.

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Finally, I would like to dedicate this work to my family, in particular my parents. Their love and support has allowed me to reach this point in my academic career. They have always stressed the value of education and hard work above all else, and for that I cannot thank them enough. I've sacrificed a lot of time with them in order to achieve this goal, and their understanding has meant everything to me. I love you all more than I could put into words here.

Abstract

Altering Quantum Confinement in Semiconductor Nanocrystals Using Strongly Interacting Exciton-Delocalizing Ligands

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Abstract: Semiconductor nanocrystals have long been studied as alternatives to traditional bulk semiconductor materials as active components in optoelectronic devices due to their size-tunable absorption and emission properties, as well as their ability to be processed into thin films from colloidal solutions. However, creating highly conductive nanocrystal solids remains a substantial challenge due to the presence of long ($\sim 2\text{-}3$ nm), insulating “native ligands” that are used to terminate nanocrystal growth and provide colloidal stability following their synthesis.

In this work we have used a variety of structural and spectroscopic characterization to investigate the chemical and physical changes associated with exchanging these native ligands for ligands that have the proper energetics and orbital symmetry conditions to interact strongly with nanocrystal electronic states, termed “exciton-delocalizing ligands”. This interaction is proposed to allow for delocalization of carriers beyond the nanocrystal core and into the ligand shell by reducing the potential energy barrier at the nanocrystal-ligand interface, which can be used to improve transport properties in nanocrystal solids.

Colloidal nanocrystal samples were investigated to determine if this strong interaction impacts carrier cooling rates, as this would provide insight into the degree of mixed nanocrystal-ligand character of these states. Using transient absorption spectroscopy we measured the change in electron and hole cooling rates following ligand exchange with the exciton-delocalizing ligand phenyldithiocarbamate and found that when excited near the nanocrystal band edge, the valence band states of the nanocrystals interact more strongly with the ligand than those in the conduction band.

Solid-state ligand exchange with phenyldithiocarbamate was then carried out on nanocrystal films to determine if the strong nanocrystal-ligand interaction of these exciton-delocalizing ligands impacts the exciton mobility in nanocrystal solids. Using a combination of transient absorption spectroscopy and kinetic Monte-Carlo simulations we have found that treatment with phenyldithiocarbamate yields a drastic increase in the diffusivity of excitons in nanocrystal films, and this improved transport occurs via a unique tunneling-type mechanism rather than more traditional Förster Resonance Energy Transfer.

A combination of multidimensional spectroscopy and transient absorption were used to probe the electronic structure and dynamics of ligand-exchanged nanocrystals in both solution and films. Contributions to homogeneous broadening are assigned as primarily due to ligand fluctuations in solution and energy transfer between NCs in solids. Finally, by varying the initial excitation energy in the nanocrystal we find that more highly excited carriers exhibit a greater degree of delocalization resulting from a greater degree of mixed nanocrystal-ligand character of these states.

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Chapter 1: Introduction

1.1 COLLOIDAL SEMICONDUCTOR NANOCRYSTALS

Colloidally-synthesized semiconductor nanocrystals (NCs) are a class of nanoscale materials that have garnered massive research interest since their discovery in the 1980s due to their novel optical and electronic properties.^{1,2} It was discovered that these materials allow for their absorption and emission properties to be tuned through synthetic control over their size,³ shape,⁴ and morphology (0D, 1D, etc.).⁵ This independent control over the band gap energy of a semiconductor is unique to nanoscale materials, whereas their bulk counterparts maintain a fixed bandgap energy for a given semiconductor material.

These unique effects arise in nanoscale materials due to the property of “quantum confinement”, in which the wavefunction of the electron, hole, or both carriers are spatially confined by the physical dimensions of the NC. This localization of one or both carrier wavefunctions leads to the appearance of excitonic features in the semiconductor absorption spectrum due to a spreading out of the energy levels near the conduction and valence band edges, shown in **Figure 1.1**. This effect gives rise to the absorption and emission tunability that have made NCs an active area of research for over three decades.

In addition to their tunable optical properties, their facile processability into thin film architectures makes NCs an attractive platform for many optoelectronic applications including LEDs,^{6,7} lasers,^{8,9} sensors,^{10,11} and photovoltaic devices.^{12–14} Whereas traditional bulk semiconductor materials require high-temperature, costly processing techniques, colloidal NCs can take advantage of low-cost, scalable processing methods such as dip coating,¹⁵ spin casting,¹⁶ or spray coating¹⁷ which can be carried out under ambient conditions.

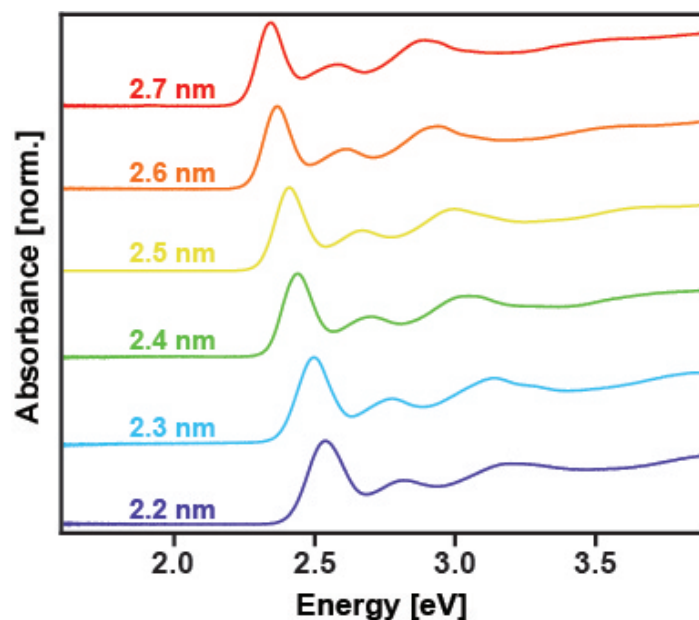


Figure 1.1: Waterfall plot displaying size dependent absorption of CdSe NCs synthesized in our lab with diameters ranging from 2.3 - 2.7 nm.

Despite these desirable properties, NCs have yet to find widespread commercial integration into many of these applications due to the substantial challenge of creating highly-conductive NC solids. This problem arises due to the details of the synthetic procedures used for producing high-quality, size and shape uniform NCs.³ The general synthetic route for metal-chalcogenide NCs proceed via the decomposition of an organometallic precursor at elevated temperatures ($> 200\text{ }^{\circ}\text{C}$), followed by the rapid injection of the desired chalcogenide (S, Se, Te) precursor. After a growth period that determines the NC size, and therefore absorption and emission properties, “native ligands” (NLs) are injected into the reaction mixture to arrest NC growth. These NLs are long (typically 12 - 30 carbon) alkyl-chain ligands that passivate the charged NC surface

and impart solubility and stability to the colloids for dispersal in a variety of organic solvents.

However when processed into a NC solid, these NLs have several adverse effects on the films' ability to conduct charge carriers. First, the long NLs ($\sim 2 - 3$ nm) create large physical separations between NCs in the film, forcing carriers to tunnel across large gaps between neighboring NCs. Additionally, the inherent stability of C-C bonds makes these NLs resistant to accepting charge carriers from the excited NC to then pass to neighboring NCs. This means that NLs act as an insulating shell around the NC and limit the efficiency of carrier mobility in NC solids. Typically carrier mobilities in NL capped NC films are on the order of $10^{-2} - 10^{-4}$ $\text{cm}^2/\text{V}\cdot\text{s}$,¹⁸ orders of magnitude below that of commercially viable bulk semiconductors.¹⁹⁻²¹

To circumvent this issue, researchers have devised procedures for exchanging these long, insulating NLs for ligands that promote more favorable carrier transport. One strategy has been to exchange NLs for shorter ligands that reduce the effective gap carriers must traverse by decreasing the average inter-particle separation within the film.²²⁻²⁵ While this strategy has improved the transport properties in NC films, the measured mobilities remain one to two orders of magnitude below bulk semiconductors.¹⁹⁻²¹

More recently, an approach that builds upon this strategy in which NLs are exchanged for ligands that not only decrease inter-particle separation, but also possess properties that allow the wavefunctions of one or both carriers to extend beyond the core of the NC and into the ligand shell. This extension of the carrier into the ligand shell can improve the wavefunction overlap between neighboring NCs. The major development of this approach is that if chosen properly, the ligand can act as a conductive pathway for charge carrier transfer. However, while use of these so called "exciton-delocalizing

ligands” (EDLs) has seen success in the literature,^{26,27} a systematic study of the properties of these ligands that allow for this delocalization effect has yet to emerge.

In the remainder of this Chapter we will derive the origin of the size-dependent electronic structure of NCs, and classify these materials based on their “confinement regime”. Next, major advancements in understanding the impact of ligands on NC electronic structure are outlined along with a discussion of the current open questions in the field. Then, a new ligand class that is able to tune NC-ligand interactions through engineering of the chemical and electronic structure is introduced, and mechanisms describing these interactions are discussed. Finally, the remainder of this work is outlined by Chapter.

1.2 ELECTRONIC STRUCTURE THEORY

Based on the details of the material dielectric constant and carrier effective masses, bulk semiconductors exhibit a characteristic length scale for the exciton wavelength called the “bulk exciton Bohr radius”. This parameter, abbreviated “ a_B ”, can be used to approximate the length scale at which quantum confinement effects begin to arise in a material. One can estimate a_B for a semiconductor using Equation 1-1

$$a_B = \frac{4\pi\epsilon\epsilon_0\hbar^2}{\mu q^2} \quad (1-1)$$

where ϵ is the material optical dielectric constant, ϵ_0 is the permittivity of free space, $\hbar$ is Planck’s constant, μ is the exciton reduced mass, and q is the charge of an electron in units of coulombs.²⁸ Plugging in values of $\epsilon \sim 9.7$ and $\mu = 9.2 \times 10^{-32}$ kg for CdSe,²⁸ our semiconductor of interest, we find that $a_B = 5.07$ nm. This indicates quantum effects arise when the diameter of the NC falls below approximately 5 nm in CdSe. Indeed, many studies have shown NCs below this threshold exhibit characteristics of quantum

confinement, including spectrally tunable absorption and emission onsets as well as the appearance of excitonic bands in their absorption spectra.^{2,29}

The bulk exciton Bohr radius can be further broken down into its component electron and hole contributions. The confinement of zero, one, or both carriers defines the “confinement regime” of the material for a nanostructure of a particular radius. In the weak confinement regime the critical dimension of the nanostructure (defined here as generic radius “ a ”) is greater than both the electron and hole Bohr radii such that $a > a_e, a_h$. In this scenario the electron and hole feel essentially no effects of quantum confinement and the exciton binding energy is exceptionally weak, similar to that of bulk systems. In the intermediate confinement regime the critical dimension of the nanostructure is smaller than one of the two carriers, more commonly the hole due to its larger effective mass relative to the electron ($a_h > a > a_e$), which leads to the onset of confinement effects. Our system of study for this report, CdSe, is an example of a material that resides in the intermediate confinement regime. Finally, a material resides within the strong confinement regime when both carrier Bohr radii are larger than the nanostructure’s critical dimension ($a < a_e, a_h$). In this regime the optical and electronic properties of the material are dominated by confinement effects. Materials found in this regime frequently exhibit small electron and hole effective masses as well as large dielectric constants, leading to large exciton Bohr radii. The large Bohr radii exhibited by these materials makes achieving critical dimensions necessary to exhibit strong confinement quite facile with modern synthetic techniques. For example both PbS ($a_B \sim 18$ nm) and PbSe ($a_B \sim 46$ nm) reside in this regime due to their large exciton Bohr radii.

However, the composition of the semiconductor material is not the only determining factor in a NC’s electronic structure. Other factors such as surface coverage by native ligands,³⁰ crystal structure of the semiconductor,^{31,32} and deviations from ideal

size and shape³³ all play a role in determining the electronic structure of individual NCs that contribute to the ensemble behavior of a NC sample. While many reports have focused on how each of these factors influence electronic structure at both the single NC^{34,35} and ensemble levels,^{32,33} only recently has the choice of surface ligand and its impact on NC electronic structure been considered.

1.3 LIGAND CONTRIBUTIONS TO ELECTRONIC STRUCTURE

Guyot-Sionnest and co-workers³⁶ were the first to determine that the type of ligands that bind to a NC surface could impact its electronic dynamics. Carrying out ligand exchanges to replace the native phosphonate ligands of CdSe NCs with either amines or thiols, they were able to show intra-band electronic cooling dynamics were altered by the types of ligands on the surface. Indeed, this laid the groundwork for a new push to develop ligand exchange chemistries that further tune the optical and electronic properties of these NCs beyond their size and shape. Initial efforts in this area focused on one main factor; the type of ligand binding group as this portion of the ligand contributes most to the overall electronic structure of the NC-ligand complex through donation of its frontier orbitals to dangling bonds of either metal or chalcogenide atoms at the NC surface.

This donation of electrons, or lack thereof, can introduce a variety of different “trap states” in the material. A “trap state” refers to the formation of a mid-bandgap state that forms for a number of reasons, including surface defects, lattice defects, and dangling bonds at the NC surface due to unpassivated surface sites. Depending on the nature of these states they can be close to the VB or CB edge (shallow), or fall further into the energetic gap between the two (deep). Regardless of their type, charges tend to

localize in these states, hurting device performance in both photovoltaic and light emitting applications.

This discovery that the binding moiety of the ligand affects the electronic structure of the NC was the first indication that one could use the ligand as an *additional parameter* to tune both the individual and ensemble properties of these materials. Early work in this area was carried out by Koole et al., who showed that using crosslinking-dithiol ligands to physically tether two NCs together improves energy transfer in colloidal NC dispersions.³⁷

Following this work, researchers began to study how the energetics of the non-binding portion of the ligand could be used to affect the potential energy barrier at the NC-ligand interface. One of the first examples of this was a systematic study of p-substituted aniline ligands carried out by Knowles et. al.³⁸ By changing the chemical functionalization of the *para*- substitution of the aniline ligand, it was observed that the amount of photoluminescence quenching varied systematically based on the HOMO energy of the aniline derivative via the creation or destruction of electronic trap states induced by the ligand exchange. This result demonstrated that the binding group of the ligand was not the only factor to consider when designing ligands to participate in a particular photo-physical process within a NC. This was one of the first works to try and develop principles for rational ligand design.

However the properties of ligands able to induce this behavior are poorly understood. What should the energetics of the ligand be relative to NC electronic states to maximize this effect? What role does orbital symmetry play in the strength of these interactions? How does this strong interaction affect the excited state dynamics of carriers in these materials? These are the types of questions we sought to answer in this work.

1.4 EXCITON-DELOCALIZING LIGANDS

Following the discovery of ligands interacting with NC states, researchers attempted to understand which molecules exhibited these properties and how they could be chemically tuned to optimize this effect. It was shown that depending on the alignment of their HOMO or LUMO levels relative to NC band edge states, different molecules could act as either hole³⁹ or electron acceptors.^{40,41} Soon after it was hypothesized that these rational design principles could be used to engineer electronic coupling between NCs in a solid, reducing the energetic barrier for charge transfer at the NC-ligand interface, and help to overcome the inherent low conductivity found in the NL capped NCs.

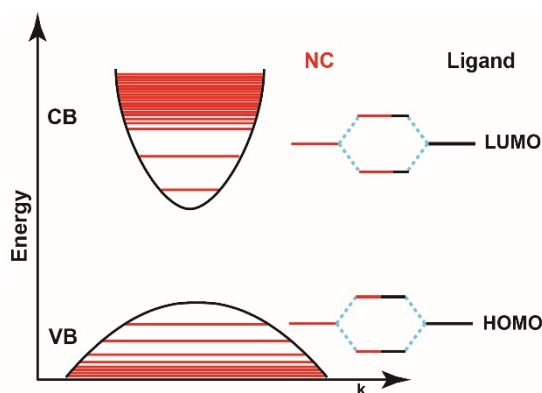


Figure 1.2: Cartoon depicting NC band structure interacting with ligand HOMO and LUMO states. Note the NC-HOMO interaction produces new states that are a mixture of NC and ligand character, while the NC-LUMO states are primarily NC-based due to the energetic mismatch of the LUMO state with the CB excitonic states.

In this study we report on the impact of one particular class of EDLs, known as dithiocarbamates, first utilized by the Weiss group.⁴² This set of ligands exhibit this carrier delocalization effect through the appearance of redshifted absorption and emission spectra of NCs upon their exchange for the NCs' NLs. This redshift appears due to a

relaxation of the quantum confinement felt by the carriers due to an increase in accessibility to ligand centered states, schematically illustrated in **Figure 1.2**.

As the wavefunction of the carriers is no longer strictly confined to the core, the energy of the NC VB states is decreased, resulting in the observed redshift of the absorption spectrum. The reason that this class of EDLs is proposed to have such a strong effect on the electronic structure of NCs is due to the resonance of HOMO states with the valence band edge states of CdSe NCs. Additionally the HOMO of the ligand has the proper orbital symmetry to mix with the valence band states, which calculations have suggested leads to the formation of hybrid electronic states shared between the ligand and CdSe NC core.⁴²⁻⁴⁵

We have characterized the interaction of these EDLs with CdSe NCs through the use of various time-resolved and steady-state spectroscopies to determine if the proposed hypothesis governing these interactions holds, and what effect this strong interaction has on the dynamics of carriers in these materials. While one might assume the strong NC-ligand interaction should be favorable for charge or energy transport, the higher density of states imparted by the dithiocarbamate ligand can potentially accelerate recombination,^{43,46} hurting performance in photovoltaic devices, while improving it in light emitting applications. Experiments that appear in Chapters 2 and 3 address these competing effects.

1.6 SUMMARY

In this dissertation we study the properties of phenyldithiocarbamate (PDTC). Specifically, we use a variety of steady-state and time-resolved optical spectroscopies to investigate its effect on the electronic structure and dynamics of both colloidal CdSe NC dispersions as well as CdSe NC films. In Chapter 2 we discuss relevant synthetic

procedures for creating CdSe NCs as well as the PDTC ligand. Ground-state characterization of these materials is included as well as interpretation of the spectral changes seen upon ligand exchange. We also discuss the processing of colloidal NCs into high-quality NC films and subsequent PDTC ligand exchange, as the majority of working optoelectronic devices require fabrication of conductive films. Chapter 3 details how PDTC impacts carrier cooling behavior in colloidal NCs, as revealed by state-resolved transient absorption spectroscopy. Our data indicates the relaxation rate is extremely sensitive to NC surface chemistry. We also use the change in cooling rate as a probe of the degree of ligand character of the CB and VB states. Chapter 4 quantifies how ligand exchange for PDTC affects carrier transport in NC solids using a combination of time-resolved spectroscopy and kinetic Monte-Carlo simulations to extract diffusion lengths and carrier hopping rates for comparison to NL-capped NCs. Finally, Chapter 5 describes the development and use of two-dimensional electronic spectroscopy (2DES) to understand the electronic structure of both colloidal NCs and NC films. We use 2DES to understand how heterogeneity plays a role in driving carrier transport in electronically coupled NC solids. We also compare results from 2DES and transient absorption to understand how the excitation energy impacts the mobility of excited carriers in the film. The result of this work is a deeper insight into the mechanism of how ligands can impact the electronic structure and transport properties of next generation quantum-confined materials.

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Chapter 2: Synthesis of Colloidal Semiconductor Nanocrystals and Ground-State Characterization

2.1 INTRODUCTION

The synthesis of high-quality nanocrystals (NCs) and the subsequent characterization of their optical and structural properties provide the basis for the remainder of this work. Studies have shown NC size and shape uniformity has a tremendous impact on their ability to self-assemble into ordered, long-range structures.¹⁻³ This self-assembly into structures with micro- and mesoscale order is critical to the development of NC solids capable of conducting charge over long distances,⁴⁻⁶ making it crucial that we develop methods to reliably produce size-uniform NCs ensembles.

In this chapter we describe the synthesis and characterization of NCs and NC solids used in the rest of this work. First, we discuss methods for synthesis of high-quality, size and shape uniform CdSe NCs capped with the native ligand (NL) oleate, and briefly describe experimental methods used for both their electronic and structural characterization. Next, we outline synthesis of the exciton-delocalizing ligand (EDL) phenyldithiocarbamate (PDTC), and subsequent characterization to confirm its successful preparation. As described in Chapter 1, we have chosen to use PDTC as a model system due to its proposed effect on CdSe NC band structure that relaxes the confinement of charge carriers, rendering them more accessible to carry out catalytic, photovoltaic and other desirable processes.⁷⁻¹⁰

With our materials in hand, we detail the process of exchanging highly insulating oleate ligands for PDTC on colloidal NCs. In solution, NC-ligand coupling dominates over potential longer range NC-NC coupling that can occur in NC-based solids. To distinguish effects of ligand exchange in solution from those in solids, we first characterize NC solutions to look at the impact of the PDTC ligands on isolated NCs. We

designed experiments in this way to build a bottom-up understanding of our system before considering PDTC's impact on exciton transport in solids. Solution-phase experiments are described in Chapter 3 and portions of Chapter 5.

After characterization of these NC-ligand interactions in solution we extend this knowledge to the study of NC solids. By processing colloidal NCs into thin films on SiO₂ substrates and developing procedures for the exchange of ligands in the solid state, we can study the impact of PDTC on exciton behavior in architectures resembling those that would be used in a working NC device. The optical and structural characterization of PDTC-exchanged NC solids is discussed further in Chapters 4 and 5. By understanding each level of this hierarchy prior to adding complexity, we have been able to separate effects of relaxation of quantum confinement, heterogeneity, improved electronic coupling, and improved energy transport and assign them as derived from ligand exchange, from processing into a thin film architecture, or a combination of the two.

2.2 SYNTHESIS AND CHARACTERIZATION OF CDSE NANOCRYSTALS

Synthesis of CdSe Nanocrystals

CdSe NCs used in this research were prepared via a modified literature method.¹¹ Briefly, 420 mg of cadmium(myristate)₂ and 20 mL of 90% technical grade 1-octadecene were added to a three-neck round-bottom flask, vacuumed for 1 hour, then purged under N₂ gas. After purging for 1 hour, the reaction was heated to 250 °C under positive N₂ flow while being stirred vigorously throughout (500 RPM). Once the solution had reached 250 °C, 5 mL of a 0.1 M Se suspension (24 mg selenium in 6 mL 1-octadecene) was rapidly injected into the reaction, nucleating NC growth. The reaction was maintained at 240 °C until the solution reached a color indicative of NCs of a

desired size. At this point, 3 mL of 90% technical grade oleic acid was injected into the reaction mixture. The solution was then stirred for an additional 3 min at 240 °C before cooling to room temperature. To remove the supernatant, the resulting mixture was dispersed in ethanol and centrifuged at 3200 RPM for 10 minutes. This process was repeated until a NC pellet had formed. NCs were then washed using 1:1 (v/v) n-hexane:ethanol and centrifuged for 10 minutes at 3200 RPM to remove excess oleate ligands and unreacted cadmium precursor. The liquid phase was removed, and this process repeated until the NCs became difficult to disperse in the n-hexane phase. The resulting NCs were then dispersed in 1 mL of 1:1 (v/v) n-hexane:octane for film preparation (~50 mg/mL), or dichloromethane for solution characterization.

Optical Characterization of CdSe Nanocrystals

Steady-State UV-Vis Absorption Spectroscopy

Samples were prepared by dissolving purified NC pellets in DCM and absorption spectra collected on a Shimadzu UV-2600 spectrometer using a 1 mm or 1 cm path length near-IR transmissive quartz cuvette. Prior to collecting each spectrum, a DCM blank was obtained in the same cuvette for each sample such that the spectra were baseline corrected from sample to sample.

Structural Characterization of CdSe Nanocrystals

Grazing Incidence Wide Angle X-Ray Scattering (GIWAXS)

GIWAXS patterns were collected on a Rigaku Ultima IV X-Ray diffractometer ($\lambda = 1.5461 \text{ \AA}$). Measurements were conducted with a collinear beam with an angle of incidence of $\omega = 0.2^\circ$. GIWAXS was used to identify the crystal structure of CdSe NCs

based on the synthetic route chosen.¹¹ The route we employ in this work yields CdSe NCs with a zinc blende crystal structure, rather than the more common wurtzite structure obtained via most synthetic routes. Using GIWAXS on NC films we were able to confirm the presence of NCs with zinc blende crystal structure in the ensembles. A GIWAXS pattern displaying diffraction from the {111}, {220}, and {311} atomic planes confirming zinc blende structure is shown in **Figure 2.1**.

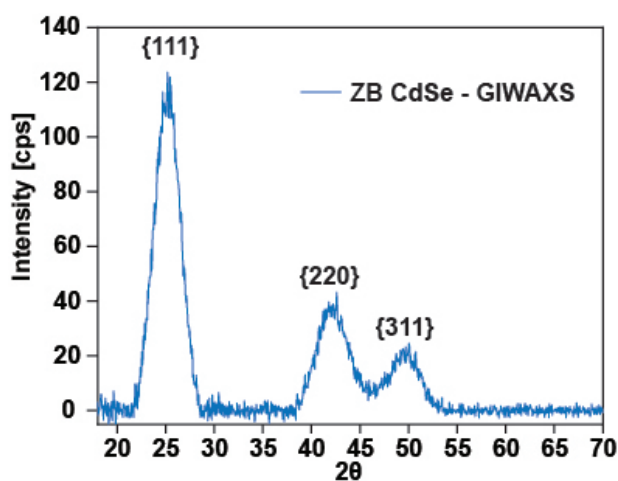


Figure 2.1: GIWAXS spectrum of CdSe NCs displaying diffraction of {111}, {220}, and {311} atomic planes consistent with zinc blende structure.¹²

2.3 SYNTHESIS AND CHARACTERIZATION OF PHENYLDITHIOCARBAMATE (PDTC)

Synthesis of PDTC

Phenyldithiocarbamate (PDTC) was synthesized via a modified literature procedure⁷ by chilling 5 mL of aniline in 30 mL of 30 w/w% ammonium hydroxide to 0 °C, maintained via an external ice bath, while stirring vigorously under N₂ flow. To this solution, 5 mL of carbon disulfide was added drop-wise over 15 minutes. Following carbon disulfide addition, the solution was stirred for 45 minutes at 0 °C before returning

to room temperature. The resulting yellow-white precipitate was subsequently isolated via vacuum filtration, washed with dichloromethane, and stored in a desiccator in the dark. The final product was a fine white powder. Successful synthesis was confirmed via ^{13}C NMR. PDTC was synthesized as an ammonium salt, and its structure is shown in

Figure 2.2.

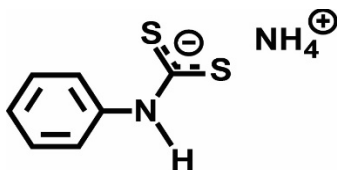


Figure 2.2: Chemical Structure of PDTC ammonium salt

Optical Characterization of PDTC

Steady-State UV-Vis Absorption Spectroscopy

Samples were prepared by dissolving PDTC powder in DI H₂O and diluting until the peak absorbance was less than 0.2 OD. Absorption spectra were collected on a Shimadzu UV-2600 spectrometer using a 1 cm path length near-IR transmissive quartz cuvette. Prior to collecting each spectrum, a DI H₂O blank was obtained in the same cuvette for each sample for baseline correction. Prominent absorption peaks at 292 and 254 nm indicated successful synthesis of PDTC as these peaks match features in PDTC's previously reported absorption spectrum.^{8,13}

2.4 SOLUTION-PHASE LIGAND EXCHANGE AND GROUND STATE CHARACTERIZATION

To separate out effects on NC absorption spectra arising from processing NCs into a thin film, we first characterized colloidal NCs ligand exchanged with PDTC. Based

on work from Weiss and co-workers^{7-10,14} we have developed a strategy for the colloidal exchange of PDTC ligands, and subsequent surface repair. While the experimental procedure is outlined below, a discussion of surface repair with cadmium (II) acetate ($\text{Cd}(\text{Ac})_2$) and its impact on NC photophysics is expanded in Chapter 3. Briefly, due to dynamic equilibrium between bound and unbound PDTC ligands upon exchange, defects tend to arise in PDTC-exchanged NCs as the strength of the cadmium-sulfur bond can result in the stripping of cadmium atoms from the NC surface. Previous reports have used $\text{Cd}(\text{Ac})_2$ to repair these surface defects induced by the ligand exchange and enhance the fluorescence quantum yield of the samples.¹⁵ While our interpretation of the effects of $\text{Cd}(\text{Ac})_2$ differ from this previous report, we find similar effects on the optical properties of our NCs upon its addition to solutions of CdSe NCs. These results are discussed in detail in Chapter 3.

Solution-Phase Ligand Exchange and Surface Repair ***PDTC Ligand Exchange on NCs in solution***

Solution PDTC ligand exchanges were performed in DCM. 125 - 5000 molar equivalents of PDTC were added to a solution of $\sim 10\ \mu\text{M}$ NCs that was then stirred in the dark for 4 - 24 hours depending on the sample. Following the exchange, the solution was passed through a $0.45\ \mu\text{m}$ syringe filter to remove any undissolved PDTC or aggregated NCs from solution.

$\text{Cd}(\text{Ac})_2$ Addition

NC surface repair with $\text{Cd}(\text{Ac})_2$ was performed by adding $50\ \mu\text{L}$ of methanol and 1000 molar equivalents of $\text{Cd}(\text{Ac})_2$ to a solution of $\sim 10\ \mu\text{M}$ NCs in DCM. The

resulting solution was then sonicated in the dark for two hours. Following sonication, the solution was passed through a 0.45 μm syringe filter to remove any undissolved $\text{Cd}(\text{Ac})_2$ or aggregated NCs.

2.5 IMPACT ON ELECTRONIC STRUCTURE IN SOLUTION

Weiss and co-workers were the first to introduce the terminology of “exciton-delocalizing ligands” and propose the idea that such ligands could be used to lower the confining potential at the NC-ligand interface.^{7–10,15} They also proposed that the resulting carrier delocalization could be used to drive catalytic reactions by increasing the accessibility of electrons or holes to the bath. We have attempted to use this effect to improve conductivity of solids by creating a more continuous density of states between NC units in a close-packed array.

These effects are proposed to arise due to the formation of new hybrid states between NC orbitals and frontier orbitals of coordinating ligands. These new states are formed when two conditions are satisfied; (1) when the HOMO or LUMO energy of the ligand is in resonance with either the valence band (VB) or conduction band (CB) states, respectively, and (2) the frontier orbitals of the ligand have the proper symmetry to mix with the surface states of the NC. In the case of our system, PDTC’s HOMO has been calculated at -6.2 eV relative to vacuum, which sits up to 100 meV above or below the VB edge of CdSe, depending on the NC size, placing it close resonance with the $1\text{S}_{3/2(\text{h})}$ state.⁷

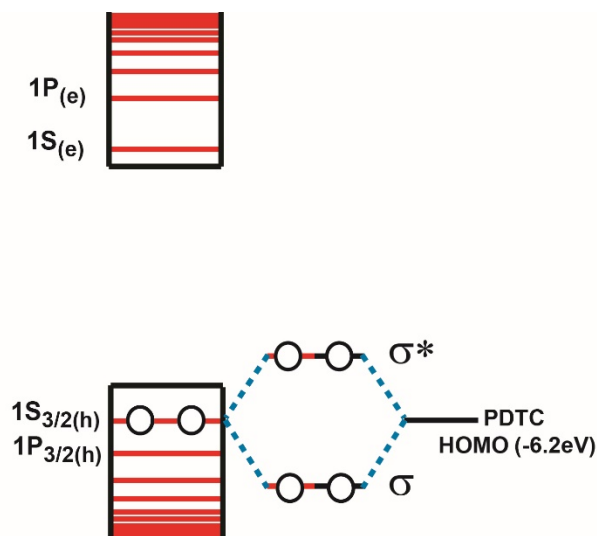


Figure 2.3: Cartoon CdSe NC band structure showing mixing between the PDTC HOMO and $1S_{3/2(h)}$ VB state.

Additionally, the π -type symmetry of the frontier orbitals of PDTC carbamate binding moiety provides strong orbital overlap with the Se 4p orbitals that comprise CdSe's VB. In fact, PDTC has the proper energetics and symmetry to impact the electronic structure of other metal-chalcogenide NCs, such as CdS, PbSe, etc. to varying degrees.⁹

As a result of the combination of close energetic matching and orbital overlap at the NC surface these new states form in a “molecular orbital” theory like fashion in which both bonding and antibonding orbitals are formed from a linear combination of atomic orbitals, as shown in **Figure 2.3**. The energy of these states can be predicted using a simple relation described by Equation 2-1:

$$E_{\sigma} = \frac{V^2}{\Delta E} \quad (2-1)$$

in which V^2 is the coupling strength of the interaction, governed by the spatial overlap of

the orbitals, and ΔE is the energetic difference between the ligand orbital and the NC states. Due to the continuous density of states found in semiconductor materials this interaction produces a number of new states that share both ligand and NC-centered character. This mixed-orbital character is hypothesized to lower the NC bandgap by providing the VB hole access to lower-energy, hybrid NC-ligand excitonic states.⁹ This is in stark contrast to the NL case in which the frontier orbitals of NLs, such as trioctylphosphonate or oleate, have HOMO and LUMO energies far from the band edges of these materials.¹⁶ In this case a very high potential energy barrier is presented to carriers in the NC, preventing them from accessing the ligand shell due to the states remaining explicitly centered on either the NC or the ligand.¹⁶

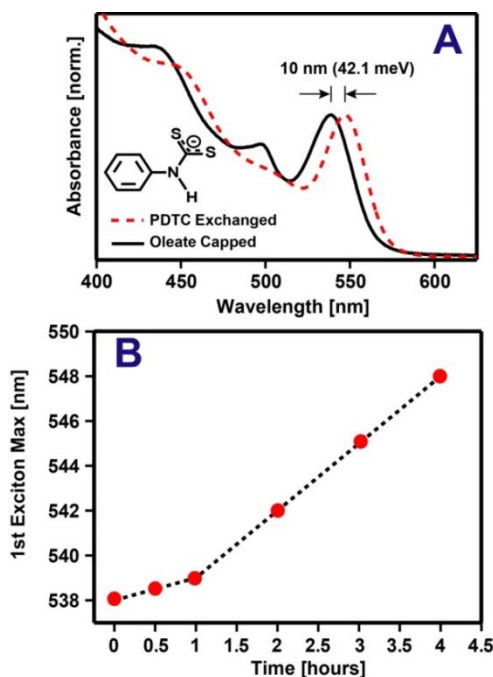


Figure 2.4: (A) Steady-state absorption spectra of 2.8 nm diameter CdSe NCs before (black) and after (dashed red) a 4 hour PDT exchange. (B) Kinetics of 1st exciton maximum shift as a function of exchange time.

This relaxation of NC quantum confinement results from the ability of carriers to access the ligand shell and no longer strictly be confined to the NC core. Spectroscopically, this effect manifests as a redshift of the NC absorption spectrum, as shown in **Figure 2.4**. Here, two main features arise as a result of the ligand exchange with PDTC: (1) the lowest energy excitonic band (X1), along with the rest of the absorption spectrum is redshifted from the NL capped NC solution, and (2) the oscillator strength of the 2nd excitonic band (X2) decreases. While we have discussed the physical reasoning for the first effect, the second is more subtle. This decreased absorption of X2 is attributed to the mixing of X1 and X2 states in the VB caused by the addition of PDTC.¹⁶ This mixing is theorized to push the energetic states of the VB associated with X2 down into the X1 band.

In solution we have achieved bathochromic shifts of up to 75 meV for NCs of the smallest size in our synthetic capabilities (~2.3 nm diameter) by allowing the exchange to proceed for >48 hours. However, to maintain colloidal stability and preserve the structure of NC surfaces we choose to terminate the exchange after 4 hours, as during this time window the majority (~60%) of the total shift occurs. At exchange times much longer than 4 hours we find significant decrease in solubility and major restructuring of the NC surface due to displacement of Cd²⁺ - oleate complexes by PDTC ligands.

While the Weiss group and others have investigated many of the ground state properties of NCs functionalized with PDTC and other EDLs, a systematic study of how they impact excited state dynamics has been lacking. Active components in electronic devices require mobile charges to either recombine or separate depending on their

application. Thus, information regarding timescales for charge separation, recombination, migration, and trapping that will aid in understanding how these materials perform in a device application require techniques that can monitor these processes in real time.

In Chapter 3 we measure and analyze how ligand exchange with PDTC impacts the rates of “hot” intraband carrier cooling in these materials. Due to the strong association of PDTC with CdSe VB states, and the formation of these new hybrid orbitals discussed above, one may hypothesize that carrier cooling may be highly accelerated due to an increased density of states and/or new electronic to vibrational energy transfer (EVET) pathways available due to new ligand vibrational modes available upon PDTC exchange. In either case this accelerated carrier cooling would hurt device performance by limiting the amount of energy available to carry out catalytic reactions or to be harnessed for photovoltaic applications. In Chapter 3 we use methods of chemical passivation with $\text{Cd}(\text{Ac})_2$ to elucidate the origin of these effects.

2.6 NANOCRYSTAL FILM PREPARATION AND CHARACTERIZATION

Working NC optoelectronic devices require formation of highly ordered NC structures as lattice defects and disordered solids tend to localize charges in low-energy sites.¹⁸ Here we detail the procedures used for preparing high-quality NC films and carrying out solid-state ligand exchange used throughout Chapters 4 and 5. We also detail the techniques used for steady-state optical and structural characterization of our NCs. This characterization is used to make predictions about changes in both optical and structural properties of NC films induced by PDTC ligand exchange. We will use these

optical and structural changes to aid in our interpretation of the dynamics that manifest in transient spectra of the samples as discussed in Chapter 4.

Film Deposition

Substrate Cleaning Procedure

Prior to deposition of NC films, SiO₂ substrates were cut into $\sim 1'' \times 1''$ squares using a diamond tip pen. The substrates were then cleaned via sonication in chloroform, isopropyl alcohol, acetone, and toluene for 20 minutes each, in that order. Following sonication, the substrates were stored in toluene until used for film deposition. Prior to spin-casting, the films were removed from the toluene bath and dried under N₂ flow.

Nanocrystal Film Preparation

To produce the CdSe-Oleate films used in this study, 60 μ L of a ~ 50 mg/mL solution of NCs in 1:1 (v/v) n-hexane:octane were dropped onto the spinning SiO₂ substrate. The spin-coating procedure used consists of spinning the substrate at 1000 RPM for 1 minute, followed by an increase in the spin rate to 4000 RPM for an additional 10 s. This procedure produced optically clear, homogeneous films over a $1'' \times 1''$ square area.

2.7 SOLID STATE LIGAND EXCHANGE

To carry out ligand exchange on NC films a new procedure was developed to circumvent several issues. While one possibility is to process films from NCs that were exchanged with PDTC in solution, as this would result in more uniform exchange of PDTC ligands across the NC ensemble, we find this method produces poor quality films. The colloidal ligand exchange requires the use of dichloromethane as the solvent as it is

able to solubilize NCs and has the proper pK_a to solubilize the PDTC salt that results from its synthesis.⁷ While dichloromethane is a good solvent for the colloidal exchange, its high vapor pressure results in fast evaporation of the solvent, leading to bubble formation that disrupts NC long-range ordering and degrades film optical quality.

Instead, we have developed a solid-state ligand exchange method in which a spun-cast film is soaked in a solution containing PDTC ligands. We have chosen this method as the optical quality of the film following ligand exchange is greatly improved. Additionally, studies have shown the long-range order of solid-state ligand-exchanged films can exceed that of films produced from pre-exchanged NCs suspensions, due to the heterogeneity in solution-phase ligand exchange disrupting the regularity of inter-particle spacing.³

PDTC Ligand Exchange

Ligand exchange for PDTC was carried out by submerging as-cast CdSe-oleate films in a 10 mM PDTC solution in methanol (46.7 mg PDTC/25 mL methanol). During ligand exchange, films were kept in the dark and allowed to exchange for up to 4 hours as this period was found to lead to a saturation of the observed redshift while yielding films with a high degree of optical transparency. Ligand exchanges that extended beyond this 4 hour time window showed marked decrease in film optical quality.

2.8 OPTICAL FILM CHARACTERIZATION

Steady-State UV-Vis Spectroscopy

Transmission and reflectance spectra were collected on a Shimadzu UV-2600 spectrophotometer with an ISR-2600 integrating sphere attachment. Both transmission

and reflectance spectra were collected to properly account for reflective losses from the front face of sample films, and used to calculate their absorption spectra.

Steady-State Emission Spectroscopy

Emission spectra were collected on a Horiba Fluorolog3 fluorimeter over a range of 2.58 – 1.55 eV using a integration time of 2 s. Spectra were collected in a right-angle geometry, where the film was tilted 30° from normal to the excitation source. Films were excited using an excitation energy of 3.08 eV. Excitation and emission slit widths were set to yield 2 nm spectral resolution.

2.9 STRUCTURAL FILM CHARACTERIZATION

Profilometry Measurement

Profilometry measurements were collected on a KLA Tencor Alpha-Step D-500 stylus profilometer. Prior to these measurements, CdSe-Oleate and CdSe-PDTC films described above were scribed down to a 1 cm × 1 cm square and a small portion of the film was removed by a razor blade, creating a step edge that exposed the SiO₂ substrate below each film. The stylus was scanned 0.4 mm across the step edge at a scan speed of 0.01 mm/s with a stylus force of 1.0 mg.

Scanning Electron Microscopy

Samples for scanning electron microscopy (SEM) were prepared using the same procedure described in the “Nanocrystal Film Preparation” section apart from the use of a conductive ITO substrate. Images were collected on a Hitachi S5500 SEM with an accelerating voltage of 5 kV.

Scanning Transmission Electron Microscopy

Samples for scanning transmission electron microscopy (STEM) were prepared by submerging a lacey carbon-coated 200 mesh copper grid (SPI Supplies) into a $\sim 10\ \mu\text{M}$ solution of oleate-capped NCs in hexane for 30 s. For images of the ligand exchanged samples, the grid was then dipped into a 10 mM PDTC solution in methanol for an additional 30 s prior to imaging. Scanning transmission electron microscopy (STEM) images were collected with a high-angle annular dark field (HAADF) detector on a JEOL 2010f Transmission Electron Microscope. Images were analyzed for center-to-center NC distances using the Gwyddion Image Analysis software package.²³ Inter-NC distances were extracted using the profile tool to determine the average separation between NCs in each sample.

2.10 DISCUSSION OF LIGAND-EXCHANGED NC FILMS

The CdSe NC films used in this study¹⁹ were produced via a facile, room temperature spin-coating procedure that yields highly uniform and optically transparent thin films ($\sim 220\ \text{nm}$ thickness) on SiO_2 substrates. The ability of this spin-casting process to produce NC films with long-range order was confirmed via Scanning Electron Microscopy (SEM), which showed films display uniform topography over tens of microns (**Figure 2.5**, top). The bottom panel of **Figure 2.5** displays a NC film before (left) and after (right) ligand exchanged with PDTC. This image highlights the high degree of optical quality retained post-exchange, leading to transparent films suitable for optical studies. We also note the color change associated with the pre- and post-exchange

indicating that the electronic structure of the material has been altered by ligand exchange with PDTC.

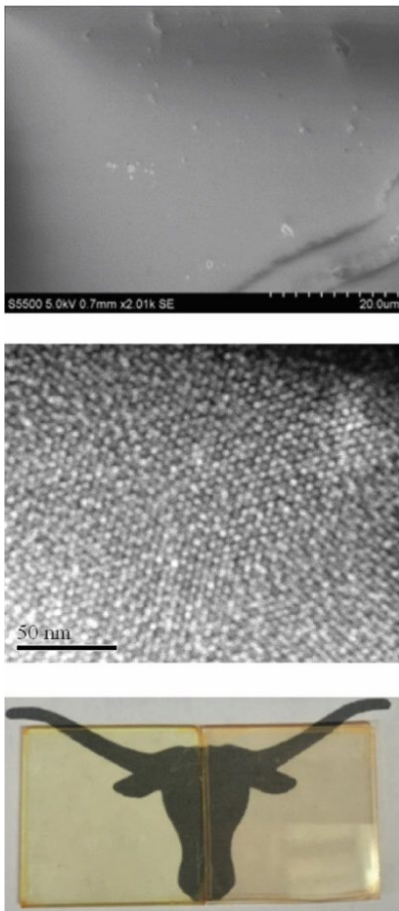


Figure 2.5: (Top) SEM image of CdSe-Oleate film showing long-range order and film homogeneity. (Middle) STEM image showing NC packing structure. (Bottom) Photograph highlighting the optical clarity of CdSe-Oleate (left) and CdSe-PDTC (right) films. Note the color change of the film post ligand-exchange.

After preparing oleate-capped NC films, solution-phase PDTC ligand exchange was carried out, which alters both the packing of the film as well as its electronic structure. Profilometry measurements revealed PDTC ligand exchange results in a decrease of the film's height to 90 nm, a 59% reduction in film thickness (**Figure 2.6**).

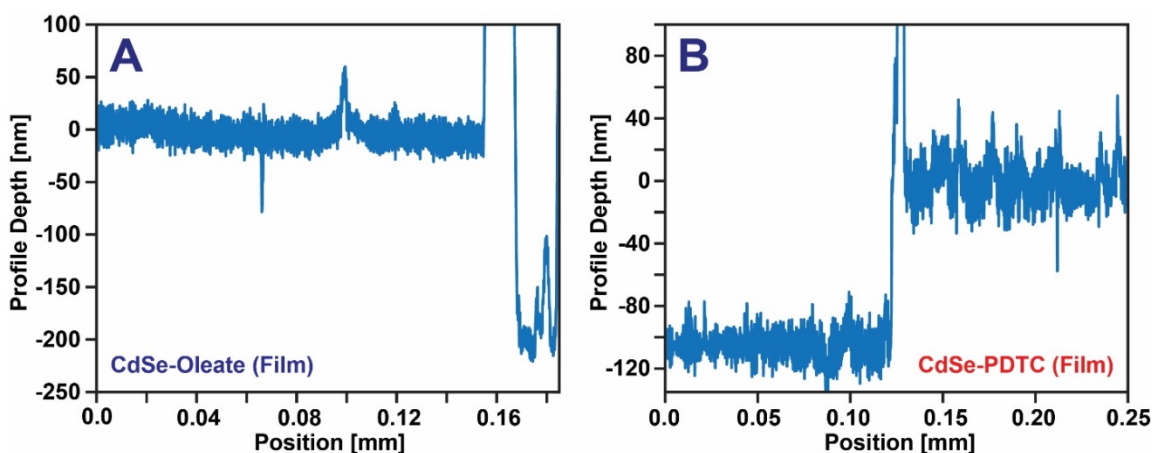


Figure 2.6: Representative profilometry profiles of (A) CdSe-Oleate and (B) CdSe-PDTC films. Several CdSe-Oleate and CdSe-PDTC films were measured and were found to have average thicknesses of 218 ± 8 nm and 91 ± 13 nm, respectively.

Assuming no NC loss during ligand exchange, this procedure yields a film with an average center-to-center separation of 3.7 ± 0.5 nm. We note this degree of compression is consistent with the difference in end-to-end length between PDTC (0.7 nm) and oleate ligands (2 nm) estimated from geometry optimized DFT calculations using a B3LYP functional and 6-311+G** basis set. Assuming NC films can be described as a collection of close-packed spheres with diameters given by the NC diameter plus a single ligand predicts the film should decrease in volume by $\sim 65\%$ upon full PDTC exchange if the ligands were perfectly interdigitated. This change is supported by STEM measurements that show following ligand exchange the NC center-to-center distance decreases from 4.7 ± 0.5 nm to 4.1 ± 0.7 nm (**Figure 2.7**). The decrease in the average center-to-center distance of the CdSe-PDTC sample reflects the shorter end-to-end length of PDTC relative to oleate, ~ 0.7 nm versus 2.0 nm, respectively.

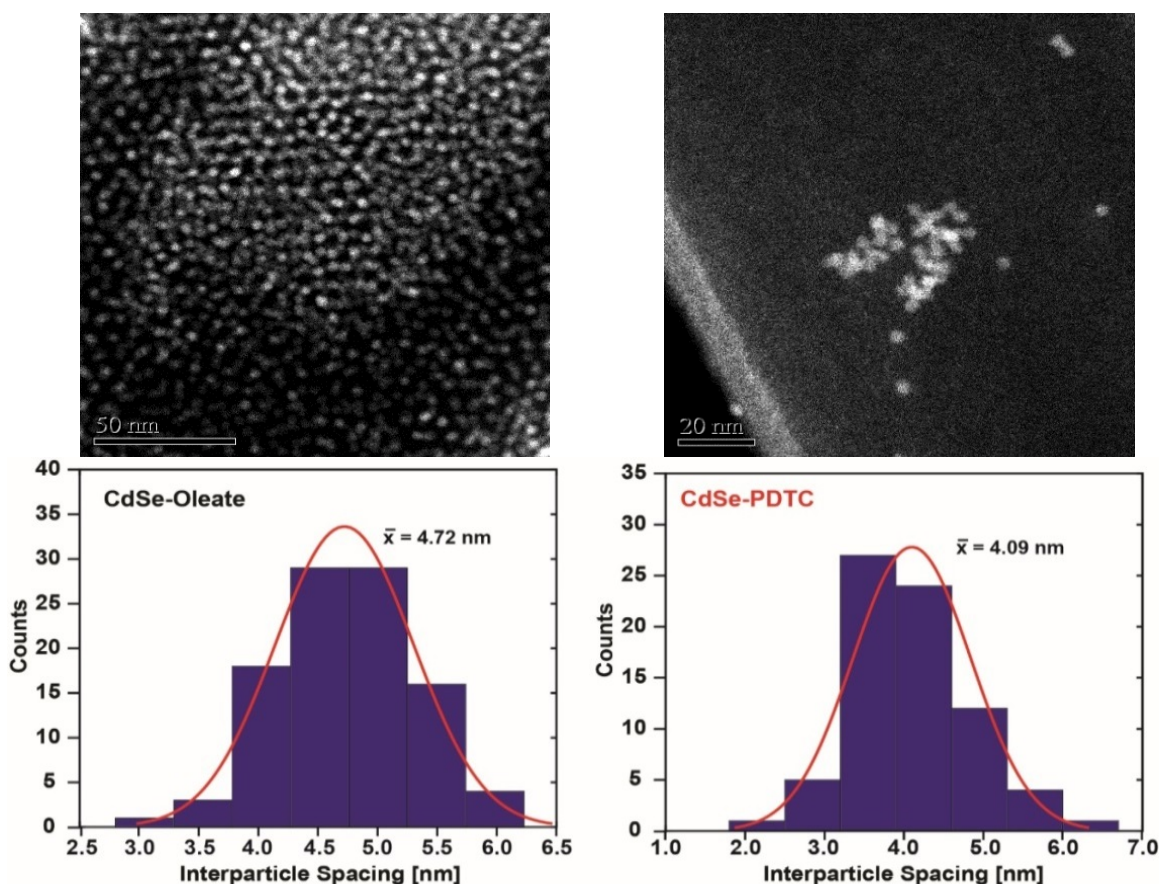


Figure 2.7: Representative STEM images of (Top Left) CdSe-Oleate and (Top Right) CdSe-PDTC treated TEM grids. Measured distributions for center-to-center distances of CdSe-Oleate (Bottom Left) and CdSe-PDTC (Bottom Right) samples.

While our transient absorption results described in Chapter 4 highlight that different NCs within the film bind varying amounts of PDTC following solid-state ligand exchange, our profilometry and TEM measurements imply the amount of oleate that remains in the film is somewhat small.

In addition to structural changes, ligand exchange with PDTC also modifies the optical properties of CdSe films. **Figure 2.8** compares optical spectra of CdSe films comprised of 2.3 nm NCs, both before and after ligand exchange to replace oleate with

PDTC. Upon PDTC treatment, the lowest energy exciton band (X1) of a CdSe film undergoes a redshift shift of ~ 110 meV. A similar shift of the emission lineshape of the film is also seen (**Figure 2.8B**), as well as broadening of both the absorption and emission bands of the ligand-exchanged NC solid. While the redshift has been previously attributed to a relaxation of confinement at the NC-ligand interface due to mixing between the electronic states of the NC and PDTC ligand, broadening of the X1 band and emission linewidth upon PDTC exchange have not previously been reported for solution-phase ligand exchanges.^{7,16,20}

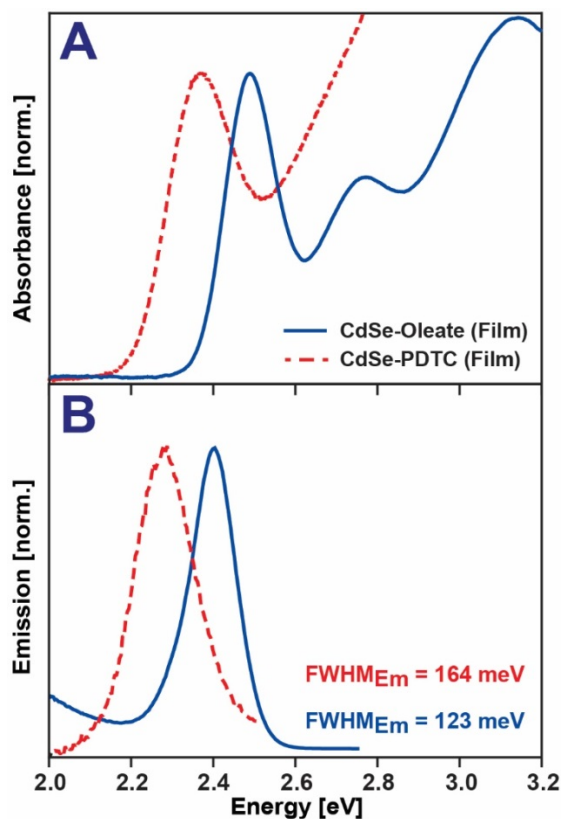


Figure 2.8: (A) Absorption spectra of CdSe-Oleate (blue) and CdSe-PDTC (dashed red) films. (B) Emission spectra of CdSe-Oleate (blue) and CdSe-PDTC (dashed red) films. FWHM values for the band edge emission of each film are reported.

Two different effects could give rise to this observed broadening. First, PDTC's ability to allow carriers to partially extend into the CdSe ligand shell could enhance electronic coupling between neighboring NCs, leading to a modification of their spectra. Prior work on NC superlattice films and ligand-exchanged solids provides some precedence for this scenario. In particular, PbSe superlattices display similar broadening of their optical spectra that has been attributed to necking between particles within the lattice.⁶ Likewise, CdSe films subjected to a solid-state ligand exchange process in which native ligands were exchanged for tert-butylthiol ligands and subsequently annealed display similarly broadened spectra that were assigned to an increase in connectivity between NCs within the film.²¹ Alternatively, as the magnitude of the change in the X1 exciton energy depends on the number of PDTC molecules that coordinate to a NC's surface,²² heterogeneity of PDTC exchange within the film could produce a distribution of exciton energies that would similarly give rise to a redshifted, but broadened X1 absorption band. In this latter case, exciting the ensemble of NCs that comprise a film could lead to a net migration of energy from high energy to lower energy sites over time if the exciton transfer rate is fast relative to the exciton lifetime. We will explore these two possible scenarios in detail in Chapters 4 and 5.

2.11 CONCLUSIONS

In this Chapter we have described the synthetic methods used throughout this work for producing high-quality, size and shape uniform NCs, as well as their steady-state optical and structural characterization. This method produces oleate-capped CdSe

NCs with a zinc blende crystal structure with diameters in the range of $\sim 2.3 - 3$ nm based on empirical sizing curves from Yu et. al¹⁷ and confirmed via TEM.

We also describe the synthesis of our EDL of interest, PDTC, and confirm its successful synthesis using a combination of UV-Vis and NMR spectroscopies. This ligand serves as the basis for our investigation of how EDLs affect the excited state dynamics of semiconductor NCs. The process for carrying out ligand exchange in solution is outlined and we describe how PDTC affects the NC band structure.

It is proposed that PDTC's HOMO has the proper energetics and symmetry to mix with CdSe VB states, creating new states with mixed NC and ligand-based character that allow for wavefunction extension into the ligand shell. We see this effect appear spectroscopically as a redshift of the NC absorption due to the relaxation of quantum confinement.

We have also described the procedures used to prepare and characterize CdSe NC films on SiO₂ and their subsequent ligand exchange with PDTC. We find that using this spin-casting procedure we are able to produce films of NCs typically ~ 200 nm in thickness with high optical quality and long range structural order, confirmed by both SEM and TEM.

Optical spectroscopy was employed to determine changes in the electronic structure of NC films upon ligand exchange with PDTC. We find that, similar to solution-phase exchanges, the X1 band of the NCs shift to lower energy. However, in addition to larger redshifts than those measured in solution, we also observe a broadening of the X1 and emission bands in solids. We propose that this broadening can be attributed to a

combination of inter-NC coupling, due to the proximity of NCs in a solid relative to solution, and heterogeneity in ligand exchange. This redshift and broadening are also reflected in emission spectra of NC films.

Structural characterization allows us to understand what physical changes occur in NC films when treating with PDTC, such as changes in the surface morphology and average inter-particle distance that can lead to changes in exciton hopping rates, which will be discussed in Chapters 4 and 5.

In the next Chapters, we will discuss the effects of these ligands on the excited state dynamics in both solution (Chapter 3) and films (Chapter 4), as well as the effect on electronic coupling and energy transfer (Chapter 5). In each of these cases we use spectroscopic evidence to make predictions regarding ligand contributions to the NC states being excited and how the energetic structure of NC ligands impacts the degree of exciton delocalization.

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Chapter 3: Influence of PDTC on Nanocrystal Intraband Cooling Dynamics*

* Work previously published as “Can Exciton-Delocalizing Ligands Facilitate Hot Hole Transfer from Semiconductor Nanocrystals?” *J. Phys. Chem. C* **2016**, 120 (49), 28224–28234.

3.1 INTRODUCTION

While reports examining the impact of exciton-delocalizing ligands (EDLs) on mobility and device efficiency have appeared, only a handful of studies examined the kinetics of charge carrier transfer facilitated by these ligands.^{1–3} A recent report has demonstrated sub-picosecond transfer of photo-excited holes in CdS nanocrystals (NCs) to a molecular acceptor linked to the NC surface by the EDL phenyldithiocarbamate (PDTC).⁴ The rapid timescale observed for this transfer suggests that it may be fast enough to compete with carrier cooling to the NC band edge. If EDLs can facilitate hot carrier transfer, this would be an exciting development as it would provide unique opportunities for advancing both photocatalysis⁵ and solar energy applications.⁶ Here, harvesting hot carriers could both improve the efficiency of these processes and provide access to previously inaccessible photo-driven reactions.

While hot electron cooling in CdSe NCs occurs through Auger energy transfer to holes,⁷ no such relaxation channel exists for excited holes due to the larger energy level spacing in the conduction band (CB) with respect to the valence band (VB).^{8,9} Therefore it is expected that hole cooling primarily occurs through electronic-to-vibrational energy transfer (EVET) pathways, some of which involve direct energy transfer to vibrational modes of surface bound ligands.^{10,11} Thus, one potential cause for concern is that the

strong association between charge carriers and EDLs that extends carrier wavefunctions into the ligand shell may also facilitate rapid carrier cooling via EVET, hindering the prospects of using EDLs to harvest hot carriers. However, a study by Schnitzenbaumer and coworkers³ found that while carrier cooling rates are impacted by surface-bound EDLs, the origin of these changes is not obvious, suggesting that despite stronger coupling to ligands, EDLs may prove viable conduits for hot carrier transfer.

As a test system for evaluating EDL-facilitated carrier transfer we have elected to examine PDTC. PDTC has been studied extensively by Weiss and coworkers^{12–15} because of its large impact on metal-chalcogenide NC absorption. When bound to CdS NCs, PDTC can lower the bandgap of these materials by nearly 1 eV through mixing of its HOMO with occupied states near the NC band edge, forming hybrid states wherein holes partially reside in the PDTC ligand shell.^{12,16} This strong association of the NC and ligand states should provide a strong test case for evaluating the influence mixing between these states on carrier relaxation rates.

One hypothesis is that this strong NC-ligand interaction should have a large impact on cooling rates, and could be used as a way to determine the ligand-centered character of the NC excitonic state. Understanding this effect would also provide insight into the mechanism of this enhancement of the cooling rate. By comparing the cooling rates of the oleate-capped NCs, which are incapable of NC-ligand state mixing, with PDTC exchanged NCs, we can make predictions about the degree of hybrid NC-ligand character to the NC excitonic states following ligand exchange. For example, calculations predict that states near the VB edge of CdSe NCs treated with PDTC have more

contribution from ligand-centered states than those near the CB edge due to the favorable energetic alignment of CdSe's VB with PDTC's HOMO.¹⁶ By contrast PDTC's LUMO is predicted to fall well above the CdSe CB edge, and therefore contributes less to the density of states in this region.¹⁶ Therefore we would expect that for band edge excitations that hole dynamics would be affected more strongly than those of electrons. Conversely, if we were to excite well above the band edge we would expect electronic dynamics to be strongly impacted. By varying the excitation pulse energy to change the energy of the initial excitation we can potentially identify which NC states have a high degree of ligand-centered character upon ligand exchange.

Previously, to determine the impact of ligands on carrier cooling, three-pulse experiments were carried out in which the decay of hot carriers was directly monitored with mid-IR pulses following above bandgap excitation.¹⁷ These pump-repump-probe experiments measured carrier cooling in CdSe NCs by directly pumping and probing intraband transitions as a function of surface ligand identity. While this experiment directly measures intraband cooling, the difficulty of generating short mid-IR pulses, lack of efficient detectors in this spectral region, and three pulse nature of this experiment have limited its usage in studying NC carrier cooling. To alleviate these issues, Kambhampati and coworkers developed a method of measuring NC carrier cooling dynamics using two-pulse transient absorption experiments.¹⁸ By preparing different initial excitonic states and watching how spectral features evolve shortly after photo-excitation, differences between measured kinetic traces can be used to extract timescales that reflect the intrinsic carrier cooling rates of a system. With this technique, denoted

State-Resolved Transient Absorption (SR-TA), we can address questions regarding how surface coverage impacts NC cooling dynamics.

We have used SR-TA^{3,18–20} to determine the effect of PDTC on cooling dynamics in 2.8 nm diameter CdSe NCs. To do so we have investigated three samples: CdSe NCs capped with oleate (CdSe-OA), CdSe NCs initially capped with oleate that has been partially exchanged for PDTC (CdSe-PDTC), and CdSe-PDTC samples treated with cadmium acetate (PDTC+Cd(Ac)₂) to remove unbound PDTC as prior reports¹⁵ have suggested diffusive quenching of CdSe-PDTC by free PDTC molecules in solution. Using SR-TA, we find an apparent increase in the hole cooling rate of CdSe-PDTC by nearly a factor of two relative to CdSe-OA. This effect is reversed upon treatment of NCs with Cd(Ac)₂, yet these NCs maintain a red-shifted absorption spectrum indicating that PDTC remains bound to the NC surface after Cd(Ac)₂ treatment.

Thus, rather than ascribing the enhancement of the hole cooling rate to EVET, we assign it to fast ligand associated trapping by PDTC bound to NC surfaces in CdSe-PDTC. This fast trapping pathway is then eliminated via modification of these PDTC trap sites by Cd(Ac)₂. Evidence for this picture is supported by DFT calculations as well as FT-IR and steady-state and time-resolved photoluminescence measurements. This data suggests that hot carrier extraction may be feasible in PDTC-capped NCs, as we see fast trapping pathways in CdSe-PDTC that are competitive with hole cooling to the band edge. Our results also support calculations suggesting that VB states near the band edge are more strongly impacted by ligand exchange with PDTC than CB states.

3.2 EXPERIMENTAL METHODS

Transient Absorption Spectroscopy

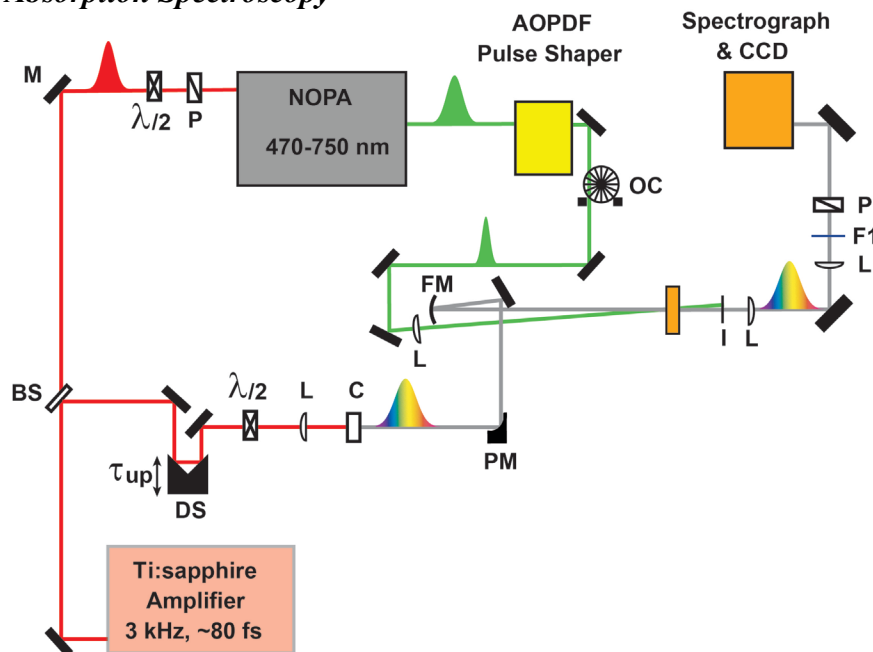


Figure 3.1: Setup depicting the transient absorption spectrometer. Abbreviations are as follows (BS) beam splitter, (M) mirror, (DS) delay stage, ($\lambda/2$) half-wave plate, (L) lens ($f=15, 25$ cm), (C) c-cut sapphire, (PM) parabolic mirror, (FM) focusing mirror ($f=25$ cm), (I) iris, (F1) 0° angle of incidence 800nm HR mirror, (P) polarizer, (OC) optical chopper.

Transient Absorption spectroscopy (TA) is a nonlinear spectroscopic technique that extends ground-state absorption spectroscopy by resolving absorption events in time using ultrashort laser pulses. In a typical TA experiment, two pulses interact with a sample of interest in order to initiate, and then read out the ensuing dynamics of the absorption feature of interest. The first pulse, called the “pump” or excitation pulse, excites one or more electronic transitions within the sample, while the second pulse measures the changes in transmission of the sample as a result of excitation. By scanning this “probe” pulse to interact with the sample at longer and longer time delays following the pump, one can watch how the spectral features of the sample evolve as a function of

this time delay. The evolution of the spectra can then be analyzed to understand electronic kinetics and population of various states within a sample of interest. This allows us to understand information regarding not only excited-state dynamics, but the excited-state electronic structure as well, which is inaccessible in ground-state characterization techniques.

A schematic of the TAS set up used for the experiments in Chapter 3 is shown in **Figure 3.1**. Briefly, a femtosecond Ti:sapphire regenerative amplifier (Coherent Legend Duo Elite, 3 kHz, 4.5 mJ) was used to generate ~ 90 fs pulses centered at 804 nm with a bandwidth of 160 cm^{-1} (FWHM). A small portion of the amplifier output ($\sim 1\text{ }\mu\text{J}$) was focused into a 1 cm path length flow cell filled with distilled H_2O to produce broadband probe pulses (390 - 780 nm) via self-phase modulation. Tunable pump pulses (470 - 540 nm) were generated using a home-built Non-collinear Optical Parametric Amplifier (NOPA). Broadband pulses produced by the NOPA were temporally compressed and spectrally narrowed to 10 nm bandwidth (FWHM) using a Fastlite Dazzler[®] Acousto-Optic Programmable Dispersive Filter (AOPDF) Pulse Shaper. Pump pulse fluence was adjusted such that all samples maintained an excitation density of less than 0.01 excitations per NC. All samples were diluted in a 1 mm path length cuvette and stirred vigorously throughout data collection. Wavelength dependent instrument response functions (IRFs) for each scan were obtained using a 1 mm path length cuvette filled with DCM. Collection of frequency-dependent IRFs allowed for chirp correction of the supercontinuum probe pulse. Chirp correction is necessary as the spectral components of the probe pulse interact with the sample at different pump probe delays due to group velocity dispersion in the generation medium.²¹ The group velocity dispersion is fit and subtracted off in order to ensure a common time origin ($t = 0$ fs) for each frequency component of the probe spectrum. The temporal cross-correlation of the pump and probe

was found to be ~95 fs (FWHM) averaged across the probe spectrum (Appendix, **Figure 3.10**).

Steady-State UV-Vis Absorption Spectroscopy: Samples were prepared by dissolving purified NC pellets in DCM and absorption spectra collected on a Shimadzu UV-2600 spectrometer using a 1 mm or 1 cm path length near-IR transmissive quartz cuvette. Prior to collecting each spectrum, a DCM blank was obtained in the same cuvette for each sample such that the spectra were baseline corrected from sample to sample.

Steady-state Photoluminescence Spectroscopy: Solutions for photoluminescence were diluted in DCM to an optical density below 0.05 in a 1 cm quartz cuvette at the excitation wavelength of $\lambda_{\text{Ex}} = 402$ nm. Emission spectra were collected on a Horiba Fluorolog3 spectrofluorimeter in a front face collection geometry. Emission and excitation slit widths were set to 5 nm.

FT-IR Spectroscopy: FT-IR measurements were carried out on a Bruker Vertex 70 Infrared Spectrophotometer over a spectral window of 500 cm^{-1} to 4000 cm^{-1} with a resolution of 0.5 cm^{-1} . FT-IR samples were prepared by drop casting 60 μL of a 50 mg/mL solution of CdSe-OA in 1:1 (v/v) hexane:octane on 1 mm thick CaF_2 substrates. Ligand-exchanged samples were prepared by submerging CdSe-OA films deposited on CaF_2 substrates in a solution of 10 mM PDTC in methanol for 4 h.

Time-resolved Photoluminescence Spectroscopy: Time-correlated single photon counting measurements (TCSPC) were performed using a Horiba Jobin Yvon Fluorolog3. NC sample solutions were placed in a 1 cm pathlength quartz cuvette excited

using a nanoLED with a peak emission wavelength of 402 nm. Emission from sample solutions was collected at a right angle relative to the path of the excitation source using a slit width commensurate with a 2 nm spectral window. To prevent reabsorption of photons emitted by each sample solution, NC solutions were diluted such that they had an optical density below 0.05 at the excitation wavelength of 402 nm. Emission traces were collected over a 200 ns window, resulting in a bin width of 0.0549 ns/collection channel.

3.3 ASSIGNMENT OF FEATURES IN NC TRANSIENT ABSORPTION SPECTRA

The top portion of **Figure 3.2** shows a representative absorption spectrum of oleate-capped CdSe NCs (CdSe-OA). Inset in this figure is a diagram of the electronic structure of CdSe NCs that assigns the three lowest energy peaks in the measured spectrum to transitions that excite the three lowest optically accessible excitonic states of the NC.²² These excitonic states are labeled X1, X2, and X3 and the transitions that generate them are represented by red, green, and blue arrows from low to high energy. These “molecular-like,” discrete excitonic states arise from quantum confinement of the electron and hole wavefunctions by the physical dimensions of the NC, which causes their energy level spacing to spread out near the band edge.²² This leads to the appearance of discrete absorbance peaks that are superimposed on a bulk semiconductor-like absorption spectrum.

Using State resolved–transient absorption (SR-TA) we are able to extract rates for both hot electron cooling between the lowest energy states that comprise the CB edge, $1P_{(e)}$ and $1S_{(e)}$, and hot hole cooling from the excited $2S_{3/2(h)}$ to the $1S_{3/2(h)}$ state at the VB

edge. In SR-TA, a femtosecond excitation pulse is used to excite a specific excitonic state and its ensuing dynamics are read out by measuring spectral changes in the transmission of a white light supercontinuum probe pulse. In principle, this is no different than conventional transient absorption spectroscopy. However, information tied to hot carrier cooling can be isolated by comparing two measurements wherein different initial excitonic states are prepared.^{3,18} Rates for charge carrier recombination and hole trapping can also be extracted from this data and will be discussed below.

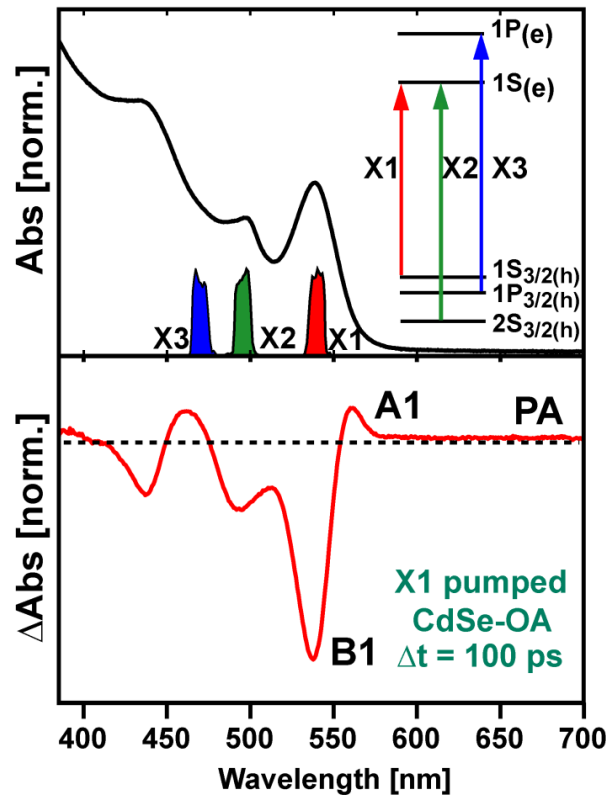


Figure 3.2: (Top) Pump pulse spectra used for X1 (red), X2 (green), and X3 (blue) excitation overlaid on the absorption spectrum of CdSe-OA. (Inset) Energy level diagram of CdSe NCs that highlights the X1, X2, and X3 excitonic states prepared by each pump pulse. (Bottom) Transient absorption spectrum of CdSe-OA measured for a pump-probe time delay of 100 ps following X1 excitation. Important spectral features include: B1 - population of the 1S_(e) electronic state; A1 - absorption of an X1 exciton in the presence of hot carriers; PA - trapped holes.

Plotted below the absorption spectrum in **Figure 3.2** are excitation pulse spectra used for SR-TA measurements. The tunability of our excitation laser allows us to selectively excite either X1, X2, or X3. Following excitation of any of these excitonic bands, changes occur in the absorption spectrum of the NC sample that are highlighted by the transient absorption difference spectrum plotted in the lower portion of **Figure 3.2**. The relevant spectral features for extracting the rates described above are assigned as follows. The feature labeled B1 (~540 nm) is attributed^{7,23} to the ground state bleach of the band edge (X1) excitonic state. Due to the 8-fold degeneracy of the $1S_{3/2(h)}$ band edge hole state, the amplitude of the B1 feature reports directly on the population of the $1S_{(e)}$ electron state. The feature denoted A1 (~570 nm), commonly referred to as the “biexciton feature”, arises due to a shift in the band edge transition energy due to charge screening by a hot exciton.^{7,24} The weak, broad, photoinduced absorption to the red of the A1 feature (~575 - 700 nm) labeled PA^{20,25,26} has been assigned to trapped holes in CdSe NCs by many authors due to observation of an increased decay rate of this feature upon addition of hole-accepting molecules to NC suspensions.^{3,26}

Figure 3.3 schematically depicts the use of SR-TA to measure both electron (top panel) and hole (bottom panel) cooling processes. In the case of electron cooling, the transient kinetics of the B1 feature are compared following photoexcitation of the X1 and X3 excitons (see **Figure 3.2**). As the B1 feature is sensitive to the population of the $1S_{(e)}$ state, and not the cooling of the hole from $1P_{3/2(h)} \rightarrow 1S_{3/2(h)}$, the only difference in the kinetic traces for each of these excitations should be due to electron cooling from

$1P_{(e)} \rightarrow 1S_{(e)}$. By taking the difference of kinetic traces for the B1 feature following X1 and X3 excitation, we can extract a timescale for $1P_{(e)} \rightarrow 1S_{(e)}$ cooling.

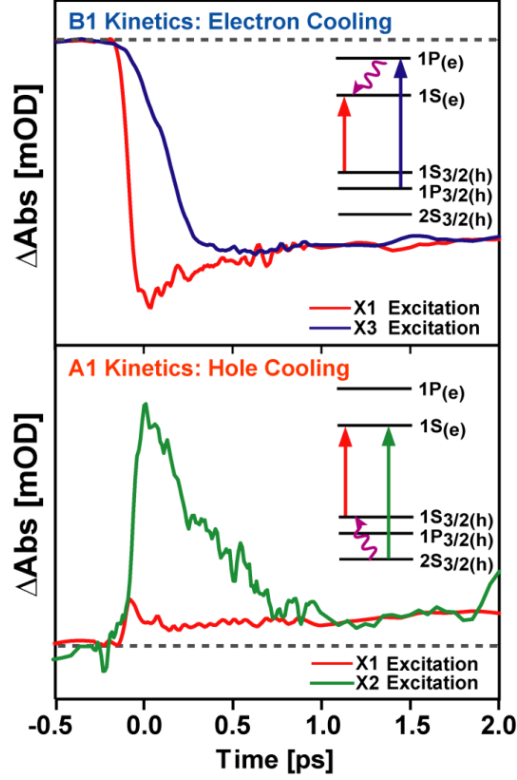


Figure 3.3: (Top) X1 (red) and X3 (blue) pumped B1 kinetics of CdSe-OA. (Inset) Energy level diagram of CdSe NCs depicting how electron cooling is isolated using X1 and X3 excitation. (Bottom) X1 (red) and X2 (green) pumped A1 kinetics of CdSe-OA. (Inset) Energy level diagram that highlights how hole cooling is isolated using X1 and X2 excitation.

Similarly, hole cooling kinetics from $2S_{3/2}(h) \rightarrow 1S_{3/2}(h)$ can be obtained by detecting changes in the A1 induced absorption following X1 and X2 excitation (**Figure 3.2**, bottom). Since the A1 band arises due to the coulombic interaction between charge carriers and is dependent on their spatial separation, the difference of the A1 kinetics for these two pump frequencies should reflect the decay of the $2S_{3/2}(h)$ hole to the band edge. For both the B1 and A1 features, decay following the initial cooling of hot carriers should

be identical after very short time delays (<2 ps). Therefore the spectra were normalized between 3 and 4 ps to isolate carrier cooling dynamics at short time delays. In the following section we discuss the results of using this approach to determine variations in electron and hole cooling rates as a function of surface treatment.

3.4 MEASURING CARRIER COOLING RATES WITH SR-TA

Using SR-TA we measured the dependence of carrier cooling rates on surface treatment with the EDL, PDTC, as well as treatment of the CdSe-PDTC system with $\text{Cd}(\text{Ac})_2$ to remove unbound PDTC molecules in solution.¹⁵ Following procedures employed by others for SR-TA experiments,^{3,18–20} **Figure 3.4** shows the $\Delta\Delta A$ traces obtained from taking the difference of the corresponding kinetic traces for each sample: CdSe-OA, CdSe-PDTC, and PDTC+ $\text{Cd}(\text{Ac})_2$. Fitting these $\Delta\Delta A$ traces allows us to extract the carrier cooling timescale for each sample.

Examining the $1P_{(e)} \rightarrow 1S_{(e)}$ electron cooling rates for each of our 3 samples (**Figure 3.4**, top row) we find that across the series the cooling rate is largely independent of surface treatment. Electron cooling timescales for our measured samples are ~ 170 fs, in good agreement with previously reported values for CdSe NCs of this size,³ and is likely due to Auger energy transfer to the photogenerated hole.^{7,10,27} These results indicate PDTC has little effect on CB states near the band edge, as is expected based on previous reports that PDTC's LUMO energy is too high to effectively mix with CdSe CB states.¹⁴ Additionally results suggest electron and hole wavefunctions maintain spatial overlap, at short time delays, due to efficient Auger energy transfer to the VB hole.

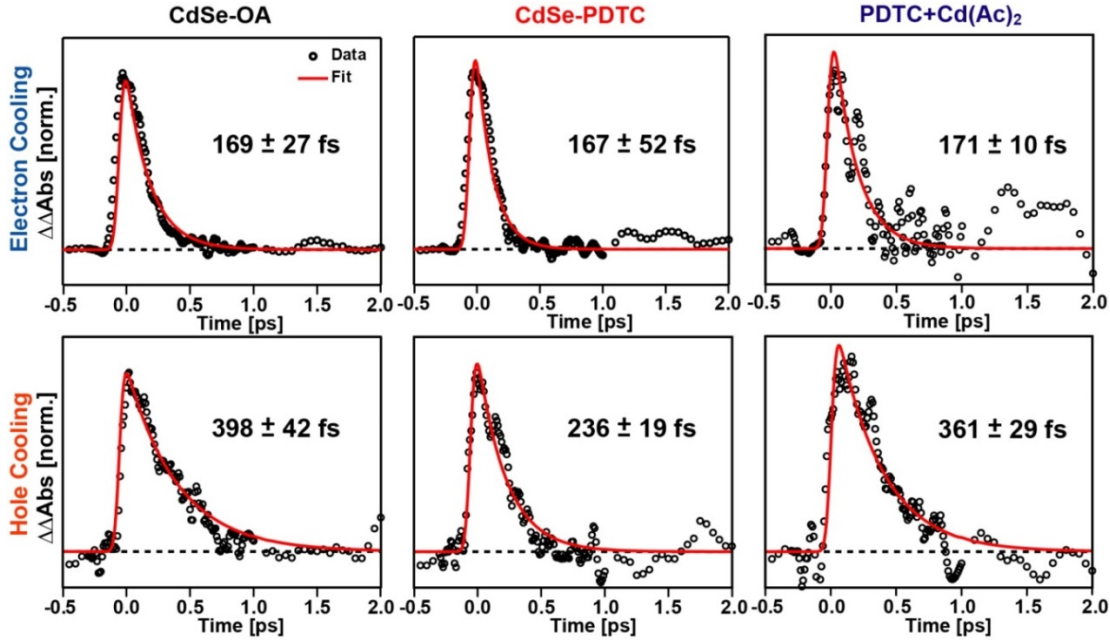


Figure 3.4: (Top) Representative $\Delta\Delta A$ traces obtained for $1P_{(e)} \rightarrow 1S_{(e)}$ electron cooling rates. (Bottom) Representative $\Delta\Delta A$ traces obtained for $2S_{3/2(h)} \rightarrow 1S_{3/2(h)}$ hole cooling rates. (Inset) Average cooling timescales for multiple data sets with standard deviation.

Figure 3.4 (bottom) plots $2S_{3/2(h)} \rightarrow 1S_{3/2(h)}$ hole cooling rates for the same three samples discussed above. Across the series we see that the hole cooling time scale varies greatly with NC surface coverage, decreasing by $\sim 2\times$ from CdSe-OA to CdSe-PDTC. This result is significant for several reasons. First, PDTC speeding up the hole cooling rate is consistent with a picture wherein the VB states excited in our experiment acquire more ligand character. If carrier density is shared between the ligand and NC states this should provide a faster avenue for hole cooling as this interaction results in a higher density of states in this region of the NC band structure.^{14–16} This is evidence that supports hybrid NC-ligand state formation upon introduction of the PDTC ligand to the NC solution.

However, when treating the CdSe-PDTC sample with $Cd(Ac)_2$, we find that the

hole cooling timescale recovers to match the CdSe-OA sample, while *maintaining* the red-shifted absorption spectrum induced by the PDTC exchange (Appendix, **Figure 3.12**). As we describe below, the reversibility of the increased hole cooling rate in CdSe-PDTC upon treatment with Cd(Ac)₂ is consistent with a scenario where at least *two* unique PDTC species bind to the NC surface.

Calculations have shown have shown PDTC can bind to CdSe surfaces in monodentate, chelating, and bridging geometries,^{16,28,29} and that each of these species has a different impact on a NC's radiative and non-radiative decay rates.²⁸ When CdSe-OA is treated with PDTC, it is likely that a mixture of these different species form. Further treatment of these NCs with Cd(Ac)₂ may preferentially remove one or more of these species. If the species removed is responsible for the change in hole cooling rate, this would explain the restoration we observe of the hole cooling rate upon treatment of CdSe-PDTC with Cd(Ac)₂. This hypothesis is supported by prior work that noted photo-brightening of CdSe-PDTC solutions upon treatment with Cd(Ac)₂.¹⁵ While this work ascribed photo-brightening to removal of unbound PDTC molecules that diffusively encounter NCs and quench their emission by scavenging holes, our observation of changes in NC cooling dynamics on femtosecond timescales suggests PL quenching by PDTC is unlikely to be a diffusion-limited process but rather one involving molecules directly bound to the NC surface.

To explore the possibility that distinct PDTC species may be attached to our NC surfaces, we measured FT-IR spectra of dropcast NC films. **Figure 3.5A** compares spectra of a CdSe-OA film before and after soaking in a methanol solution of 10 mM

PDTC.

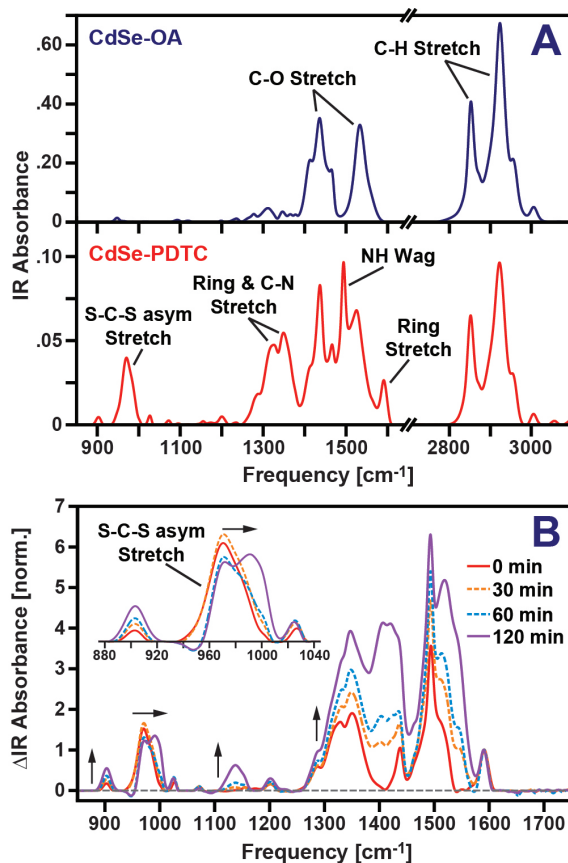


Figure 3.5: (A) FT-IR spectra of CdSe-OA films before (top, blue) and after PDTC ligand exchange (bottom, red). Mode assignments are based on DFT calculations (B) Difference FT-IR spectra of PDTC exchanged CdSe-OA films as a function of time following Cd(Ac)₂ treatment. Plotted spectra have had contributions from oleate vibrational peaks removed by subtracting the CdSe-OA spectrum shown in panel (A) following normalization to the alkyl stretching transitions between 2800 and 3000 cm⁻¹. The resulting difference spectra are then normalized to the PDTC ring stretching transition at 1590 cm⁻¹.

Prior to PDTC treatment, peaks due to the alkyl stretches of oleate ligands appear just below 3000 cm⁻¹ and a pair of peaks are observed at 1432 cm⁻¹ and 1539 cm⁻¹ that are assigned to the symmetric and asymmetric carboxylate stretches of oleate bound to surface Cd atoms.³⁰ Upon PDTC treatment, each of these peaks undergo a noticeable

decrease in amplitude, indicating that oleate is displaced from the NC surface. As these peaks disappear, three narrow peaks at 1590 cm^{-1} , 1494 cm^{-1} , and 970 cm^{-1} are observed to grow in that, on the basis of DFT calculations (Appendix, **Figure 3.13**), are assigned to C=C ring stretching, N-H wagging, and S-C-S asymmetric stretching modes of PDTC. In addition, a broad band centered at 1337 cm^{-1} can be seen that arises from a combination of ring and C-N stretching modes. These results suggest that PDTC indeed displaces oleate and binds to the surface of our CdSe NCs. While the magnitude of the decrease in the oleate stretching features should in principle allow us to estimate the amount of oleate displaced by PDTC, extracting a quantitative value for the number of displaced ligands is complicated by the fact that our films experience some degree of NC material loss when treated with methanol. Hence, we are only able to provide an upper bound of this value which we estimate at about 80%.

Figure 3.5B plots how FT-IR spectra of CdSe-PDTC films change upon exposure to $\text{Cd}(\text{Ac})_2$. With increased exposure time, we observe a decrease of all peaks in our spectra due to partial desorption of NCs from our film. To account for this effect, we have normalized our plotted spectra to the PDTC C=C ring stretching peak at 1590 cm^{-1} as this peak is predicted to display only a minimal shift between different PDTC binding geometries. The normalized spectra reveal that the asymmetric S-C-S stretching peak at 970 cm^{-1} decreases in amplitude and shifts to higher frequency with increasing exposure time to $\text{Cd}(\text{Ac})_2$, suggesting $\text{Cd}(\text{Ac})_2$ alters the average geometry through which PDTC molecules attach to CdSe. DFT calculations of PDTC molecules bound to a CdSe {110} surface in chelating and two different bridging geometries likewise show the asymmetric

S-C-S stretch shifts between these different geometries (Appendix, **Figure 3.13**). While the lack of quantitative agreement prevents us from assigning the shifts we see in our measured FT-IR spectra to specific changes in the populations of different surface bound species, our spectra and calculations suggest that different PDTC species are present on our NC surfaces, one of which may be responsible for the rapid hole cooling we observe in SR-TA measurements.

3.5 DISCUSSION

Excited holes often relax via electronic-to-vibrational energy transfer (EVET) as they cannot access Auger channels due to the larger energy level spacing of the CB relative to the VB. Though the exact details of this hole cooling mechanism are debated, recent reports have shown EVET to both phonon modes^{31,32} and surface bound ligands^{11,33,34} contribute to hot carrier cooling. In particular, vibrations involving atoms directly anchored to the NC surface are expected to be important acceptors of excess energy due to their close proximity to the NC core. Examining the FT-IR spectrum in **Figure 3.5A** of CdSe-OA, we see that the symmetric and asymmetric carboxylate stretches fall at 1432 cm⁻¹ and 1539 cm⁻¹, respectively, placing both these modes close to the energy difference between the 2S_{3/2(h)} and 1S_{3/2(h)} states (~1685 cm⁻¹). Likewise, as these modes are associated with the oleate head group, they should be readily accessible to photoexcited holes. Taken together, these two effects suggest that EVET to these vibrational modes likely accounts for the observed rapid hole cooling in CdSe-OA.

Assuming EVET similarly drives hole cooling upon PDTC exchange, there are

two explanations that may account for the increased hole cooling rate in CdSe-PDTC; (1) hole cooling is facilitated by a single or collection of PDTC modes that lie in close resonance with the $2S_{3/2(h)} - 1S_{3/2(h)}$ energy gap when PDTC is bound to CdSe in one particular geometry but not others or (2) spatial extension of the hole increases the coupling strength of the carrier and ligand via direct wavefunction overlap. However, taking stock of the two-species model suggested by the recovery of the hole cooling kinetics, both of these scenarios can be ruled out.

Based on the energy gap between the X1 and X2 exciton states, whose value represents the energy spacing between the $2S_{3/2(h)}$ and $1S_{3/2(h)}$ states, we expect a vibrational mode with a frequency of $\sim 1685\text{ cm}^{-1}$ would have the proper energetic alignment to accept excess energy from a hot hole. Examining the FT-IR spectrum of CdSe-PDTC spectrum (**Figure 3.5A**), we see that modes assigned to stretching and bending of PDTC's aromatic ring fall close to this energy difference and could possibly serve as accepting modes for the excess energy of a hot hole. To address scenario 1 we have examined how the vibrational spectrum of PDTC changes when it is bound in both chelating and bridging geometries to the $\{110\}$ surface of CdSe to determine if any of the modes described above experience large shifts tied to binding geometry. While many of the ring modes do indeed display frequency shifts between these two geometries, many of these changes are small ($< 20\text{ cm}^{-1}$) and are likely insufficient to rationalize a $2\times$ change in hole cooling rate due to the removal of PDTC molecules that preferentially bind in one of these two different geometries.

The spectrum shown in **Figure 3.5A** also provides a hint as to why we can

exclude scenario 2. While PDTC does possess vibrational modes with frequencies close to 1600 cm^{-1} , these modes are primarily associated with stretching and bending motions of PDTC's phenyl ring. However, prior work that has examined exciton delocalization imparted by PDTC has shown that its $\text{S}_2\text{C-NH}$ bridging group is responsible for most of the change in the density of states of CdSe's VB upon binding,¹⁶ indicating that hole density is preferentially associated with this group rather than PDTC's phenyl ring. The spatial separation of the hole and phenyl ring would suggest that ring stretching and bending modes should be poor acceptors for the excess energy of hot holes. While vibrations involving the $\text{S}_2\text{C-NH}$ binding group would be expected to couple strongly to hot holes and facilitate EVET, the spectra shown in **Figure 3.5A** indicate these modes are significantly detuned from the $2\text{S}_{3/2(\text{h})} - 1\text{S}_{3/2(\text{h})}$ energy gap. This suggests EVET involving these modes must involve the simultaneous excitation of multiple lattice phonons, reducing the likelihood of this event. Based on these arguments, we believe we can rule out EVET to PDTC as the primary pathway leading to hole cooling.

As vibrational relaxation appears to be insufficient to explain our results, we have developed an alternative scenario to explain this rapid hole cooling phenomenon. SR-TA tracks hole cooling by measuring a loss of amplitude of the A1 induced absorption band. However, if excited holes were to be physically removed from a NC, this would similarly lead to a loss of A1 induced absorption. Thus, a scenario that can explain our results is one wherein PDTC molecules bound to the NC core in a particular geometry trap hot holes, extracting them from the NC. This picture is consistent with prior work that demonstrated PDTC can quench the photoluminescence (PL) of CdSe NCs.¹⁵ However,

while this work assumed PDTC quenching was diffusive in nature, involving unbound PDTC molecules in solution, the femtosecond rate of quenching suggested by our results indicates it must involve a species directly bound to the NC surface. Hence, we hypothesize that rather than unbound PDTC scavenging holes as previously reported, a subset of PDTC molecules bound to the surface can rapidly remove photoexcited holes from the NC core, quenching PL, and increasing the apparent rate of carrier cooling.

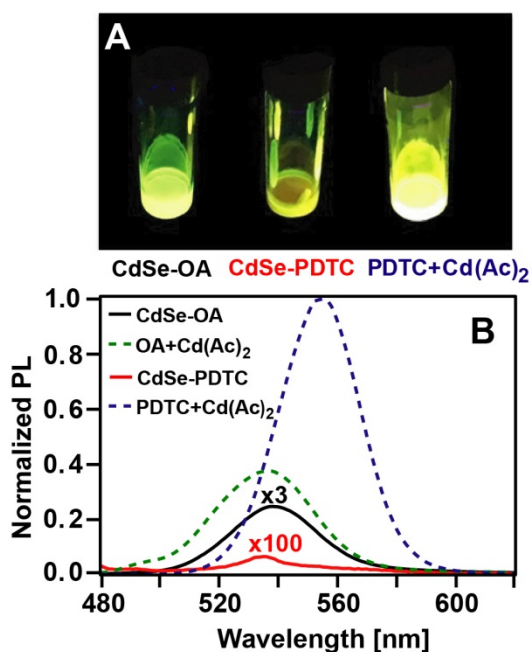


Figure 3.6: (A) Photograph depicting photoluminescence of CdSe-OA, CdSe-PDTC, and PDTC+Cd(Ac)₂ under 365 nm excitation. (B) PL spectra of CdSe-OA (black), OA+Cd(Ac)₂ (green dashed) CdSe-PDTC (red), and PDTC+Cd(Ac)₂ (blue dashed) relative to PDTC+Cd(Ac)₂ maximum.

This mechanism for fast hole trapping in CdSe-PDTC is supported by steady-state PL measurements, shown in **Figure 3.6**. **Figure 3.6B** shows the relative emission spectra of CdSe-OA, CdSe-PDTC, PDTC+Cd(Ac)₂, and a control sample comprised of CdSe-OA with added Cd(Ac)₂ (denoted OA+Cd(Ac)₂). From the relative quantum yield (QY)

from each sample we see that PDTC-capped NCs are highly quenched, displaying a QY that is only 0.79% of that of CdSe-OA. However, this effect is clearly reversed upon addition of Cd(Ac)₂. In the PDTC+Cd(Ac)₂ sample we see recovery of the photoluminescence QY exceeding the CdSe-OA sample as well as the control sample OA+Cd(Ac)₂. This increased photoluminescence intensity of PDTC+Cd(Ac)₂ shows that only a small portion of the gain in photoluminescence intensity can be attributed to passivating surface electron traps. Therefore it is likely that some oscillator strength is borrowed from the PDTC ligand, as predicted by previous work,^{15,16} which would account for the remaining increase in photoluminescence QY.

In addition to the PL data, transient absorption and time-correlated single photon counting (TCSPC) kinetics provide evidence for a hole-trapping mechanism induced by PDTC exchange. Examining the PA absorption feature that reports on the presence of trapped holes,^{20,25,26} we find that for each of the CdSe samples described above this feature develops with a ~180 fs time constant (Appendix, **Figure 3.14**), indicating that all of our CdSe suspensions rapidly trap holes. To determine the percentage of holes that populate trap sites, we can compare the amplitude of the PA band to the initial amplitude of the B1 bleach as the latter reports on the number of excited electrons placed in the 1S_(e) state by our excitation pulse (**Table 3.1**). Interestingly, we find that the PA:B1 ratio decreases by nearly 2× for CdSe-PDTC relative to CdSe-OA. This suggests that CdSe-PDTC traps *fewer* holes at sites that contribute to the PA absorption feature.

While this result may at first seem counterintuitive if PDTC treatment induces additional hole traps, it is consistent with a picture wherein PDTC-induced traps are

strongly *ligand-associated* rather than residing on the NC surface or core. The PA absorption feature arises from lattice defects and unpassivated surface sites that generate mid-gap states. As these species reside on the NC itself, they can optically access states within the NC VB, leading to the appearance of the PA absorption band. In contrast, if PDTC creates hole traps that primarily reside on the ligand, absorption transitions between these PDTC-centered states and deeper states within the NC valence band are expected to have low oscillator strength due to their spatial separation. Thus, trapping a hole on a PDTC molecule would lead to a decrease of the PA feature rather than an increase. Treatment of CdSe-PDTC with Cd(Ac)₂ increases the PA:B1 ratio, suggesting that it removes PDTC-associated hole traps.

Sample	PA Peak Amplitude [mOD]	B1 Peak Amplitude [mOD]	PA:B1 Ratio
CdSe-OA	0.185	18.8	0.98%
CdSe-PDTC	0.11	19.4	0.57%
PDTC+Cd(Ac) ₂	0.18	13.5	1.33%

Table 3.1: Maximum amplitude of the PA (averaged from 600 - 750 nm) and B1 spectral features. The ratio of these amplitudes reflects the relative number of photoexcited holes trapped in each sample. Absolute values of the B1 amplitude have been used in calculating the PA:B1 ratio due to the opposite sign of these features.

The long time kinetics of the B1 feature also support a scenario wherein PDTC creates additional ligand-associated hole traps. **Figure 3.7A** shows the recovery of the B1 feature up to 1.65 ns after photoexcitation for each of the three NC samples (Appendix, **Figure 3.15, Table 3.2**). The CdSe-PDTC sample shows a rapid, non-exponential decay of the B1 amplitude within the first 100 ps followed by an additional slow decay that can

be fit well by an exponential with a 2.7 ns time-constant. This rapid decay is echoed by TCSPC measurements (**Figure 3.7B**) that are dominated by an instrument-limited decay followed by a slower decay over 2.7 ns (Appendix, **Table 3.3**). This behavior is in stark contrast to that of CdSe-OA, which after a short ~ 30 ps decay, exhibits a 5.2 ns exponential decay that is consistent with TCSPC measurements (**Figure 3.7B**). As the B1 amplitude tracks the population of electrons in the $1S_{(e)}$ state, these results indicate PDTC treatment creates a new pathway that either traps electrons or leads to their recombination with holes.

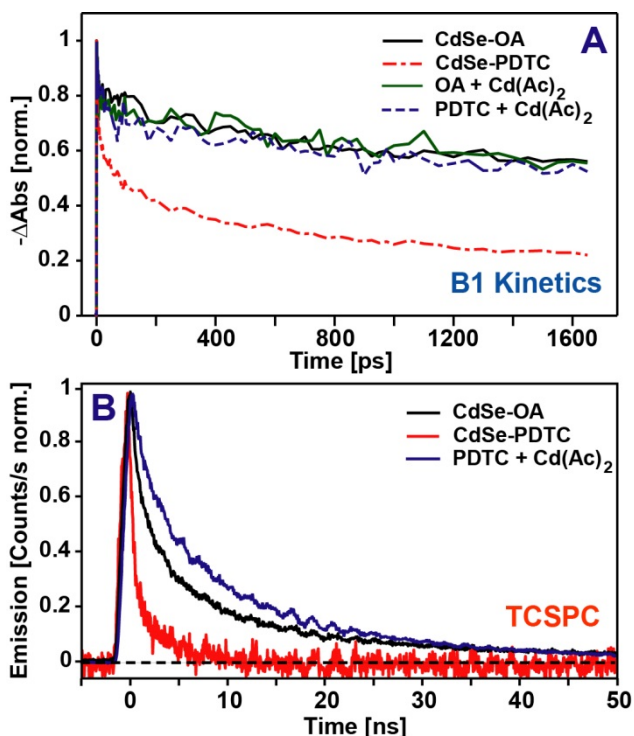


Figure 3.7: (A) Normalized decay traces of the B1 spectral feature for X1 pumped CdSe-OA (black), CdSe-PDTC (red dash dot), and PDTC+Cd(Ac)₂ (blue dashed), and OA+Cd(Ac)₂ (green). (B) TCSPC decays for the three samples above. PDTC shows an instrument limited decay, indicating relaxation occurs primarily through nonradiative pathways.

While we do not have definitive evidence that can differentiate electron trapping from electron-hole recombination, one piece of data that suggests PDTC-trapped holes nonradiatively recombine with $1S_{(e)}$ electrons comes from the PA band, which shows a decay that matches the recovery of the CdSe-PDTC B1 bleach (Appendix, **Figure 3.16**). This is consistent with a scenario wherein nonradiative recombination between PDTC-associated trapped holes and $1S_{(e)}$ electrons occurs rapidly, leading to the sub-100 ps B1 bleach decay. Transfer of trapped holes from NC defects to PDTC-associated traps over longer timescales would then lead to a decay of the PA and B1 features that closely track one another due to rapid recombination of $1S_{(e)}$ electrons with PDTC-associated traps. As with the PA:B1 ratio described in **Table 3.1**, upon addition of $Cd(Ac)_2$ to CdSe-PDTC, we see that both the rapid decay of the B1 amplitude and TCSPC decay recover, suggesting elimination of PDTC-associated traps.

To summarize, this work suggests there are likely two different PDTC species attached to the NC surface following ligand exchange. Treatment of CdSe-PDTC with $Cd(Ac)_2$ induced a drastic change in both intraband hole cooling and global relaxation rates from transient absorption experiments, as well as increased photoluminescence QY and lifetime. This led us to conclude that the species removed by $Cd(Ac)_2$ provides non-emissive, low-energy charge trap states that are rapidly populated on a sub-picosecond timescale following photoexcitation. Removal of this species eliminates access to this trapping pathway, leaving photoexcited holes to cool via an EVET pathway, similar to CdSe-OA.

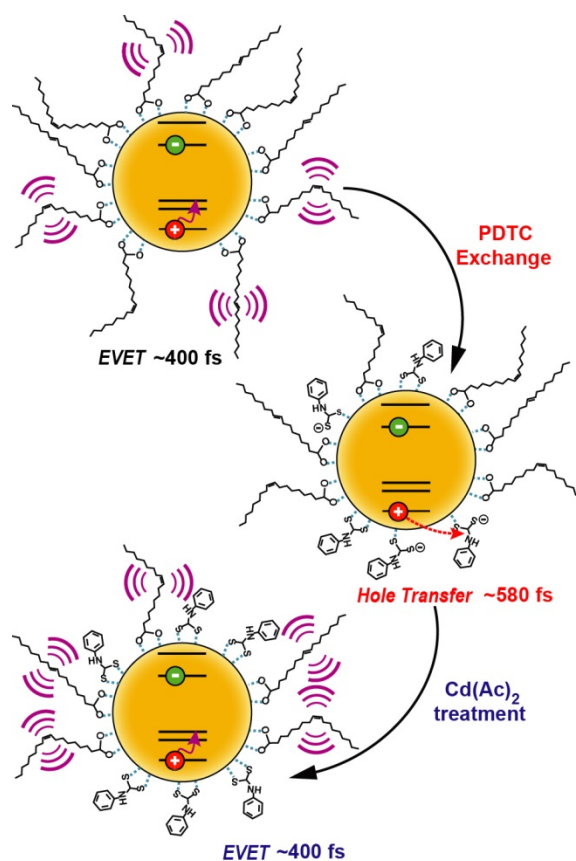


Figure 3.8: Cartoon depiction of ligand-dependent hole cooling mechanisms. PDTC exchange induces fast hole transfer (~ 580 fs) to PDTC in CdSe-PDTC with monodentate PDTC as the hole acceptor. Removal of monodentate PDTCs via $\text{Cd}(\text{Ac})_2$ chelation leads to hole cooling via an EVET pathway, similar to CdSe-OA.

Although definitive assignment of the hole trapping to a particular species is not possible with our data, PDTC bound in a monodentate geometry is most likely to serve as a hole trap as it has an exposed lone pair. The existence of such species is supported by simulations by Azpiroz and de Angelis that showed their presence on CdSe NCs, albeit in small numbers.¹⁶ Moreover, a scenario wherein monodentate PDTC molecules act as hole traps is also consistent with our observation that $\text{Cd}(\text{Ac})_2$ treatment results in a removal of these traps. The addition of Cd^{2+} atoms repairs surface defects, as indicated by an

increase in PL quantum efficiency and a slight red-shift in the absorption maximum of CdSe-OA samples. The addition of Cd^{2+} atoms to a NC surface would provide additional attachment sites for PDTC molecules, likely reducing the number coordinated to the surface in a monodentate geometry. **Figure 3.8** depicts our proposal for how PDTC treatment and subsequent $\text{Cd}(\text{Ac})_2$ treatment modify the surface of CdSe NCs. EVET to oleate ligands dominates hole cooling in CdSe-OA NCs. Following PDTC exchange fast transfer of photoexcited holes to monodentate PDTC molecules can occur. Hole relaxation is again dominated by EVET following removal of monodentate PDTC molecules by $\text{Cd}(\text{Ac})_2$.

As the observed hole relaxation rate in CdSe-PDTC represents a sum of the rates for both the formation of PDTC-associated traps and hole cooling, we can extract a rate for PDTC-associated trap formation (k_{trap}) assuming the intrinsic timescale for hole cooling ($k_{\text{cool}} = 1/398 \text{ fs}$) is unchanged by PDTC treatment ($k_{\text{observed}} = k_{\text{trap}} + k_{\text{cool}} = 1/236 \text{ fs}$). Under this assumption, we find that the timescale for PDTC-associated trap population is 580 fs ($1/236 \text{ fs} = 1/580 \text{ fs} + 1/398 \text{ fs}$). As our measurements cannot determine the number of PDTC-associated traps per NC, this timescale represents an upper bound on the rate of trapping at these sites ($k_{\text{trap}} \cdot \text{int}$) as it is the product of the rate of populating a single PDTC-associated trap and the number of trap sites on a NC.

3.6 CONCLUSIONS

We have presented evidence that PDTC binds to CdSe NC surfaces in multiple geometries, and that these geometries greatly impact the NC's excited state dynamics.

Specifically, we have used FTIR, and a combination of time-resolved emission and TA to isolate the effects of two different species by using $\text{Cd}(\text{Ac})_2$ to alter the average binding geometry of PDTC molecules bound to the surface of CdSe NCs. By measuring the hole cooling rate for different NC samples, we have shown that a subset of PDTC molecules bound to a NC surface can trap photoexcited holes and facilitate non-radiative recombination. In contrast, NCs that have been treated with $\text{Cd}(\text{Ac})_2$ relax primarily through radiative recombination, suggesting removal of these quenching PDTC species.

Based on SR-TA measurements, we find that in CdSe-PDTC holes populate trap states in ~ 580 fs, indicating fast hole transfer to PDTC ligands can compete with carrier cooling to the band edge. Upon treatment of CdSe-PDTC with $\text{Cd}(\text{Ac})_2$ we see the hole cooling rate recover to similar values measured for CdSe-OA (~ 400 fs), and the photoluminescence QY greatly increase beyond that of the NL-capped NCs. This data indicates that $\text{Cd}(\text{Ac})_2$ removes a surface-bound species that introduces ligand associated trap states, while maintaining the absorption redshift induced from PDTC addition to the NC solution.

This result is interesting in that it shows that EDLs do not *necessarily* drive rapid carrier cooling via EVET despite extended wavefunction overlap between the NC core and these ligands. Rather, we see that hot carrier cooling dynamics appear to be highly dependent on both the binding geometry of PDTC and the details of its vibrational density of states. Indeed, we find oleate is likely a major contributor to hot hole relaxation in CdSe NCs due to good energetic matching of the vibrational frequencies associated with its carboxylate binding group and the splitting between the NC $2\text{S}_{3/2(\text{h})}$

and $1S_{3/2(h)}$ states. Exchange of oleate for a different NLs coupled with careful control of the PDTC binding geometry could further extend the lifetime of hot holes and allow for their extraction.

Perhaps the most insightful information we have gained through this study is regarding the electronic structure changes that occur upon ligand exchange with PDTC. The changes in the hole cooling rates provide strong evidence that PDTC-associated trap states arise as a result of the strong VB – ligand interaction predicted by theory and experiment.^{4,12–16} The mixed NC-ligand character of these states confirms the potential of NC-EDL composites as promising materials for thin film optoelectronics as this could circumvent the issue of charge carriers remaining localized to the NC core due to poor energetic overlap with their surface ligands. In Chapter 4 we will test this hypothesis by carrying out ligand exchange with PDTC on CdSe NC films, and use TA to measure the dynamics of carrier transport in these films.

3.7 APPENDIX

Steady-State Absorption Spectra: Ligand Exchange and Kinetics

We have carried out PDTC exchanges over multi-day time scales to determine the maximum bathochromic shift that can be induced by PDTC. For the size regime studied (diameter ~ 2.8 nm) we find that the maximum shift saturates at 73.2 meV (**Figure 3.9A**), over ~ 2.5 days (**Figure 3.9B**). Eventually, however, all investigated NCs crash out of solution, which we attribute to the poor solubility of PDTC in dichloromethane relative to oleate capping ligands.

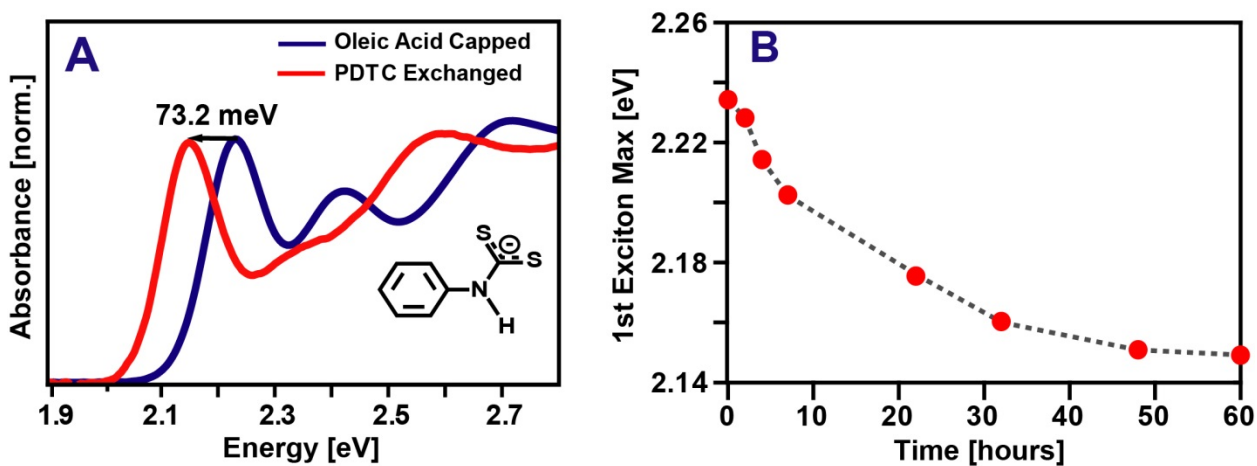


Figure 3.9: (A) Absorption spectra of CdSe-OA NCs before (blue) and after PDTC exchange (red). The exchange was allowed to proceed for 60 hours. (B) Band edge exciton energy as a function of the exchange time. The total red shift over the course of the 60-hour exchange was 73.2 meV.

Chirp Correction and Determination of IRF for SR-TA Measurements

Following convention for femtosecond transient absorption experiments^{21,35} we have used the nonlinear response of solvent molecules, in our case dichloromethane, induced by the pump pulse to measure and correct for the chirp of the broadband supercontinuum probe. The solvent response, which reflects the chirp of the supercontinuum probe pulse, is fit with a cubic polynomial (Figure 3.10, dashed red, Raw Data) using an in-house MATLAB script. The extracted polynomial fit is then used to adjust the $\Delta t = 0$ point for each probe wavelength channel, resulting in the interpolated, chirp-corrected spectrum (Figure 3.10, Interpolation). This process is repeated for each of the three excitation pulses described in the main text and applied to the appropriate data set. By taking a slice through the solvent response at a specific frequency, we can determine the instrument response function (IRF) for that given frequency channel. This

is done by fitting the kinetics of the solvent response to the sum of a gaussian and its first and second derivatives^{21,35} (**Figure 3.10**, dashed blue, bottom right). In the region used for SR-TA temporal analysis, we find that the FWHM of our instrument response is 95 fs.

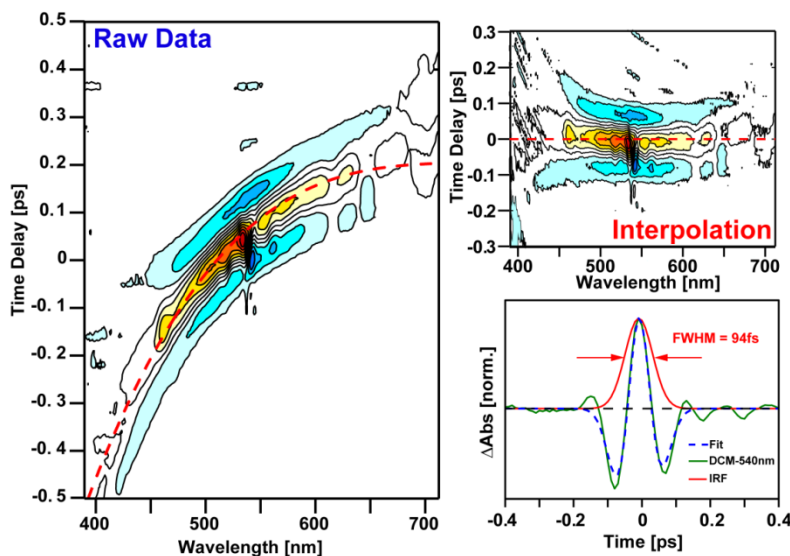


Figure 3.10: Example of chirp correction using a 1 mm pathlength cuvette filled with DCM for a pump pulse centered at 540 nm with 10 nm bandwidth (FWHM). A cubic function (dashed red, Raw Data) is applied to adjust the $\Delta t = 0$ position of each collected wavelength channel (Interpolation).

Control Experiments - OA+ Cd(Ac)₂

To determine if treatment with Cd(Ac)₂ alone changes the relaxation dynamics in CdSe NCs, we carried out control SR-TA experiments on CdSe-OA treated with Cd(Ac)₂ (denoted OA+Cd(Ac)₂). Shown in **Figure 3.11** are representative $\Delta\Delta A$ traces that report 1P_(e)→1S_(e) electron (left) and 2S_{3/2(h)}→1S_{3/2(h)} hole cooling rates (right) for OA+Cd(Ac)₂. The spectra are fit using Equation 3-1:

$$\Delta\Delta A(t) = IRF \otimes e^{-t/\tau_{cooling}} \quad (3-1)$$

where the IRF is extracted using the method described in the previous section. We see that both electron and hole cooling are in agreement with values reported for CdSe-OA in the main text as well as previously reported literature values for CdSe NCs of a similar size.³

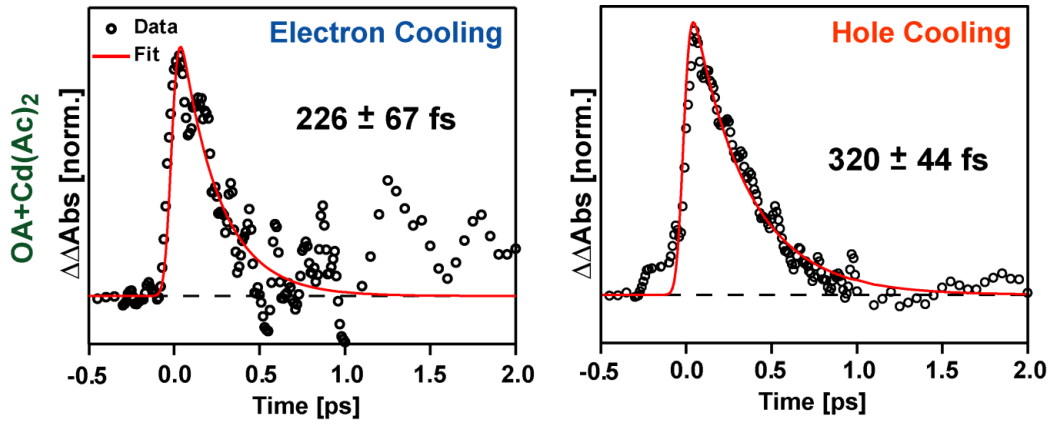


Figure 3.11: Representative $\Delta\Delta A$ traces obtained for $1P_{(e)} \rightarrow 1S_{(e)}$ electron cooling and $2S_{3/2(h)} \rightarrow 1S_{3/2(h)}$ hole cooling for OA+Cd(Ac)₂. (Inset) Average cooling timescales for multiple data sets with standard deviation.

PDTC+Cd(Ac)₂ vs PDTC Absorption Spectra

Figure 3.12 shows representative linear absorption spectra of both CdSe-PDTC (dashed red) and PDTC+Cd(Ac)₂ (blue) samples. Following treatment of CdSe-PDTC with Cd(Ac)₂, we find minimal difference in the absorption spectra of the two species, indicating the PDTC species responsible for exciton delocalization remains covalently tethered to the NC surface. Typically upon treatment with Cd(Ac)₂, we see a small ($\sim 2 - 4$ nm) red-shift of the absorption spectrum for both PDTC+Cd(Ac)₂ and OA+Cd(Ac)₂

samples, consistent with prior results reported by Jin *et. al.*¹⁵ This shift is likely due to Cd^{2+} surface defects repaired by the introduction of $\text{Cd}(\text{Ac})_2$.

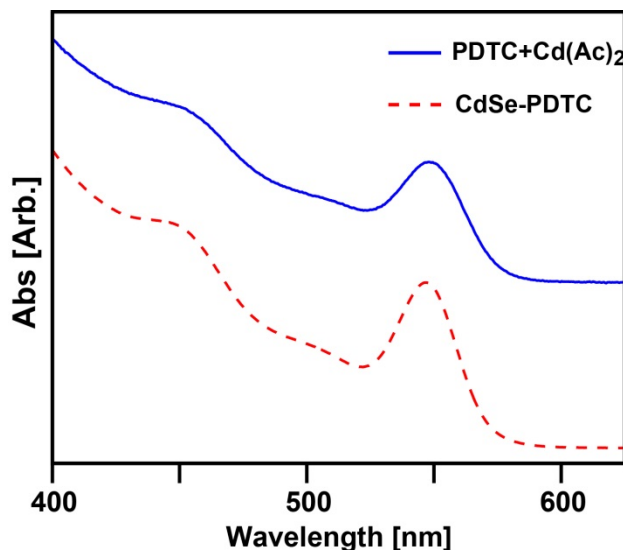


Figure 3.12: Comparison of CdSe-PDTC (dashed, red) and PDTC+ $\text{Cd}(\text{Ac})_2$ (blue) absorption spectra. Upon addition of $\text{Cd}(\text{Ac})_2$, we see a small red-shift (~ 2 nm) of the absorption.

Calculated CdSe-PDTC Vibrational Spectra as a Function of Binding Motif

Density functional theory (DFT) was used to calculate binding motifs of PDTC to a Cd-rich CdSe {110} surface and to determine the magnitude of shifts of the vibrational modes of PDTC between different surface binding motifs. These calculations were performed using the Vienna Ab-Initio Simulation Package.³⁶ Exchange and correlation were modeled within the generalized gradient approximation of the Perdew, Becke, and Ernzerhof form.³⁷ Core electrons were described within the projector augmented wave framework,³⁸ valence electrons were expanded in a plane wave basis up to an energy cutoff of 400 eV. The Cd-Se slab was modeled with four layers and eight atoms per layer with the bottom two layers frozen in their bulk lattice positions. All other atoms were

relaxed until the residual force was less than 0.001 eV/Å. A k-point mesh of 2x2x1 was used to integrate over the electronic states within the Brillouin zone. A Gaussian smearing was applied with a width of 0.05 eV to improve convergence of electronic states near the Fermi level. Equivalent vibrational modes were found using DFT perturbation theory and a finite difference displacement method using a step size of 0.001 Å (see **Figure 3.13C**).

Three stable binding geometries were found, one chelating geometry wherein both sulfur atoms of PDTC are coordinated to a single Cd atom (**Figure 3.13A**) and two bridging geometries wherein each of PDTC's sulfur atoms coordinate to different Cd atoms. In the first of these geometries, labeled “bridging-top” (**Figure 3.13A**), each PDTC sulfur atoms bonds to a single Cd atom, while in the second, labeled “bridging-twisted” (**Figure 3.13A**), each PDTC sulfur atom coordinates to two surface Cd atoms. While prior computational studies that examined dithiolcarbamate ligands attached to CdSe NCs have reported the existence of chelating and bridging-top geometries for dithiocarbamates,^{16,39} bridging-straddling geometries were absent from these reports. The identification of this geometry in our study may reflect the low surface coverage of PDTC that we, for simplicity, consider in our calculations. Upon the coordination of additional ligands to a CdSe surface, PDTC binding geometries such as bridging-straddling may become highly disfavored due to steric effects. Nevertheless, we include vibrational spectra calculated for PDTC bound in this geometry as a point of comparison.

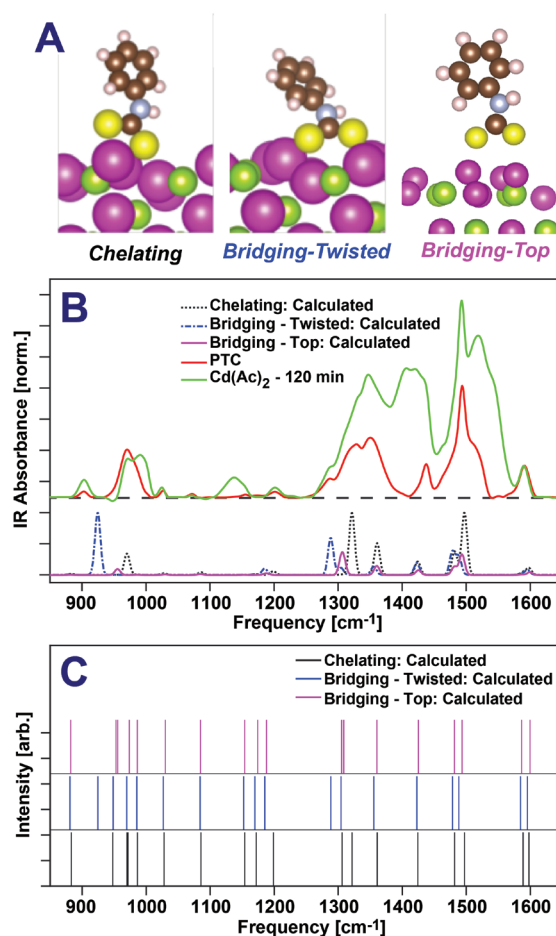


Figure 3.13: (A) DFT calculated structures of PDTC bound in chelating, bridging-twisted, and bridging-top linkages to a Cd-rich CdSe {110} surface. Atoms are colored as: C-brown, H-white, S-yellow, Cd-purple, and Se-green. (B) FT-IR spectra of CdSe-PDTC films before (red) and after (green) treatment with Cd(Ac)₂ for 2 hours (Top). Contributions from oleate peaks have been subtracted to isolate features due to PDTC and highlight changes upon treatment with Cd(Ac)₂. Spectra are normalized to the C=C ring stretching mode at 1590cm⁻¹. DFT calculated spectra for the chelating (dashed black) , bridging-twisted (dashed dot, blue) , and bridging-top (purple) geometries. Spectra have been multiplied by a Gaussian function with a FWHM of 10cm⁻¹ (bottom). (C) Calculated vibrational modes for each of the three geometries described above highlighting the minimal spectral shifts seen upon changes in binding geometry.

Figure 3.13B displays infrared absorption spectra calculated for chelating, bridging-top, and bridging-straddling geometries. **Figure 3.13C** plots the position of all

vibrational transitions for these structures irrespective of their vibrational oscillator strength. While shifts in the position of peaks associated with the vibrational modes of these structures can be identified, these shifts are typically somewhat small. Of particular importance are modes that fall within the 1400 – 1700 cm^{-1} region of the spectrum as vibrations with frequencies in this region are in close resonance with the $2S_{3/2(h)} - 1S_{3/2(h)}$ energy gap. However, comparing the location of vibrational resonances that fall in this region for chelating, bridging-top, and bridging-straddling structures, we see only small shifts in energy of each of these modes ($< 20 \text{ cm}^{-1}$) when moving from one structure to another. This observation led us to the conclusion that EVET to a specific PDTC mode available in one specific PDTC binding geometry, but not others, was insufficient to explain the rapid hole cooling ($< 250 \text{ fs}$) observed for CdSe-PDTC samples.

Kinetics Observed in Transient Absorption Measurements

As described in the main text, distinct features observed in transient absorption spectra report on the populations of different photogenerated species. Specifically, the B1 band describes the population of electrons that occupy the $1S_{(e)}$ state while the broad PA feature that appears to the lower energy side of the B1 band signifies holes that have been trapped at NC defect sites. **Figure 3.14** compares the growth kinetics of the PA feature following X1 excitation. For all of the NC samples we have investigated (CdSe-OA, OA+Cd(Ac)₂, CdSe-PDTC, and PDTC+Cd(Ac)₂) we observe a rapid rise ($\sim 180 \text{ fs}$) of the trapped hole feature, indicating that the trapping of this carrier at intrinsic NC defects effectively competes with PDTC-associated trapping.

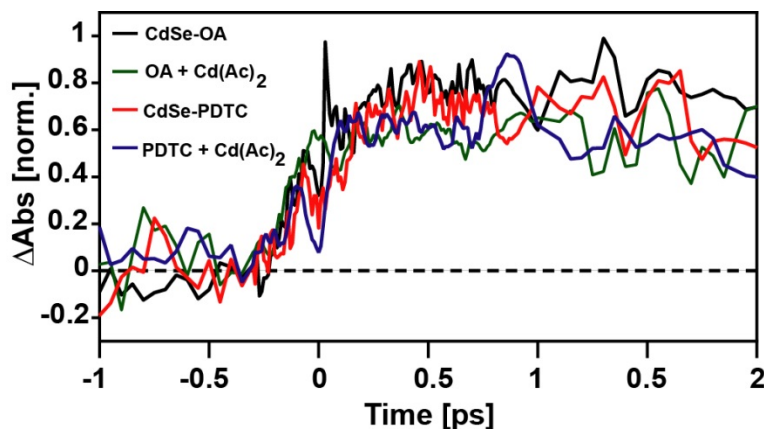


Figure 3.14: Comparison of PA rise following X1 photoexcitation. All four investigated samples display a growth of this band over ~ 180 fs.

Moving onto the B1 band, we find that the decay of this feature is nearly identical for CdSe-OA, OA+Cd(Ac)₂, and PDTC+Cd(Ac)₂ samples (**Figure 3.15**). Following a $\sim 10\%$ decay over ~ 30 ps, the B1 band for each of these samples displays a decay consistent with a 5.5 ns lifetime. To fit these decay traces, we have employed an exponential fitting function that has been modified to account for a Poisson distribution of electron trapping sites on our particles^{8,9} that can describe the rapid decay observed at short timescales. Fit parameters that result from this model are included in **Table 3.2**.

In contrast to these traces, decay of the B1 band is markedly accelerated for CdSe-PDTC. We assign this rapid decay to recombination of electrons with holes that populate PDTC-associated traps. In support of this assignment, the decay of the B1 band can be properly fit by adding an additional Poisson-distributed quenching pathway to our decay model (**Table 3.2**).

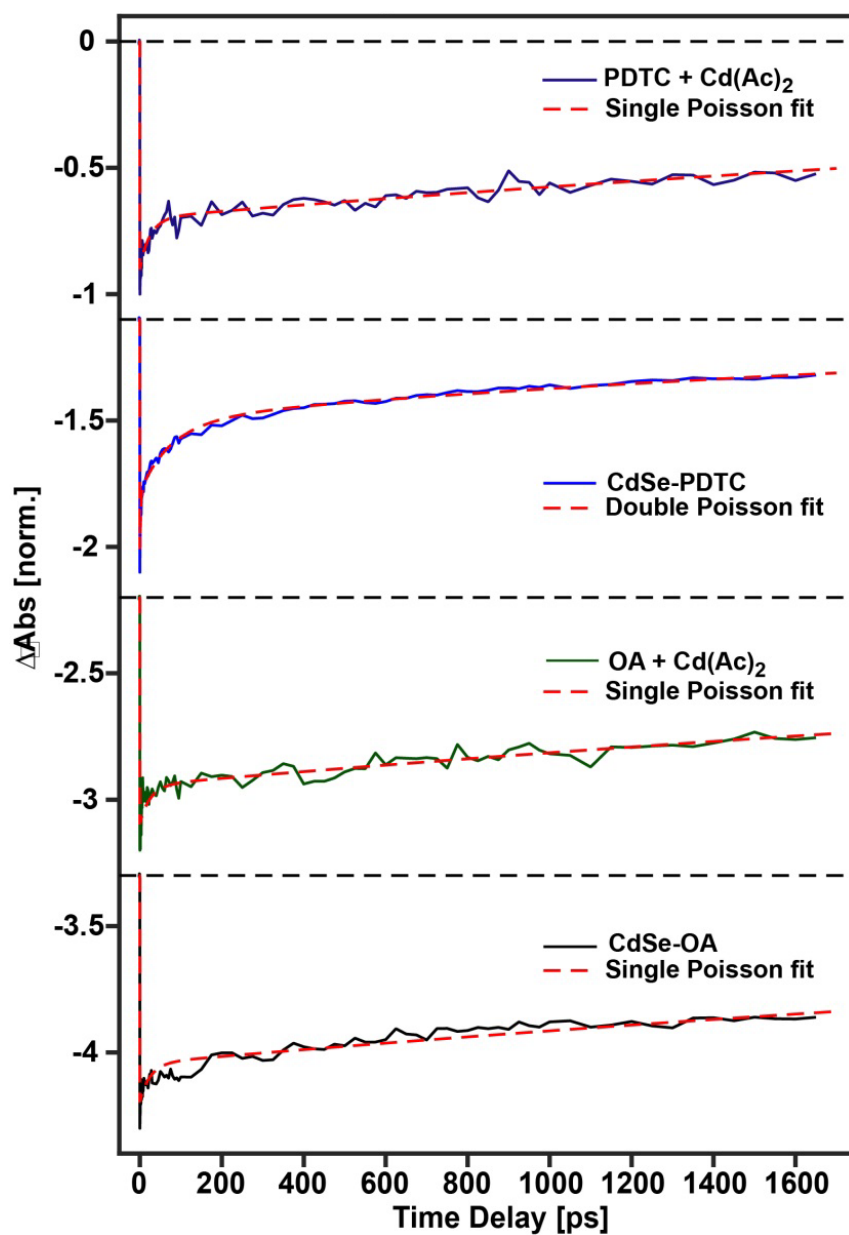


Figure 3.15: B1 recovery traces for the four NC samples described in the main text. Data shown as solid lines; fits from a function that accounts for a Poisson distribution of electron quenching sites among NCs shown as dashed red curves.

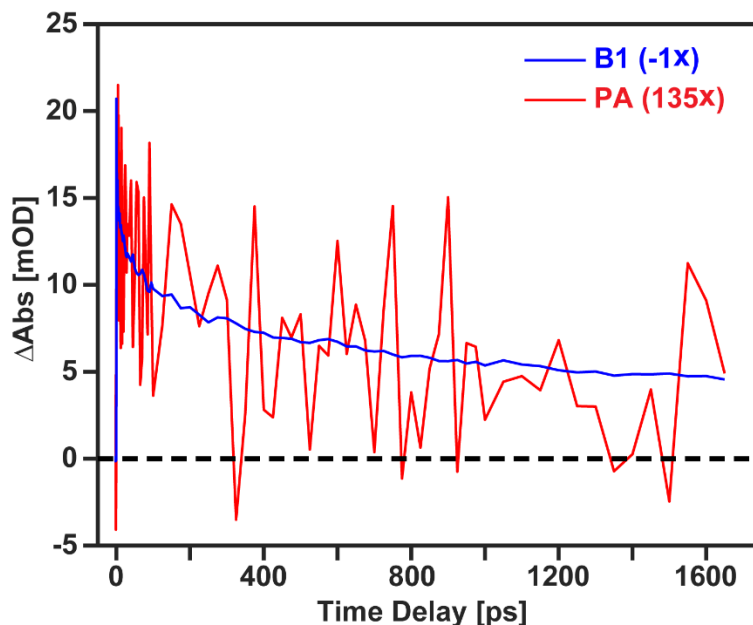


Figure 3.16: Comparison of the recovery kinetics for the B1 and PA features measured for CdSe-PDTC following X1 excitation. The sign of the B1 trace has been flipped to compare to the induced absorption band. The PA feature has been scaled by 135 $\times$ to place it on the same amplitude scale as the B1 feature.

Comparing the decay kinetics of the PA band to that of the B1 band, we find that for CdSe-OA, OA+Cd(Ac)₂, and PDTC+Cd(Ac)₂, this decay occurs on timescales longer than we can reliably resolve using our TA spectrometer given its maximum time delay 1.65 ns. Interestingly however, for CdSe-PDTC we find that the recovery of the PA feature matches that of the B1 band (**Figure 3.16**). As the PA feature tracks the population of NC-associated hole traps rather than those associated with PDTC, this implies that PDTC treatment accelerates the recombination of holes that populate NC-associated traps with 1S_(e) electrons. As we argue in the Chapter main text, we attribute this observation to hole transfer that occurs between NC-centered traps and PDTC-

associated traps over 100s of picoseconds to nanoseconds as they likely reside in equilibrium.

Fit Parameters for Transient Absorption and TCSPC Data

Table 3.2. Fit Parameters for B1 Recovery Kinetics

Sample	A	τ_{QD} [ns]	m_1	τ_1 [ps]	m_2	τ_2 [ps]
CdSe-OA	-0.743	5.25	0.186	27.0	NA	NA
OA+Cd(Ac) ₂	-0.743	5.25	0.186	27.0	NA	NA
CdSe-PDTC	-0.395	2.73	0.294	2.38	0.555	98.7
PDTC+Cd(Ac) ₂	-0.699	5.16	0.254	27.0	NA	NA

Table 3.2: Bleach recovery traces were normalized to their maximum values prior to fitting. Data were fit to a model that assumes a Poisson distribution of electron quenching sites among nanocrystals. This model has the following functional form: $\Delta Abs(t) = A \exp\left[-t/\tau_{QD} + \sum m_i e^{-t/\tau_i}\right]$, where τ_{QD} is the 1S_(e) electron decay rate in the absence of quenching sites and m_i and τ_i are, respectively, the average number of quenching sites per NC and the quenching rate at these sites. For CdSe-OA, OA+Cd(Ac)₂, and PDTC+Cd(Ac)₂ samples, only a single type of quencher was needed to reproduce the experimental B1 decay traces. Two types of quenchers with different trapping rates were needed to adequately fit CdSe-PDTC. Fits were convolved with a Gaussian instrument response function with a FWHM of 94 fs. Given the strong overlap between the B1 traces for CdSe-OA and OA+Cd(Ac)₂, the fit to these traces was constrained to be the same.

Table 3.3. Fit Parameters for TCSPC Decays

Sample	A ₁	τ_1 [ns]	A ₂	τ_2 [ns]	A ₃	τ_3 [ns]
CdSe-OA	0.511	2.32	0.316	10.8	0.068	43.4
OA+Cd(Ac) ₂	0.392	3.51	0.468	16.2	0.087	63.9
CdSe-PDTC	0.491	2.72	NA	NA	NA	NA
PDTC+Cd(Ac) ₂	0.536	2.98	0.494	13.0	0.061	41.9

Table 3.3: TCSPC decay traces were normalized to their maximum values prior to fitting. Data were fit to a multiexponential decay starting at a time delay of 1 ns, a point at which the IRF (700 ps FWHM) had largely decayed. Data for CdSe-OA, OA+Cd(Ac)₂, and PDTC+Cd(Ac)₂ could each be adequately fit by a triexponential decay. In contrast, the decay for CdSe-PDTC displayed a prominent instrument limited component followed by a tail that could be well fit by a single exponential decay.

3.8 REFERENCES

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Chapter 4: Monitoring Exciton Transport Dynamics*

*Work Previously published as “Exciton-Delocalizing Ligands Can Speed Up Energy Migration in Nanocrystal Solids” *Nano Lett.* **2018**, 18 (5), 3259–3270.

4.1 INTRODUCTION

In Chapter 3 we saw that in colloidal CdSe nanocrystals (NCs) ligand exchange with phenyldithiocarbamate (PDTC) increases the rate of hole relaxation, due to the NC-ligand interaction that results from the energetic alignment and orbital symmetry of PDTCs HOMO that allow strong mixing of this state with those within CdSe’s valence band (VB). We hypothesized that the hybrid NC-ligand character that results from this interaction improve the mobility of excitons in NC films due to enhanced spatial delocalization of these states. Here we test this hypothesis using a combination of transient absorption spectroscopy (TA) and kinetic Monte-Carlo (KMC) simulations to monitor the transport of excitons in CdSe NC solids.

Measuring energy and charge transport in NC films presents a number of practical challenges as electrical measurements require NCs be integrated into device geometries such as field-effect transistors and photovoltaic cells.^{1–4} In such devices, the nature of the electrical contacts formed to a NC film can strongly impact device performance^{5–7} and consequently the derived values for exciton diffusion rates and carrier mobilities. To circumvent this problem, researchers have devised ways to extract the diffusion lengths and hopping rates of carriers in films using optical methods as a proxy for electrical device measurements.^{8–14} A recent study by Gilmore et. al has shown time-resolved spectroscopic measurements coupled with simulations can be used to extract

energy transport parameters for ligand-exchanged PbS NC solids.⁹ In particular, TA was used to track time-dependent changes in the average energy of the band-edge exciton of excited PbS NCs by monitoring the spectral position of photobleaching bands. Using a KMC simulation to fit the transient data, they were able to follow charge transport in homogeneously broadened NC solids and extract carrier hopping rates and mobility values.

In this work, we have used a similar approach to track exciton migration in PDTC-treated CdSe films and assess the impact of this exciton-delocalizing ligand (EDL) on exciton diffusivity. TA measurements performed on PDTC-exchanged films display a rapid, sub-picosecond decrease of the average energy of excited carriers. These dynamics are not observed in oleate-capped NC films, suggesting PDTC treatment reduces barriers hindering exciton transport within NC solids. To quantitatively extract a hopping rate between NCs, we have developed a site-based KMC model that properly accounts for the NC size dispersion within our NC films as well as changes in NC exciton energy and hopping rate upon treatment with PDTC. To properly account for time-dependent changes observed in TA measurements performed as a function of temperature, we find we need to employ a Miller-Abrahams model¹⁵ to describe exciton hopping. This indicates exciton transfer occurs not by Förster Resonance Energy Transfer but rather via carrier tunneling. Trajectories computed with this model reveal hops between NCs occur as fast as 200 fs in PDTC-exchanged films, whereas excitons produced in oleate-capped films display hopping rates that are five orders of magnitude slower. Interestingly, our experimental data indicates PDTC treatment also speeds carrier recombination, which

unfolds over hundreds of picoseconds. Incorporation of a relaxation rate in our KMC simulations that scales with the number of PDTC molecules coordinated to CdSe NCs reproduces this result. This finding is in qualitative agreement with prior work that demonstrated PDTC can enhance the radiative recombination of excitons in CdSe NCs.^{16,17} Importantly, the hopping rates measured as a result of PDTC exchange fall among the fastest reported for NC solids. This suggests treating NC surfaces with EDLs can form an effective strategy for speeding energy transport.

4.2 USING SPECTRAL SHIFTS TO MONITOR ENERGY TRANSPORT

Experimental Setup

TA measurements follow exciton relaxation dynamics of PDTC-exchanged films by using, a femtosecond pump pulse excites an ensemble of NCs whose ensuing dynamics are read out by a time-delayed, broadband white light probe pulse. As the pump pulse removes carriers from the valence band and places them into the conduction band, this lowers the absorptivity of the X1 state, creating a transient photobleach of this transition, commonly referred to as the “B1 bleach” in NC studies.^{19,20} The peak position of this band reflects the average energy of excited NCs within a film.⁹ Changes in the center position of this peak can thus signal energy migration between neighboring NCs.

A schematic of the transient absorption (TA) set up used for the experiments in Chapter 4 is shown in **Figure 4.1**.

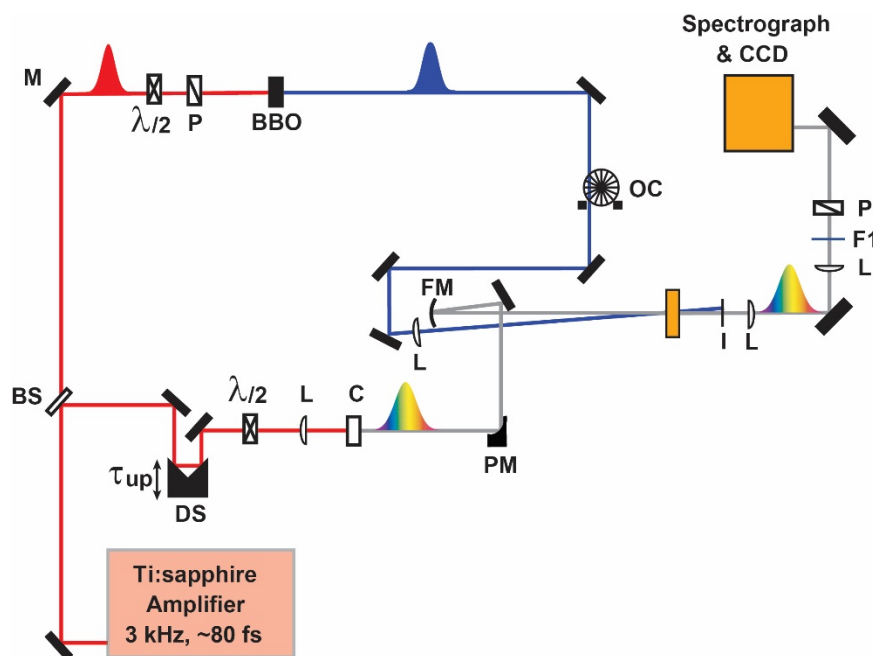


Figure 4.1: Setup depicting the transient absorption spectrometer. Abbreviations are as follows (BS) beam splitter, (M) mirror, (DS) delay stage, ($\lambda/2$) half-wave plate, (L) lens ($f=15, 25$ cm), (C) c-cut sapphire, (PM) parabolic mirror, (FM) focusing mirror ($f=25$ cm), (I) iris, (F1) 0° angle of incidence 800nm HR mirror, (P) polarizer, (BBO) β -barium borate crystal, (OC) optical chopper.

Briefly, a femtosecond Ti:sapphire regenerative amplifier (Coherent Legend Duo Elite, 3 kHz, 4.5 mJ) was used to generate ~ 90 fs pulses centered at 1.54 eV with a bandwidth of 160 cm^{-1} (FWHM). A small portion of the amplifier output ($\sim 1 \mu\text{J}$) was focused into a 3-mm thick, c-cut sapphire window to produce broadband probe pulses (1.59 – 2.76 eV) via self-phase modulation. Pump pulses (3.1 eV) were generated by frequency doubling the fundamental Ti:sapphire output using a Type-I β -barium borate crystal. The pump fluence was selected such that all samples displayed a linear scaling of the differential absorbance amplitude with changing fluence (Appendix, **Figure 4.9**). A motorized rotation mount (Thorlabs KPRM1E) was used to continuously rotate the film

at a rate of 25 degrees/s throughout data collection to prevent charging effects. For temperature-dependent TA experiments, the cryostat housing a NC film was linearly translated throughout data collection using a computer-controlled delay stage (Newport XMS50) to prevent sample charging. Frequency dependent instrument response functions (IRFs) for each scan were obtained using a cleaned SiO₂ substrate. Collection of frequency-dependent IRFs allowed for chirp correction of the supercontinuum probe pulse.

Figure 4.2A plots TA spectra of a PDTC-exchanged film following photoexcitation at 400 nm (3.1 eV). Examining the data at a pump-probe delay of 200 fs, a decrease in absorption attributed to the B1 band is observed whose maximum falls at 2.32 eV, an energy close to the peak absorptivity of the X1 state in the film's steady-state absorption spectrum. As the pump-probe delay is increased, the B1 band undergoes a rapid redshift, lowering its peak energy to ~2.24 eV over the course of 1 ps. We note TA experiments performed on PDTC-exchanged NCs in solution do not show this shifting behavior (Appendix, **Figure 4.8**), indicating it is not due to carrier cooling within individual NCs but rather must result from interactions between NCs within the film. Given our prior hypotheses for the observed broadening of the steady-state absorption spectra of PDTC-exchanged films, we note a shift of the B1 band to lower energy over time is consistent with excitations moving within PDTC-exchanged films along an energetic gradient towards lower-energy NCs with a high degree of PDTC substitution.

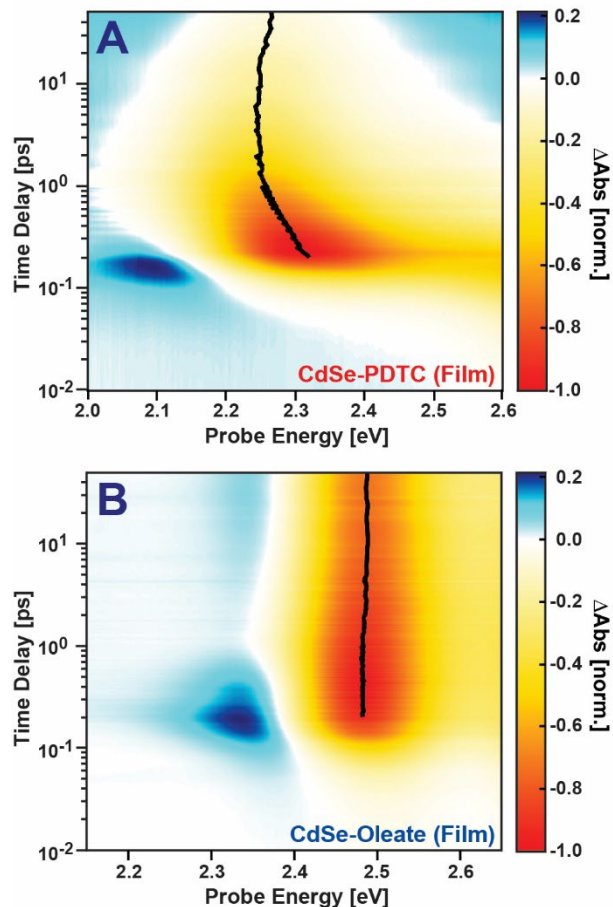


Figure 4.2: TA spectra of (A) CdSe-PDTC films and (B) CdSe-Oleate films that highlight time-dependent changes in the position of the NC's B1 band within the first 50 ps following excitation. Signal amplitudes shown in red/orange correspond to absorption decreases (photobleaching) while signals shown in blue denote absorption gains. Black lines indicate the energy of the B1 bleach maximum as a function of time.

We compare this result to similar TA measurements conducted on films comprised of NCs capped with native oleate ligands (**Figure 4.2B**). We observe no appreciable redshift of the B1 band within the first 50 ps following photoexcitation. Rather, plotting the center position of the B1 band (**Figure 4.3A**, black), we see an ~ 8 meV increase in the energy of this feature over 10 picoseconds. As isolated CdSe NCs in

solution display a similar increase in the energy of the B1 band upon excitation (**Figure 4.3A**, blue), this shift cannot be tied to energy migration within the native ligand-capped NC film. While we have focused our discussion on photobleaching contributions to the B1 band, a portion of this feature's amplitude on its lower energy side arises from stimulated emission from X1 excitons. A loss of stimulated emission can shift the B1 band to higher energy. Such a stimulated emission loss can result from the trapping of photoexcited holes, which has been shown to occur rapidly in CdSe NCs and likely explains the slight blue shift seen for CdSe-oleate in both solution and films.^{18,21}

Following its shift to higher energy, the peak of the B1 band of CdSe-Oleate films returns to its starting position over hundreds of picoseconds. This shift back towards lower energy is absent from TA spectra of individual, oleate-capped NCs in solution. While the synthetic methodology we used to produce CdSe NCs was selected due to its ability to produce NCs with a narrow size distribution, the emission linewidth measured for the oleate-capped NC film is 123 meV, which is $\sim 10 - 20$ meV larger than the predicted homogenous linewidth for uniform CdSe NCs with an exciton energy of 2.48 eV.^{22,23} Thus, the ~ 8 meV redshift we observe for the oleate-capped NC film likely results from energy migration within the film towards larger NCs with lower X1 energies. However, the timescale observed for this migration, 353 ps, is nearly three orders of magnitude slower than that found in PDTC-functionalized films, ~ 400 fs (Appendix, **Figure 4.8**), indicating PDTC-functionalization significantly speeds energy transport in NC solids.

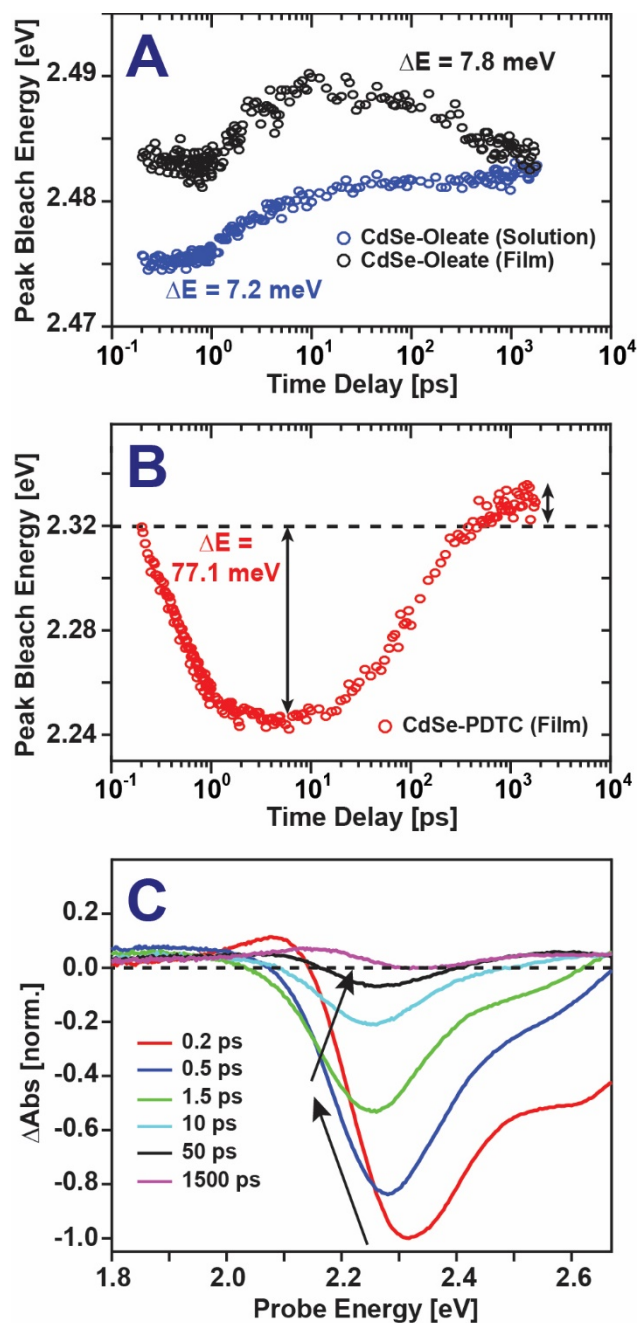


Figure 4.3: (A) Center peak B1 bleach energy of a CdSe-Oleate solution (blue) and film (black) as a function of pump-probe time delay. (B) Center peak B1 bleach energy of a CdSe-PDTC film as a function of pump-probe time-delay. (C) TA spectrum of CdSe-PDTC film highlighting the B1 bleach evolution (black arrows) over the lifetime of the experiment.

Shifting our focus back to dynamics within PDTC-functionalized films, we find that over a few hundred picoseconds, the peak of the B1 bleach increases in energy and ultimately settles on a value that is 8.6 meV higher in energy than its initial position (**Figure 4.3B**). This increase in the B1 band center position is unexpected as exciton migration within a film should only cause this band to decrease in energy rather than increase. As such, a different fundamental process must underlie the observed dynamics. Examining our TA spectra further, we note the increase in the B1 band center position is correlated with a loss of its amplitude (**Figure 4.3C**), suggesting exciton relaxation is responsible for the observed spectral shifting dynamics. Both experiments^{16,18} and theory¹⁷ have shown PDTC can increase a NC's radiative rate by enhancing the density of states at the NC band edge. Likewise, PDTC ligand exchange can induce some degree of NC surface reconstruction that accelerates nonradiative carrier recombination.^{16,18} Therefore, excitons in NCs with a high degree of PDTC substitution should decay more rapidly compared to excitons in NCs with less PDTC molecules bound to their surface. We hypothesize this effect is responsible for the long-time B1 shifting dynamics shown in **Figure 4.3B**. As more highly PDTC-substituted sites should decay preferentially, the longtime behavior is dominated by those less substituted, higher energy sites which have slower decay rates. This is reflected in the TA spectrum as a blueshift of the B1 bleach maximum at long time delays. Thus, we interpret the observed shifting of the B1 band of PDTC-functionalized films as arising from two distinct phenomena: (1) rapid exciton migration to low-energy, highly PDTC-substituted NC sites on a sub-picosecond timescale, and (2) accelerated decay of excitons at these low-energy sites.

4.3 KINETIC MONTE-CARLO SIMULATIONS OF EXCITON MIGRATION

While extracting timescales and the magnitude of the downhill energy migration from TA spectra provides some measure of PDTC's impact on the transport properties of NC films, to build a comprehensive picture of the effects of PDTC exchange we have turned to simulations to provide a deeper physical understanding of this process. To extract relevant transport parameters, such as the carrier diffusion length, transport rate, and mechanism, we have developed a KMC model that can accurately reproduce the changes we observe in TA spectra of NC films. In this model, the CdSe film is described as an ordered array of 16,000 NCs arranged at the vertices of a three-dimensional face-centered cubic (FCC) lattice comprised of 40 close-packed 20×20 layers and periodically replicated in the x and y dimensions. The inter-NC spacing is determined by the FCC lattice constant, which we set based on experimental measurements. To account for energetic variations within the NC population we assigned each NC in the model an intrinsic energy, $E_i^{(0)}$, assigned randomly from a Gaussian distribution whose width is parameterized based on experimental emission spectra.

We model the effect of PDTC substitution by assuming each PDTC ligand produces a redshift in the NC energy of $\alpha = -3.46$ meV. The value of α is obtained from linear absorption spectra of colloidal oleate-capped and PDTC-exchanged NCs and is consistent with previously reported values for colloidal CdS NCs.²⁴ We also assume each PDTC ligand increases the excited state decay rate by an amount $\kappa_D = 1.22$ ns⁻¹, which is obtained by fitting the TA spectra of colloidal PDTC-exchanged NCs (Appendix, **Figure 4.7**). In this way, if NC i has n_i substituted PDTC ligands, it will have an energy

of $E_i = E_i^{(0)} + n_i\alpha$ and an excitation decay rate of $k_D = k_D^{(0)} + n_i\kappa_D$ where $k_D^{(0)}$ is the decay rate of an unsubstituted site. We assign the PDTC substitution number, n_i , randomly based on a Poisson distribution with a mean of 24 substituted ligands, consistent with FTIR measurements of oleate loss in the exchange process¹⁸ taking into account each PDTC molecule displaces two oleate ligands.²⁴

To describe exciton transport in NC films, a model is required that predicts how the rate of exciton transfer between NCs varies with the energy difference between NC sites and their spatial separation. In weakly-coupled NC arrays, Förster Resonance Energy Transfer (FRET) has been suggested to be the dominant mechanism of energy transfer.²⁵ However, a calculation of the FRET rate between two CdSe NCs separated by a single PDTC molecule predicts a hopping rate of several nanoseconds, which is orders of magnitude slower than the shifting behavior we observe for the B1 band experimentally. For this reason, we have chosen to instead model exciton transport in NC films via a carrier tunneling mechanism. Motivated by the exponential distance dependence of carrier tunneling rates, we assume transport is dominated by incoherent next-neighbor hops from site i to site j with a Miller-Abrahams rate¹⁵ described by Equation 4-1,

$$k_{i \rightarrow j} = \begin{cases} k_T \exp\left(-\frac{(E_j - E_i)}{2k_B T}\right) & E_j > E_i \\ k_T & \text{otherwise} \end{cases} \quad (4 - 1)$$

where E_n is the energy of site n , k_T is a characteristic transport rate and $(E_j - E_i)/2$ is the energy difference between an exciton on particle j and particle i under the effective mass approximation. Direct hops between particles that do not neighbor one another are

neglected in our model as a similar KMC study of NC films found no improvement in model performance by including coupling beyond nearest-neighbor sites.⁹

The initial excitation seen in the TA spectrum of the PDTC exchanged film is significantly blue-shifted from the film's emission spectrum, indicating a non-equilibrium population of sites is prepared by the pump pulse. We therefore model the initial population of excitations by randomly selecting NCs with a bias on the intrinsic NC energy, $E_i^{(0)}$, designed to reproduce the initial TA bleach peak. Once initialized, we simulate the dynamics of individual non-interacting excitons using a KMC algorithm. For this algorithm, at each KMC step the exciton can either hop to a NC on a neighboring lattice site, with rate $k_{i \rightarrow j}$, as expressed in Equation 4-1, or can decay to the ground state (thereby terminating the trajectory) with rate k_D . The transport rates can then be fit to the initial red-shift behavior giving a transport rate of $6.7 \times 10^{-5} \text{ ps}^{-1}$ for the oleate-capped films and 4.6 ps^{-1} for the PDTC-exchanged film, indicating an increase in the transport rate by nearly five orders of magnitude (**Figure 4.4**). Correspondingly, an excitation in the PDTC exchanged film travels $\sim 10 - 12$ lattice units in its $\sim 100 \text{ ps}$ lifetime while an exciton in the oleate capped film travels ~ 4 lattice units in its $\sim 1 \text{ ns}$ lifetime. We conclude the rapid redshift seen in PDTC-treated films results from a significant enhancement of the exciton hopping rate, which our KMC simulations suggest falls on the order of 200 fs per hop. Thus, PDTC treatment appears to enhance carrier tunneling in NC films.

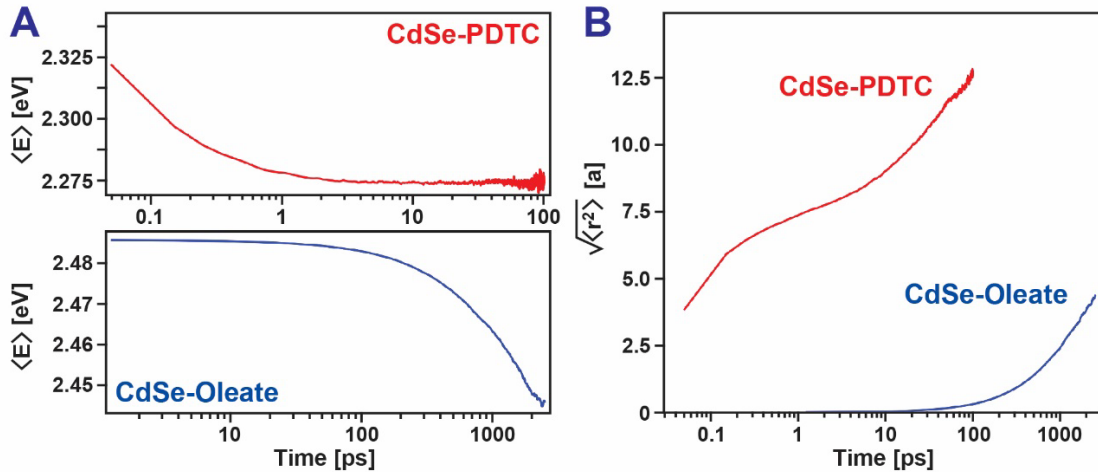


Figure 4.4: Time series of the mean exciton energy (A) and root mean squared displacement (B) for PDTC-exchanged (red) and oleate-capped (blue) NC films extracted from KMC simulations. The mean exciton energy corresponds to the bleach peak position of the TA spectra while the root mean squared displacement is reported in units of the lattice constant, a . Note the difference in axis scales for the PDTC-exchanged and oleate-capped NC films in panel (A).

Above, we hypothesized the blue shift we observe experimentally on longer timescales results from the rapid decay of excitations at highly-substituted PDTC sites. Consistent with this hypothesis, when we constrain our KMC model using experimental parameters we find many excitations decay before reaching time delays at which we experimentally find the average excitation energy to shift back to higher energy. However, this creates a practical problem associated with reproducing the return of the CdSe-PDTC film B1 bleach to high energy as this reflects the behavior of a small subset of the ensemble of excitations prepared in a film. As such, accurately reproducing this behavior requires use of long simulation times and averaging over multiple realizations of the energetic disorder in our system. To determine if our KMC model can produce a blueshift of the B1 bleach, we have explored how the behavior of trajectories change when the decay rate asymmetry, κ_D , is varied. Increasing this parameter will accelerate

the rate at which low-energy excitations decay and thereby allow shorter trajectories to be used to determine if the model predicts a bleach blue-shift. Indeed, we find as this value is increased the model exhibits a range of different behaviors, some of which display a bleach blue-shift, while others do not. This suggests the behavior predicted by our model is sensitive to the relative rates for energy transport and excitation decay.

To explore how competition between different microscopic parameters works in concert to give rise to the observed red-shift and subsequent blue-shift in PDTC-treated films, we perform a sweep through these parameters. To facilitate this sweep, a few simplifying assumptions were made to reduce the dimensionality of the model's parameter space. First, all NCs were taken to have the same intrinsic energy. The energy variance is therefore a result of PDTC substitution only. The initial exciton ensemble is then created by a uniform sampling of all NC sites. The parameter sweep is then performed across three non-dimensional ratios of the model parameters. The ratio $k_T/k_D^{(0)}$ measures competition between transport and exciton decay and is proportional to the number of hopping events in an unsubstituted film. Second, $\Delta k_D/k_D^{(0)}$, where $\Delta k_D = \kappa_D \bar{n}$, measures the preferential decay of more substituted sites where $\bar{n}$ is the mean substitution number. Finally, $k_B T/\Delta E$ is a normalized temperature measuring the size of thermal fluctuations relative to the standard deviation in site energies $\Delta E = \alpha \bar{n}$.

Representative time series showing the evolution of the average exciton energy as a function of these parameters are shown in **Figure 4.5**, which explores how varying the relative rates of excitation transfer and decay influence the mean excitation energy of the

NC ensemble.

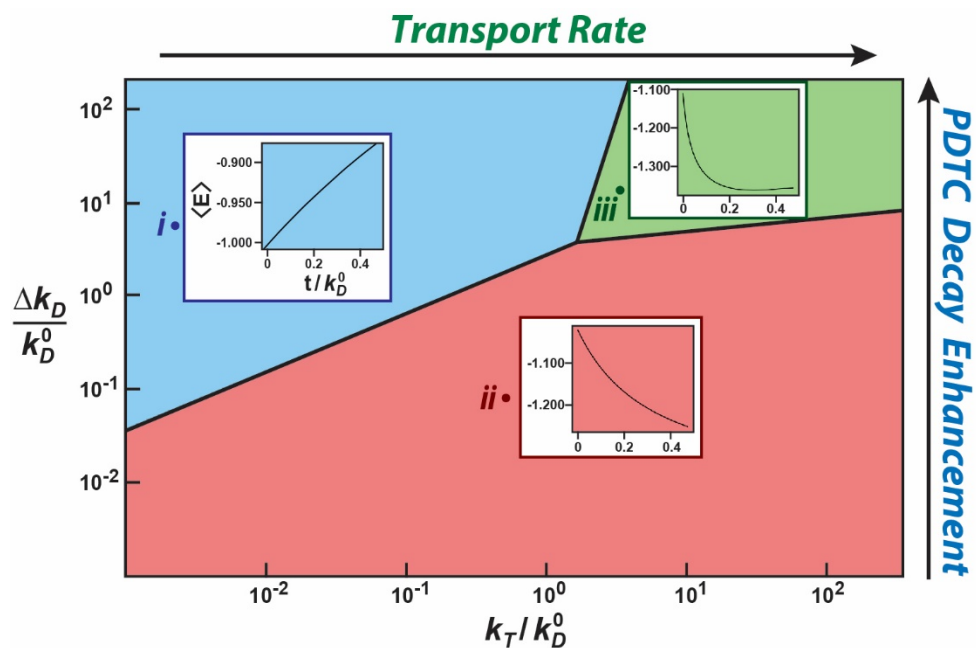


Figure 4.5: Parameter sweep showing how the behavior of the mean exciton energy in KMC simulations varies with changing exciton transport rate and PDTC decay enhancement. Regions in blue display only an increase in average exciton energy (i), regions in red, a decrease (ii), and those in green show a decrease followed by an increase (iii).

Our sweep identifies three characteristic behaviors for the photobleach of the NC ensemble: (i) red-shift only (highlighted in red), (ii) blue-shift only (highlighted in blue), and (iii) red-shift followed by a blue back-shift (highlighted in green). A red-shift of the mean excitation energy has been observed in previous studies of ethanethiol-capped NC films⁹ and can be attributed to thermalization of the exciton ensemble. This behavior is a direct consequence of the thermodynamic detailed balance condition. In contrast, a blue-shift is a new behavior, unique to the PDTC-exchanged film. This occurs due to the preferential decay of highly-substituted low-energy sites leading to an over-sampling of higher-energy unsubstituted sites at long times and a corresponding blue-shift of the

mean energy. The red-shift therefore occurs due to thermodynamic equilibration within the excited-state manifold while the blue-shift is a competing non-equilibrium effect.

Examining the results of our parameter sweep, we find when there is little decay-rate asymmetry ($\Delta k_D/k_D^{(0)} \ll 1$) a red-shift is seen when the thermal fluctuations are smaller than the standard deviation in site energies. Furthermore, the size of the shift is determined by the ratio k_T/k_D . This is consistent with previous studies⁹ and with the thermalization mechanism for the red-shift. As the decay rate asymmetry is increased, a system that initially displayed a red-shift only, first shows a smaller red-shift followed by a subsequent back-shift, then a linear blue-shift only. This illustrates the competition between the approach to thermal equilibrium and the non-equilibrium decay-rate asymmetry and is consistent with the selective-decay mechanism for the blue-shift. We find that only over a relatively narrow range of parameters do we observe a red-shift followed by a blue-shift (**Figure 4.5**, region iii).

We also note our kinetic model makes some clear predictions regarding how rates for exciton transport and relaxation change with temperature. As we cool the PDTC-exchanged film, the initial rate of downhill energy migration is expected to be unchanged as this process is not thermally activated. Over time, as excitons encounter local minima, the residence time spent in these wells increases with decreasing temperature. Thus, we expect the rate at which excitons access the lowest energy sites with the highest exciton recombination rates should slow. Projecting these dynamics onto our bleach shifting behavior, as temperature is lowered we expect to observe a negligible change in the red-shifting behavior at short time delays and a suppression of the blueshift recovery at long

delays as exciton migration to sites favoring exciton recombination is suppressed. These predictions are supported by experimental TA spectra of PDTC-exchanged films measured at 78 and 294 K (**Figure 4.6A**). This data shows the timescale associated with the initial red-shift of the NC X1 photobleach displays little change with decreasing temperature while the blue-shift that occurs over hundreds of picoseconds at 294 K is completely suppressed at 78 K. **Figure 4.12** shows the suppression of the blueshift of the NC X1 band at low temperature is correlated with a lengthening of the exciton lifetime, lending further support to our model.

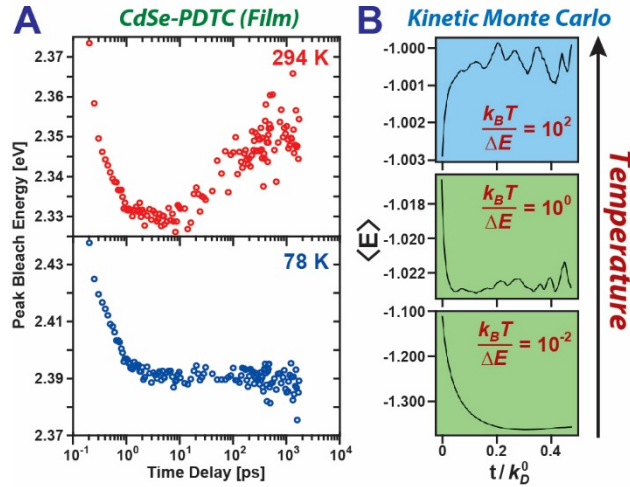


Figure 4.6: (A) Peak B1 bleach energy of a CdSe-PDTC film measured as a function of pump-probe time delay at 294 K (top, red) and 78 K (bottom, blue). (B) KMC parameter sweep showing the influence of temperature on exciton transport for a fixed $k_T/k_D^{(0)}$ ratio of 10^1 and a fixed $\Delta k_D/k_D^{(0)}$ ratio of 10^1 .

In **Figure 4.6B**, we use our kinetic model to make predictions regarding the behavior of excitations in PDTC-exchanged NC films over a larger temperature range than we can access experimentally. These calculations are performed for a set of parameters that, according to the parameter sweep in **Figure 4.5**, predict a red-shift

followed by a blueshift at temperatures where the energetic disorder in the system is similar to thermal energy ($k_T/k_D^{(0)} = \Delta k_D/k_D^{(0)} = 10$). At temperatures where the thermal energy is comparable to the distribution of site energies ($k_B T/\Delta E = 1$, **Figure 4.6B**, middle panel), our KMC model predicts a rapid red-shift of the average exciton energy followed by a slower recovery resulting from exciton decay at highly-substituted PDTC sites. This behavior is comparable to our experimental results at room temperature. According to the scaling relationships extracted from our sweep, we conclude the experimental parameters derived from PDTC-functionalized films should give rise to a blue-shift occurring on timescales on the order of 0.1 – 1 ns, which is consistent with our experimental data. As the temperature is lowered ($k_B T/\Delta E = 0.01$, **Figure 4.6B**, bottom panel), we find the blue-shift of the average exciton energy at longer delays is suppressed, similar to our results at 78 K. The plotted data trace also shows a slowing of the initial red-shift of the average exciton energy, which is not as readily apparent in our experimental data at 78 K. However, this occurs as the temperature variation shown for the model corresponds to a 100 $\times$ decrease in the temperature whereas we only explore a 4 $\times$ decrease experimentally, which would impact the extent to which local trapping of excitons during downhill energy migration influences their dynamics.

Experimentally, heating our films above 400 K leads to PDTC degradation (Appendix, **Figure 4.13**). However, using our KMC model we can predict how excitons move in a disordered NC lattice when the thermal energy exceeds the site disorder ($k_B T/\Delta E = 100$, **Figure 4.6B**, top panel). In this case, we find lowering the energetic penalty for occupying a high-energy site leads to the absence of a decrease of the average

exciton energy at short time delays as each site in the NC lattice gains similar probability for exciton occupation. Over time we observe an increase in the average exciton energy that stems from preferential relaxation at low-energy sites. The overall magnitude of this shift however, decreases with increasing temperature as the thermal energy simply outweighs the distribution of site energies, preventing exciton pooling at low-energy sites.

4.4 DETERMINATION OF TRANSPORT MECHANISM

While the model we have employed is similar to one previously used to describe exciton migration in NC super-lattices,⁹ we wish to point out two key differences with this prior work. First, the decay rate in the model we present is taken to be spatially heterogeneous. We find this drastically alters the non-equilibrium exciton statistics as the interaction between transport and spatially heterogeneous decay leads to unexpected behavior, such as the back and forth changes in the average exciton energy of the PDTC-functionalized films we explore here and enhanced near-infrared emission from PbS NCs interfaced with J-aggregate assemblies.²⁶ Second, an additional source of energetic disorder was added to account for stochastic ligand exchange. As ligand substitution also dictates the spatially heterogeneous decay rate, this leads to correlation between the decay rate and site energies. Indeed, this correlation is responsible for the novel non-monotonic behavior observed in the non-equilibrium energy of the NC exciton ensemble and suggests the potential to harness correlated transport and decay in the design of nanostructured materials, such as light-harvesting antennas.²⁷

Examining the exciton hopping timescale extracted from our KMC model for PDTC-functionalized films, 200 fs, we find it is very fast compared to values reported by other groups. For example, energy hopping timescales of 50 ps have been reported for monolayer and bilayer NC films,^{28,29} while more recently Cohen et. al. have measured transfer timescales as fast as 30 ps in layered donor-acceptor NC structures treated with a short chain dithiol that covalently links neighboring NCs.³⁰ Compared to these studies, the 200 fs exciton hopping timescale we obtain is roughly two orders of magnitude faster.

Given PDTC alters the spatial extent of photoexcited holes but not electrons,^{17,31,32} it is not immediately clear why PDTC would speed exciton transfer over simply the transfer of holes between neighboring NCs. However, our data clearly shows exciton transfer dominates our observed dynamics. We observe rapid shifting of the B1 band of PDTC-functionalized NCs even though this band selectively reports on the behavior of photoexcited electrons over photoexcited holes,²⁰ suggesting the hole and electron move together. This notion is further supported by the decay of spectral features within our TA data. As the B1 band relaxes, we observe a near complete loss of other TA spectral features, suggesting B1 band relaxation occurs due to electron-hole recombination and not carrier trapping. Such recombination necessitates correlated motion of the photoexcited electron and hole.

One potential mechanism that could explain PDTC's large impact on exciton migration was recently outlined theoretically by Reich and Shklovskii,³³ who suggested exciton migration between NCs can occur via sequential hole and electron transfer steps. As the transfer of each charge carrier can occur in a concerted fashion, the formation of a

charge transfer intermediate is not necessitated but the rate of the overall exciton transfer depends on the strength of the one-electron couplings for both electron and hole transfer. As such, increasing hole wavefunction overlap between NCs via PDTC-functionalization would be expected to enhance exciton transfer via this mechanism. We note the exciton hopping rate we obtain agrees well with sub-picosecond timescales that have been reported for hole extraction from PDTC-functionalized nanomaterials,^{34,35} suggesting the rate of hole transfer limits exciton migration. Such a scenario would be expected for a concerted charge transfer mechanism due to the hole's larger reduced mass.

Throughout this chapter, we have hypothesized that due to the strong interaction of PDTC with NC valence band states,^{31,32,36} PDTC promotes carrier wavefunction delocalization that improves electronic coupling between NCs that aids exciton transport. However, an alternate explanation for the improvement of exciton transport in NC films upon PDTC treatment is that PDTC ligands decompose within several hours after ligand exchange,³⁷ leaving behind a CdS shell on the NC surface that can direct oriented attachment between neighboring particles. Grenland et. al. have used Raman spectroscopy to show when PDTC ligands decompose they deposit a thin shell of sulfur atoms that can bind strongly to a Cd²⁺ enriched surface of a NC. They go on to propose this CdS shell is primarily responsible for carrier delocalization in this system.³⁸

Despite these reports, a series of control experiments performed on PDTC films allow us to rule out PDTC decomposition as the origin of the rapid exciton transport we observe. First, FTIR measurements we have reported previously for PDTC-treated films¹⁸ show PDTC ligands remain intact following the film preparation and ligand exchange

procedure we employ. Next, STEM images of PDTC-treated NCs show they display an average inter-particle distance greater than the expected separation for NCs that have fused epitaxially via a CdS shell (Appendix, **Figure 2.7**). PDTC decomposition via laser-induced heating is also unlikely given we need to heat PDTC-treated NC films to temperatures of 400 – 450 K to observe spectral changes attributed to particle necking,³⁹ such as the loss of a well-defined X1 band (Appendix, **Figure 4.13**). This finding is consistent with prior studies that have employed dithiocarbamates as sulfur precursors for core-shell NC growth, which find these molecules need to be heated to temperatures above 410 K to produce appreciable shell growth.⁴⁰ We estimate the maximal temperature change imparted by absorption of our pump beam falls well below this threshold (Appendix, **Figure 4.13**). Finally, based on the estimated number of PDTC molecules per NC in our films obtained from FTIR and absorption spectra, a CdS shell deposited by PDTC decomposition would only partially coat the surface of a NC due to incomplete exchange of PDTC for oleate ligands. We would anticipate such a partial shell would lead to increased exciton trapping rather than enhancing the rate of exciton transport within the film. We note PDTC decomposition to aniline is catalyzed by acidic conditions.⁴¹ As PDTC is commonly synthesized as an ammonium salt, this makes PDTC decomposition sensitive to both the concentration of PDTC used and the length of the exchange process due to ammonia outgassing. Indeed, when PDTC-functionalized NCs have been removed from acidic conditions, they have been shown to be stable for upwards of 62 hours.²⁴ Under the conditions we use for solid-state ligand exchange, which limits the exposure of NC films to PDTC solutions to only 4 hours, we find PTDC

decomposition does not play a major role in our observations. This guides us to the conclusion that improved wavefunction overlap facilitated by PDTC ligand exchange leads to the rapid energy migration we report.

4.6 CONCLUSIONS

In summary, we have measured carrier transport dynamics in CdSe NC solids treated with PDTC using a combination of fs-TA and KMC simulations. We have shown that solid-state ligand exchange with PDTC greatly improves transport properties in these films, as evidenced by a rapid decrease in the energy of photoexcited excitons on a sub-picosecond timescale. Modeling of these dynamics using KMC simulations reveals PDTC increases the exciton hopping timescale to a value as fast as 200 fs, which stands among the fastest rates reported for exciton transfer between neighboring NCs. These simulations also highlight that preferential non-equilibrium relaxation at NCs with high degrees of PDTC substitution results in unique dynamics that reflect a competition between exciton transport and recombination pathways. While charge carrier recombination at present limits the distances over which excitations diffuse in PDTC-substituted films, our results highlight that the strategy of employing exciton-delocalizing ligands to enhance energy transport in NC films is valid. Further work investigating the influence of such ligands on energy and charge transport in NC arrays is warranted.

4.7 APPENDIX

Transient Absorption Spectra of CdSe-PDTC in Solution

To verify the rapid down shifting of the NC photobleach of CdSe-PDTC films

results from energy transfer between NCs rather than processes tied to the energy relaxation of individual NCs, we have carried out TA experiments on CdSe NCs exchanged with PDTC in solution. 500 molar equivalents of PDTC salt were added to a 10 μ M NC solution in DCM and allowed to exchange for 4 h. This solution was kept in the dark and stirred throughout the exchange process. Following ligand exchange, the solution was passed through a 0.45 μ m PTFE syringe filter to remove undissolved PDTC salt and aggregated NCs. The NC solution was then diluted with DCM to an optical density of $\sim$ 0.1 in a 1 mm path length cuvette for TA experiments. The same B1 bleach shifting analysis used in the main Chapter text was performed on the TA spectra of CdSe-PDTC in solution and is shown in **Figure 4.7**.

Examining the bleach shifting dynamics of CdSe-PDTC in solution, we find no red-shift of the ground state bleach of the NCs' first exciton band can be seen following photoexcitation. Rather, a slight blue-shift ($\sim$ 6 meV) occurs over a $\sim$ 1 ps timescale that we attribute to spectral dynamics associated with exciton cooling following photoexcitation at 400 nm, similar to what we observe for CdSe-Oleate in solution. These results indicate the rapid downhill energy shift of the photobleach of the lowest exciton band of PDTC-treated CdSe films is a consequence of energy transfer between the NCs that comprise them

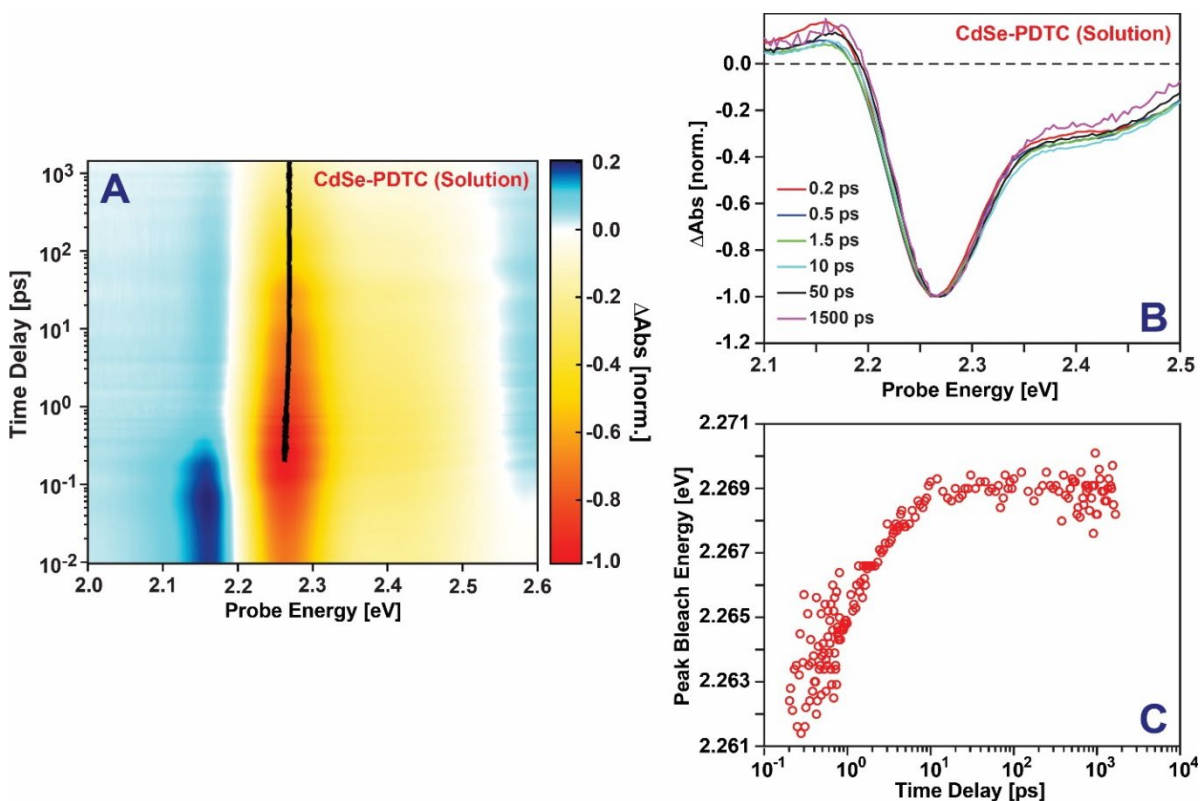


Figure 4.7: (A) TA spectra of CdSe-PDTC NCs in DCM following photoexcitation at 470 nm. (B) Temporal slices of TA spectra normalized to the B1 Bleach. These spectra highlight the lack of spectral shifting in PDTC-exchanged NC solutions. (C) B1 bleach center peak energy of CdSe-PDTC NCs in DCM as a function of pump-probe time-delay.

Exponential Fits to the B1 Bleach Shift of CdSe-Oleate and CdSe-PDTC Films

To extract time constants for the hopping prefactor (k') used in the Miller-Abrahams rate equation, the bleach shifting dynamics of both CdSe-Oleate and CdSe-PDTC films were fit to a single exponential decay (**Figure 4.8**). These fits yield time constants of 353 ps and 402 fs for CdSe-Oleate and CdSe-PDTC films, respectively. We note an apparent three orders of magnitude increase in the rate of energy migration in this CdSe-PDTC films over CdSe-Oleate, indicating much stronger electronic coupling in the ligand-exchanged NC solid.

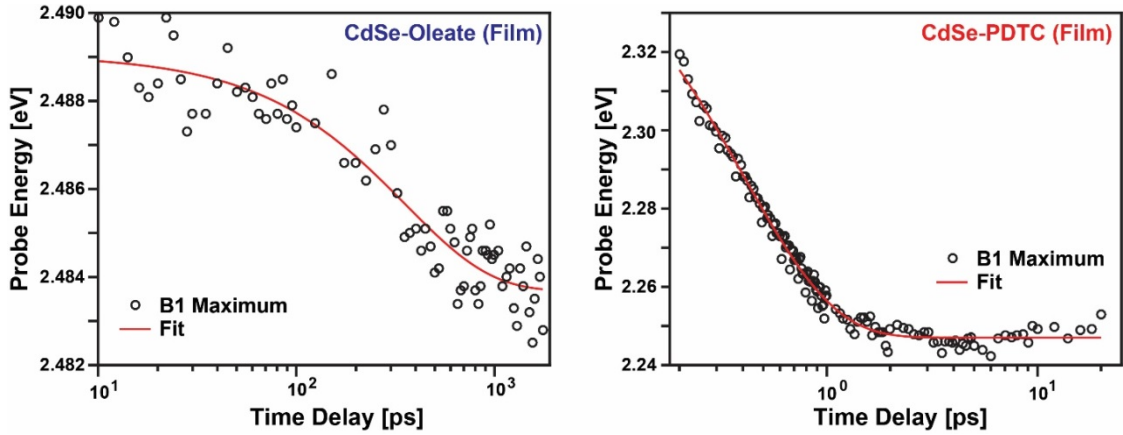


Figure 4.8: Exponential fit to bleach shifting dynamics in CdSe-Oleate (Left) and CdSe-PDTC (Right) films used to extract k' parameter for Miller-Abrahams equations.

Transient Absorption Signal Scaling with Excitation Fluence

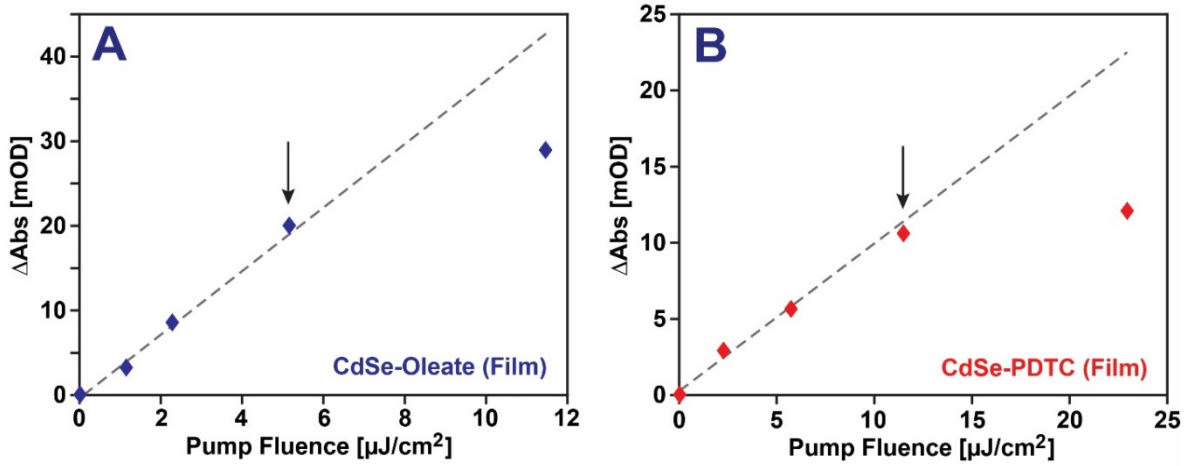


Figure 4.9: Plot of the maximum B1 band amplitude measured following excitation at 3.1 eV as a function of pump fluence for (A) CdSe-Oleate and (B) CdSe-PDTC films. Arrows denote datasets highlighted in the main text.

To suppress contributions to TA spectra from multiexciton effects, all data analyzed in this manuscript was recorded in the regime in which the TA signal amplitude scaled linearly with pump fluence. Shown in **Figure 4.9** are plots of the differential

absorbance amplitude plotted against pump fluence for both CdSe-Oleate and CdSe-PDTC films. The pump fluence employed for the data shown in the main Chapter text are indicated by the black arrows in each panel. This fluence was chosen as it falls in the linear regime of amplitude-to-fluence scaling while yielding the highest S/N ratio for analysis. Bleach shifting dynamics remained unchanged at fluences below those used for the data presented in this chapter.

Temperature-Dependent Steady-state and Transient Absorption Measurements

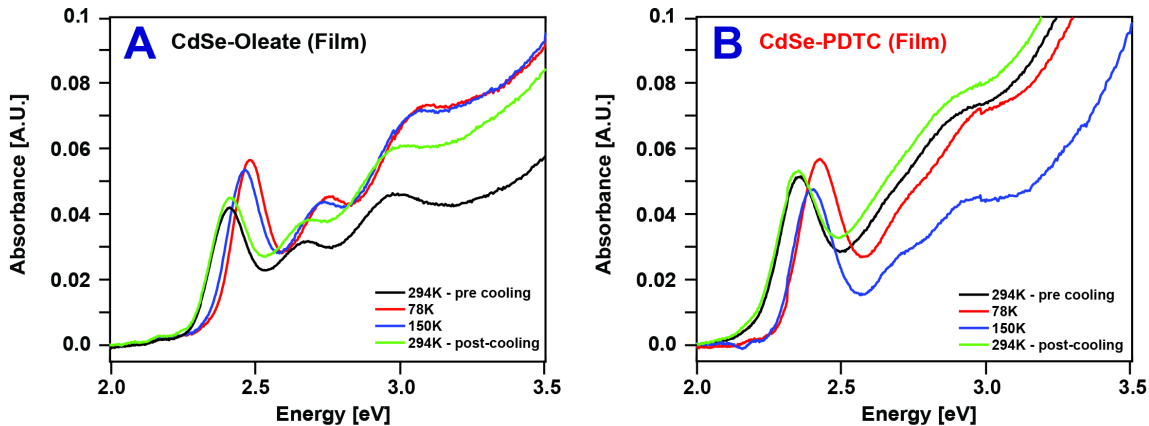


Figure 4.10: Absorption spectra of (A) CdSe-Oleate and (B) CdSe-PDTC films at 78, 150, and 294 K. The relative amplitude of spectral features, particularly at high energy, are not comparable across the series due to improper subtraction of background scatter. However, the peak of the X1 band moves to higher energy with decreasing temperature, consistent with prior work.^{42,43}

Temperature-dependent absorption spectra of CdSe-Oleate and CdSe-PDTC films were collected using a Janis ST-100 cryostat and Shimadzu UV-2600 spectrophotometer as described in the methods section of Chapter 2. Both films display a blue-shift of the X1 peak energy with decreasing temperature (**Figure 4.10**), consistent with prior reports of CdSe NCs and related nanostructures.^{42,43} This change in the energy of the X1 exciton

is reflected in the initial position of the B1 band in the transient absorption spectra highlighted in **Figure 4.6A** of the main Chapter text, which moves from 2.37 to 2.44 eV upon cooling from 294 K to 78 K.

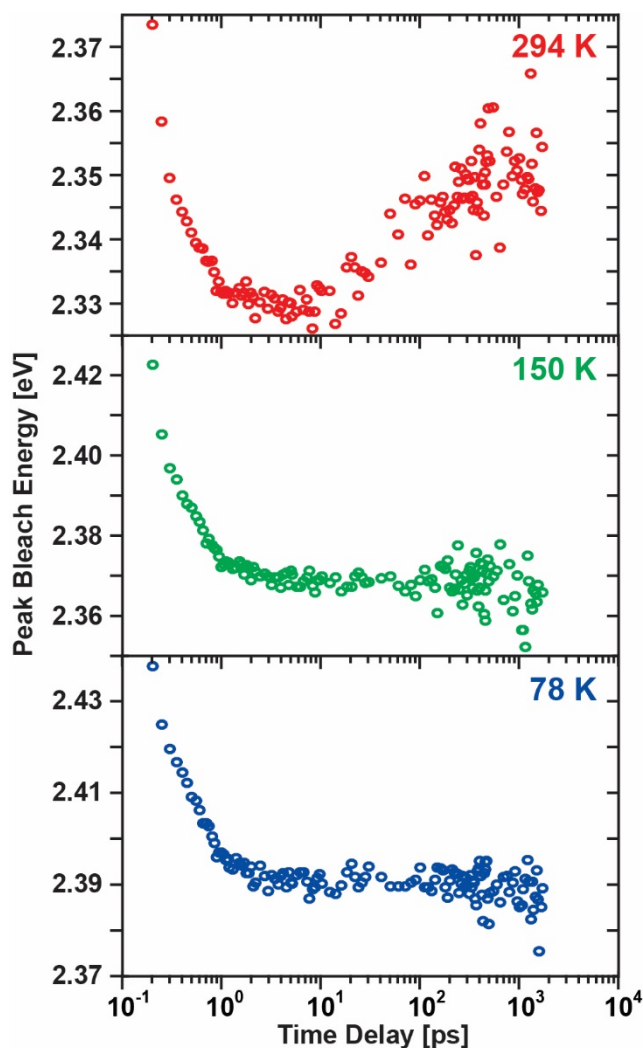


Figure 4.11: B1 bleach peak energy of a CdSe-PDTC film as a function of pump-probe time delay measured at 294 K (red, top), 150 K (green, middle), and 78 K (blue, bottom).

Traces showing time-dependent shifting of the peak of the B1 photobleach at 294 K and 78 K were highlighted in **Figure 4.6A** of the main Chapter text. For completeness, in **Figure 4.11**, we plot data recorded for an additional temperature point, 150 K. Similar

to the data measured at 78 K, we observe a decrease of the peak position of the B1 band that is largely complete within the first picosecond after photoexcitation. Blue-shifting of this band, which occurs over hundreds of picoseconds at 294 K, is suppressed at both 150 and 78 K, consistent with predictions from our KMC model as the rate of accessing low-energy sites that speed exciton recombination is slowed at low temperature. This slowing of migration to low-energy sites is reflected in a lengthening of the lifetime of the B1 photobleach with decreasing temperature (**Figure 4.12**).

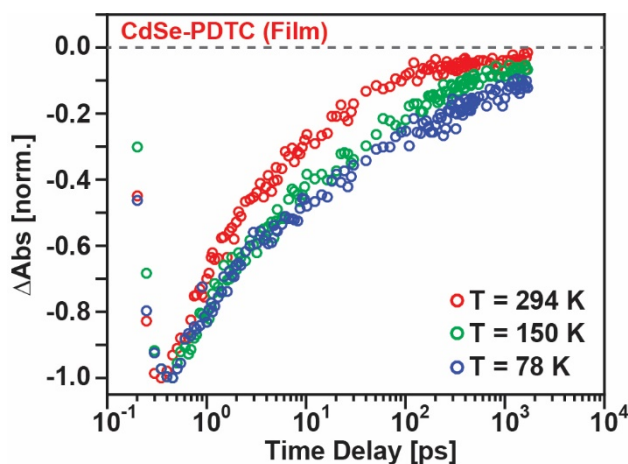


Figure 4.12: B1 bleach recovery as a function of pump-probe time delay measured for a CdSe-PDTC film at 294 K (red circles), 150 K (green circles), and 78 K (blue circles).

CdSe-PDTC Film Degradation and Spectral Changes with Increased Temperature *Temperature Dependence*

Temperature-dependent experiments were carried out using a Janis ST-100 cryostat, which was evacuated for 30 minutes prior to use. Temperatures were maintained throughout data collection using an external proportional-integral-derivative controller

and liquid N₂ dispenser.

Recent work has suggested PDTC degradation may be responsible for changes in the optical properties of CdSe NCs upon PDTC ligand exchange that have been attributed to exciton delocalization.^{45,46} On the basis of our STEM image analysis (**Figure 2.7**) and previously reported FTIR spectra⁴⁷ of PDTC-treated NC films, we conclude PDTC degradation does not occur at room temperature under the film preparation conditions we employ. However, under laser illumination such as that employed for TA, some heating of NC films is expected, which could facilitate PDTC removal and particle necking. Considering the size of our NCs, which have a radius of 1.15 nm, on the basis of CdSe's bulk heat capacity we estimate a maximum temperature rise of 27.5 K for a single NC that absorbs a 400 nm photon following carrier recombination. We note this estimate of the temperature change is an upper bound as it does not account for any thermalization of energy by the NC ligand shell or surrounding particles.

To determine if the magnitude of this temperature rise is sufficient to drive PDTC degradation, we have measured how the optical spectra of PDTC-treated films change in response to heating (**Figure 4.13**). Prior work that examined CdSe NC films containing thiol ligands demonstrated heat-induced necking between particles leads to an irreversible suppression of the NC's X1 absorption band.³⁹ As we increase the temperature of our PDTC film we indeed observe a loss of a distinct X1 band for temperatures in excess of 400 K. This is consistent with prior reports that used dithiocarbamates as sulfur precursors for core-shell NC growth as it was found that solutions needed to be heated to temperatures in excess of 410 K to drive dithiocarbamate decomposition.⁴⁰ However, for

temperatures below this value, the excitonic structure of the NCs is clearly maintained. As we estimate photon absorption will, at best, increase the temperature of a NC to ~ 320 K, we do not believe photoinduced heating is sufficient to induce necking between NCs.

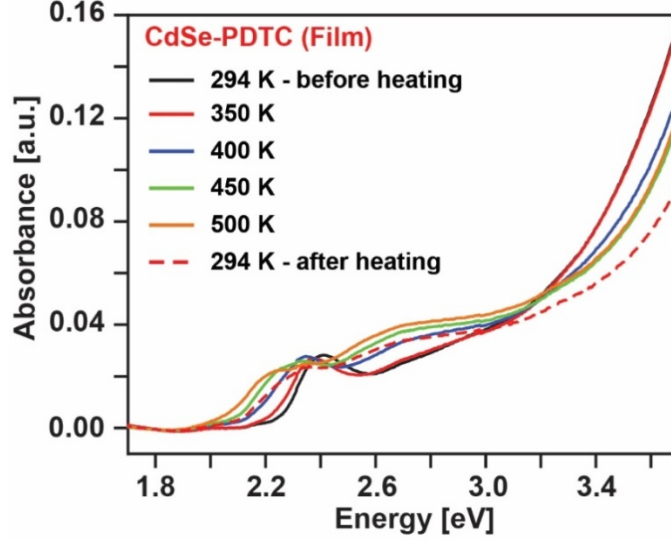


Figure 4.13: Absorption spectrum of a PDTC-functionalized CdSe film as a function of temperature. Heating the film to temperatures exceeding 400 K results in a loss of a well-defined X1 band and irreversible absorption changes that persist once the film is cooled back to room temperature (red dashed).

Kinetic Monte-Carlo Simulations

All parameters used in the KMC simulations, except for the transport rate, were directly obtained from experimental data. The mean substitution number for the PDTC exchange, $\bar{x}$, was determined by FTIR measurements of oleate loss,⁴⁷ taking into account that each PDTC molecule replaces two oleate ligands.²⁴ Using a Gaussian Fit of the emission spectrum with mean $\bar{E}_{emm}$ and standard deviation σ_{emm} , the unsubstituted exciton energy distribution's first two moments can be calculated as $\bar{\epsilon} = \bar{E}_{emm} + \frac{1}{2}\beta\sigma_{emm}^2 + \alpha\bar{x}$ and $\sigma_{\epsilon} = \sqrt{\sigma_{emm}^2 - \alpha^2\bar{x}}$. The initial energy distribution was determined directly from the

initial TA B1 bleach. The exciton decay rate enhancement per PTDC molecule, κ_D , was estimated by fitting the B1 bleach relaxation timescales for both PDTC and oleate-functionalized NC films and dividing by the average number of PDTC ligands per NC. As the decay of the B1 bleach is non-exponential for both samples, this procedure provides only a rough estimate of the exciton decay enhancement per PDTC. However, we do not expect small variations in the value of κ_D we employ to lead to large qualitative changes in the behavior our KMC model predicts.

PARAMETER	OLEATE-CAPPED PDTC-EXCHANGED	
UNSUBSTITUTED DECAY RATE (k_D^0)	$1.79 \times 10^{-3} \text{ ps}^{-1}$	
DECAY RATE ENHANCEMENT PER LIGAND (κ_D)	$1.92 \times 10^{-3} \text{ ps}^{-1}$	
RED-SHIFT PER LIGAND (α)	-3.46 meV	
TEMPERATURE (T)	298 K	
UNSUBSTITUTED ENERGY MEAN ($\bar{\epsilon}$)	2.459 eV	2.448 eV
UNSUBSTITUTED ENERGY STANDARD DEVIATION (σ_ϵ)	52.28 meV	67.60 meV
INITIAL ENERGY MEAN ($\bar{E}_0$)	2.510 eV	2.342 eV
INITIAL ENERGY STANDARD DISTRIBUTION (σ_0)	70.5 meV	142.2 meV
MEAN PDTC SUBSTITUTION ($\bar{x}$)	0	24
TRANSPORT RATE (k_T)	$6.7 \times 10^{-5} \text{ ps}^{-1}$	4.6 ps^{-1}

Table 4.1: Summary of KMC simulation parameters used to produce **Figure 4.5** in the main text.

Parameters used to produce the data shown in **Figure 4.5** of the main text are summarized in **Table 4.1**. For each trajectory, a new lattice is realized where each site's unsubstituted energy and PDTC substitution are drawn from a Gaussian and Poissonian distribution respectively. The energy distribution is then sampled using a rejection algorithm. That is, a random site is first selected by uniformly sampling the sites of the lattice. This site is then rejected, as a function of its overall energy, E , with probability $P_{reject}(E) = 1 - P_0(E)/P(E)$ where $P(E)$ is the overall site energy distribution and $P_0(E)$ is the initial energy distribution, obtained from the TA B1 bleach. Each trajectory is then propagated using a standard rejection-free kinetic Monte-Carlo (rf-KMC) algorithm (**Scheme 4.1**) with Miller-Abrahams transition rates.

1. Determine the list of the N_i outcomes $\{j\}$ of the current state i . This is comprised of the transitions to the nearest neighbors of state i and excitation decay.
2. Calculate the Miller-Abrahams rates $k_{i \rightarrow j}$ for the $i \rightarrow j$ transitions using Eq. 1.
3. Calculate the cumulative transition probability function: $K_{i \rightarrow \alpha} = \sum_{\beta=1}^{\alpha} k_{i \rightarrow \beta} / \sum_{\beta=1}^{N_i} k_{i \rightarrow \beta}$.
4. Draw a uniformly distributed random number $u \in (0,1]$.
5. Select the outcome i' such that $K_{i \rightarrow i'-1} < u < K_{i \rightarrow i'}$.
6. Draw another uniformly distributed random number $u' \in (0,1]$.
7. Update the time $t \rightarrow t + \Delta t$ by incrementing by waiting time $\Delta t = \ln\left(\frac{1}{u'}\right) / \sum_{\beta=1}^{N_i} k_{i \rightarrow \beta}$.
8. Return to step 1 until a decay event is selected.

Scheme 4.1: rf-KMC algorithm used to propagate energy transport trajectories

Energy and RMSD statistics were then collected for 1,000,000 trajectories under each set of conditions and combined to compute the mean energy and RMSD time series in **Figure 4.5** of the main Chapter text.

As discussed in the main Chapter text, the blue-shift of the average energy of the excited NC ensemble occurs due to preferential decay of excitons at low-energy sites featuring a high level of PDTC-substitution. This presents a challenge in reproducing the blue-shift in some regimes, particularly those where it is preceded by a red-shift, as the energy back-shift occurs as most trajectories decay. In particular, for the case of the PDTC exchanged films the back-shift occurs on time-scales of ~ 100 s to 1000 s of picoseconds, while excitations decay on the order of tens of picoseconds. This is shown in **Figure 4.14** where a blue-shift begins to appear for an ensemble of trajectories at delays of ~ 100 - 200 ps while the excitation half-life is ~ 25 ps. Practically, this leads to a small sample of trajectories surviving to later times when the blue back shift appears and consequently a significant increase in noise that cannot be feasibly mitigated.

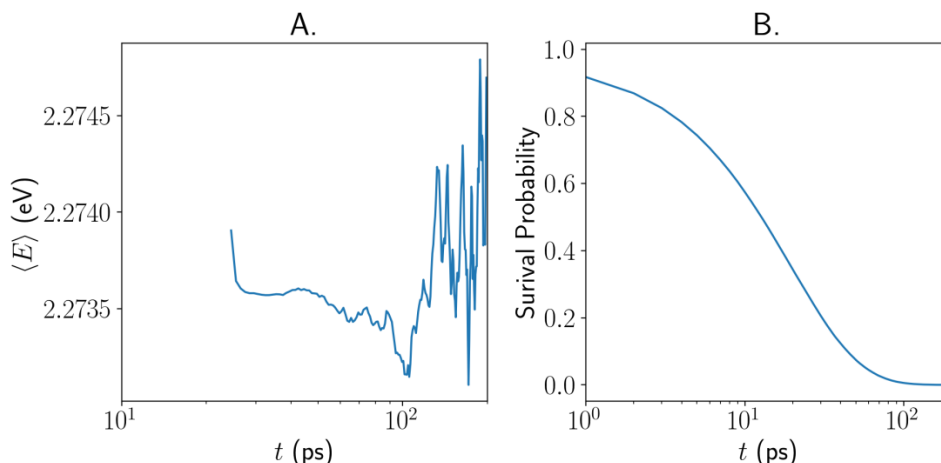


Figure 4.14: The mean energy (A) and survival probability (B) of excitations in PDTC-exchanged NC films. Results were obtained from 7,000,000 trajectories with a 25 ps moving average applied.

As such, we have conducted a parameter sweep wherein parameters such as the PDTC-induced decay rate were artificially enhanced to make this blue-shifting behavior more apparent at short delay times to determine if our KMC model correctly predicts this experimentally-measured behavior (**Figure 4.15**).

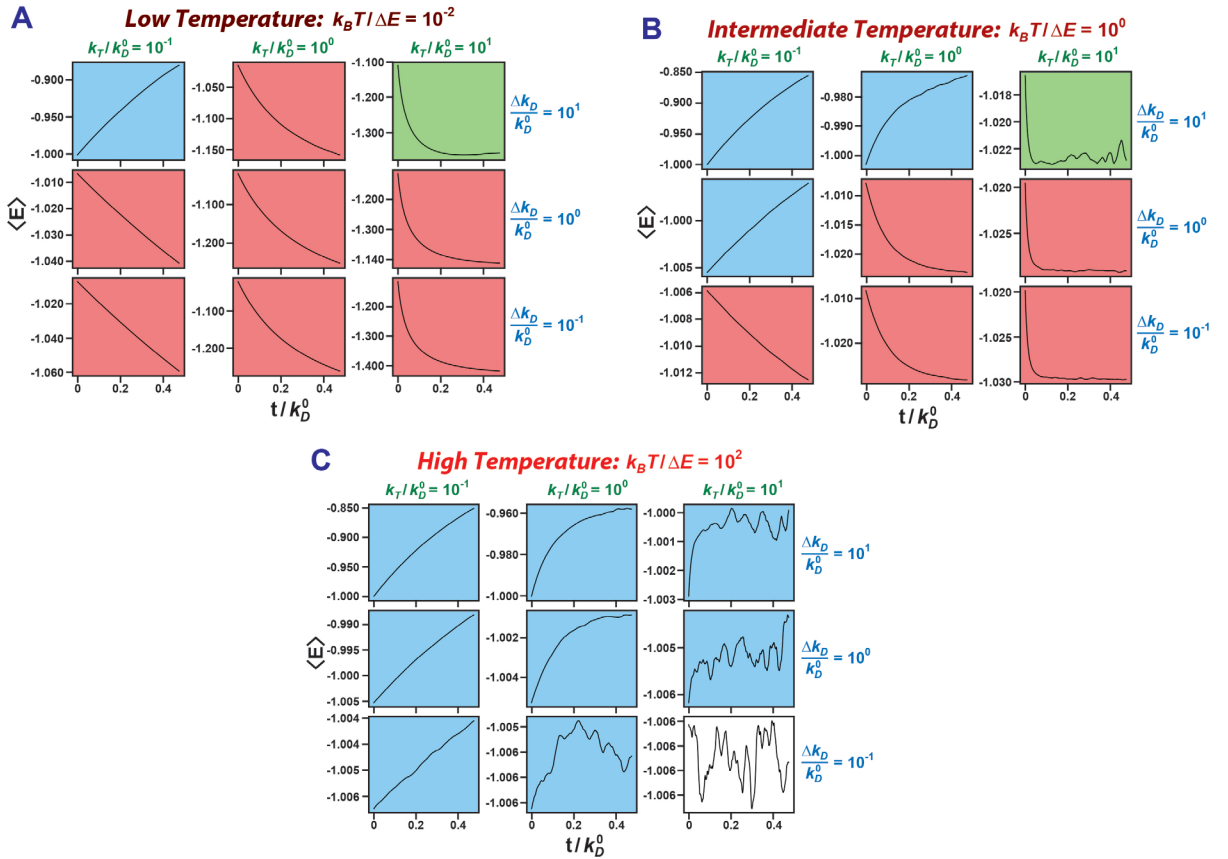


Figure 4.15: Parameter sweep of KMC simulations showing time-dependent mean energy as a function of temperature, transport rate and ligand-induced decay rate enhancement. Plots highlighted in red show only a red-shift while those in blue show only a blue-shift. Green highlighted plots show an initial red-shift followed by a subsequent blue back-shift.

In this sweep, we explore how the average energy of an ensemble of trajectories changes when the exciton transport rate (k_T), PDTC-induced decay rate enhancement

(κ_D) , and temperature (T) are varied. This sweep reveals that at low transport rates, very little red-shift is observed while higher transport rates give an increasing red-shift, eventually saturating at thermal equilibrium. Similarly, increasing the decay rate enhancement increases the rate and magnitude of the observed blue-shift. Furthermore, comparing systems with the same transport rate and increasing decay-rate enhancement shows a decrease in the magnitude of the observed red-shift, illustrating the competition between the two mechanisms. As the temperature increases, the red-shift magnitude decreases, reflecting the loss of preferential down-hill energy transport, while the blue-shift is unaffected. This leads to a total loss of the red-shift at high temperatures leaving only the blue-shift. Therefore, the mean energy displays a red-shift followed by a blue back-shift when $k_B T \lesssim \langle \Delta E \rangle$ (so that thermalization leads to a decrease in the mean energy), $k_T \gtrsim \langle \Delta k_D \rangle$ (ensuring that initial cooling is not outcompeted by the preferential decay of low energy states) and $\langle \Delta k_D \rangle > k_D^0$ (so that excitation at low-energy, highly-substituted sites decay appreciably faster than at unsubstituted sites).

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Chapter 5: Disentangling Nanocrystal Electronic Structure and Dynamics with Multidimensional Spectroscopy

5.1 INTRODUCTION

In Chapter 4 we saw phenyldithiocarbamate (PDTC) does appear to improve electronic communication between CdSe nanocrystals (NCs) as evidenced by a decrease in the average exciton energy within NC films following photoexcitation. However, our kinetic Monte-Carlo (KMC) model was unable to reproduce the blue shift of the bleach energy at long time delays we attributed to slowed exciton recombination at these higher-energy, kinetically-trapped sites. In Chapter 4 we attributed this to a sampling issue as the number of excitations that survive for hundreds of picoseconds is exceptionally low, making KMC simulations to reproduce this effect exceedingly expensive due to the need for an abnormally high number of trajectories. While this sampling issue is one potential explanation for the lack of quantitative agreement between our experiment and simulations, there are other possible reasons that could account for this discrepancy as well.

In our model we made several assumptions regarding parameters such as inter-NC separation, the distribution of PDTC across NC sites, and how PDTC impacts the energy of the NCs. While we estimated each of these parameters based on experimental data available to us, heterogeneity in the ligand exchange, such as variations in the number of ligands bound to a NC and their distribution of binding geometries, that have not been accounted for could impact all of these factors. Heterogeneity in these parameters likely plays a role in the inability of our model to reproduce the blue shift of the bleach

minimum at long time delays. For example, we assumed a Poissonian distribution of PDTC molecules where each ligand bound to the NC linearly decreases the absorption maximum of the X1 band by 3.46 meV. However, ligands bound to neighboring NC surface sites can create a nonlinear shift of the NC's absorption energy due to cooperative effects between the ligands¹ that is not currently captured in our KMC model. Heterogeneity in the spatial distribution of PDTC in the film can also affect the electron-phonon coupling and phonon density of states in the film through tuning of the NC-ligand interaction,² further altering their electronic structure in a complex manner, as we would expect sites near the surface of the film to be more highly-substituted. Finally, computational studies have shown the adsorption geometry of PDTC, such as monodentate or bidentate, is dynamic, and that changes in this binding geometry can cause fluctuations in the bandgap energy.³ Each of these processes contributes to the energetic heterogeneity of our system and further increases the complexity of the electronic structure of our films in ways that haven't been accounted for in our KMC model.

Competition between carrier cooling and exciton hopping is another potential phenomenon that could lead to the lack of agreement between our experimental data and predictions of our KMC model. Calculations carried out on PDTC-exchanged CdSe NCs have shown PDTC impacts not only hole states near the valence band (VB) edge, but also high-energy electronic states spatially separated from the conduction band (CB) edge.³ We hypothesize that by exciting excitons using these higher-energy states we could prepare excitons that are more spatially delocalized than prepared by photoexcitation at

the band edge, due to the higher degree of ligand character of these states predicted by these calculations. The ability of these high-energy excitations to access ligand-centered states could provide the basis for this non-equilibrium, ballistic type transport within the film as fast delocalization-facilitated exciton transfer could compete with electron cooling to the CB edge. Competition between these effects could lead to non-equilibrium transport tied to the excess energy of the excitation, which is not accounted for in our KMC model. One experiment to test this hypothesis is to vary the energy of the pump pulse to explore the mobility of highly excited or “hot excitons” and compare their migration dynamics to those that result when NCs are excited at their band edge, where electronic states are predicted to be more NC-centered.³

While we have focused on the impact of PDTC on NC photoexcited dynamics, more broadly, electronic heterogeneity has long been an issue in understanding NC photophysics due to the inherent size distribution of particles in a NC synthesis. While theory would predict semiconductors experiencing three-dimensional quantum confinement should display discrete, narrow, atomic-like absorption and emission spectra, a number of sources contribute to the broadened linewidths measured experimentally. Unlike molecules which are atomically precise, even the best synthetic routes typically yield NCs with a size distribution of ~3-5%.⁴ Due to the size dependent properties of NCs, this distribution yields an inhomogeneously-broadened line shape for both NC absorption and emission spectra. In this case, inhomogeneous broadening represents a *static* distribution of resonance frequencies that reflects the distribution of particle sizes in the NC ensemble, each of which contributes their own frequency to the

measured “inhomogeneous linewidth” of the sample. Ligand exchange with PDTC contributes an additional source of inhomogeneous broadening due to heterogeneity in the number of PDTC molecules exchanged. In addition the static sources of broadening, additional sources homogeneously broaden the line shape of each NC in the ensemble. Homogeneous broadening typically arises from effects such as spectral diffusion,^{5,6} exciton fine structure,^{7,8} and electron-phonon coupling.^{9,10} While techniques such as photoluminescence excitation spectroscopy,¹¹ fluorescence line narrowing,¹² and single-molecule spectroscopy^{10,13} can, in principle, separate inhomogeneous and homogeneous contributions to NC linewidths, each of these techniques has its drawbacks.

Among these techniques, perhaps the most powerful with regards to understanding NC heterogeneity is single-molecule spectroscopy as it allows for determination of inhomogeneous contributions at the single particle level.^{10,13} In single-molecule experiments, dilute NC samples are prepared, and emission spectra are collected from individual NCs. Spectra can be correlated with electron microscopy images of dilute films to build up statistics for relevant parameters of interest. For example, NC size and emission frequency are common parameters that are used to build histograms that can give information regarding the single particle contributions to a sample’s inhomogeneous linewidth. While this technique is effective, there are several drawbacks with regards to investigating our hypotheses concerning exciton migration in PDTC-treated films. First, typical single-molecule experiments measure only emission spectra due to the relative ease of detecting low signal intensities from single emitters with no background compared to measuring a small change in absorption on a large

background in a single-molecule absorption experiment. While single-molecule extinction techniques are currently available,^{14–16} the difficulty of implementing these experiments has limited their use. Additionally, these single-molecule measurements are steady-state experiments and provide no information regarding NC carrier dynamics. Finally, the use of dilute films of NCs isolated in an inert matrix, required to ensure single particle statistics for understanding sample heterogeneity, eliminates the type of coupling interactions that we are interested in distinguishing in our experiments. These factors limit the utility of single molecule spectroscopy in addressing our particular set of hypotheses for how EDLs impact exciton migration in NC solids.

To evaluate our hypotheses concerning exciton transport, we need an experiment that can address both the issue of sample heterogeneity and the excitation energy dependence of transport within PDTC-exchanged NC solids. One experiment capable of answering each of these questions is two-dimensional electronic spectroscopy (2DES). In a 2DES experiment, spectral information is encoded along two axes – excitation and emission – allowing one to disentangle effects such as energy transfer,¹⁷ electronic coupling between quantum states,^{18,19} spectral diffusion,²⁰ and homogeneous and inhomogeneous broadening of absorption lineshapes,^{21–24} each of which are often inaccessible in more traditional techniques such as absorption spectroscopy or TA. By resolving the frequencies initially excited within a sample and watching how they evolve in time, we can directly visualize energy flow from one excited chromophore to another.

A major advantage provided by 2DES is the ability to measure electronic coupling and energy transfer as an optical technique. Typically, enhanced electronic

coupling is measured through improved mobility or electrical measurements, most of which require fabrication of NC-based devices, such as field-effect transistors^{25,26} or photovoltaic cells.^{27,28} However, these measurements are highly sensitive to the presence of defects, effective formation of electrical contacts, and other factors that are indicative of the ability to engineer high-quality devices rather than the actual coupling strength present in a NC film.^{29–31} Optical techniques, such as 2DES, can probe the underlying physics of electronic motion in NC films, circumventing these device engineering challenges. This allows us to understand, at a fundamental level, the properties that govern energy transport in close-packed, ordered NC solids, as well as to directly visualize the impact of ligand exchange on film electronic structure.

2DES has been used to study a variety of chromophores including photosynthetic light-harvesting centers in chlorophyll,^{32–35} dye molecules,^{36–38} and more recently colloidal NCs.^{18,19,21,39,40} It has proven particularly useful in this last class of materials as they exhibit highly-complex electronic structure. For example, Engel and Scholes were able to show that X1 and X2 excitons in CdSe NCs are strongly coupled through the shared $1S_{(e)}$ CB state, which confirmed theory predictions for CdSe NC electronic structure.^{18,19} Others have focused on contributions of electron-phonon coupling to homogeneous linewidths and compared these values for zinc-blende and wurtzite CdSe NC structures of various diameters.⁴¹ Other studies have attempted to characterize the structure of biexcitons in colloidal CdSe NCs.^{22,24,39} While the reports above have been helpful in determining NC electronic structure, all of these reports have focused on interrogating the electronic structure of isolated, colloidal NCs while none have

attempted to characterize coupling and energy transfer in solids. As reports have shown, electronic structure in these materials is drastically altered when processed into high-quality, extended solids as there is potential for mini-band formation.^{26,42} To our knowledge, this study is the first attempt to use 2DES to characterize long-range interactions in NC solids.

In this study we use 2DES to quantify changes in NC electronic structure and dynamics due to exchanging native oleate ligands for PDTC in both colloidal NC solutions and NC films. Upon exchange with PDTC in solution we observe a fast broadening of the antidiagonal linewidth of the CdSe X1 band that we attribute to spectral diffusion due to band gap fluctuations from PDTC ligand motion that is not seen in PDTC-exchanged NC films. However in NC films, a slower timescale for this broadening is observed that we attribute to a net decrease of the average exciton energy as a function of the waiting period, T . The broadening in this case is assigned to exciton migration within NC solids. This is the first report of 2DES confirming improved electronic coupling in NC solids through the use of ligand exchange with an exciton-delocalizing ligand (EDL).

5.2 TWO-DIMENSIONAL ELECTRONIC SPECTROSCOPY

2DES is an extension of conventional TA spectroscopy where signal dependence on the frequency at which a sample is initially excited is resolved. This is done by creating a pair of excitation pulses and scanning the delay between them, called the “coherence period” (τ_1), shown in **Figure 5.1**. By scanning the excitation pulses in time,

interference between the frequencies within each pulse is varied, creating a unique excitation spectrum at each time delay that allows for the reconstruction of dynamics that stem from each frequency within the spectrum of each excitation pulse. Following this coherence period, a broadband white light pulse interacts with the sample at time delay “T” acting as the experimental “probe”. Finally, the signal is radiated during the τ_3 period and its interference with the probe pulse is detected. For a given T, or “waiting period,” which is analogous to the time delay in TA spectroscopy, we obtain the excitation frequency axis, ω_1 , by Fourier transforming the signal measured by scanning τ_1 , while the detection frequency axis, ω_3 , is provided by spectrally dispersing the transmitted probe and emitted signal in a spectrometer.

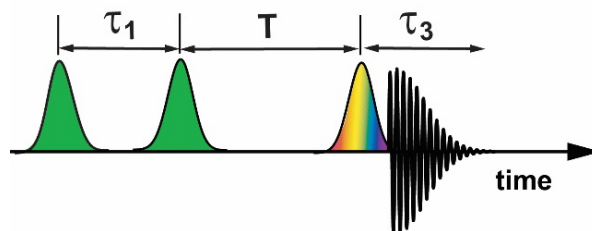


Figure 5.1: Pulse sequence for 2D electronic spectroscopy (2DES)

These 2D spectra allow us to disentangle complex spectral features that are obscured in other experiments by allowing for correlation of the initial frequency excited by the pump pulse (ω_1) with the spectral changes it induces (ω_3) at time T. Several processes that 2DES can distinguish are illustrated in **Figure 5.2**. Using 2DES one can separate contributions from homogeneous and inhomogeneous broadening to a measured

lineshape based on the diagonal and antidiagonal peak widths, respectively (**Figure 5.2A**).

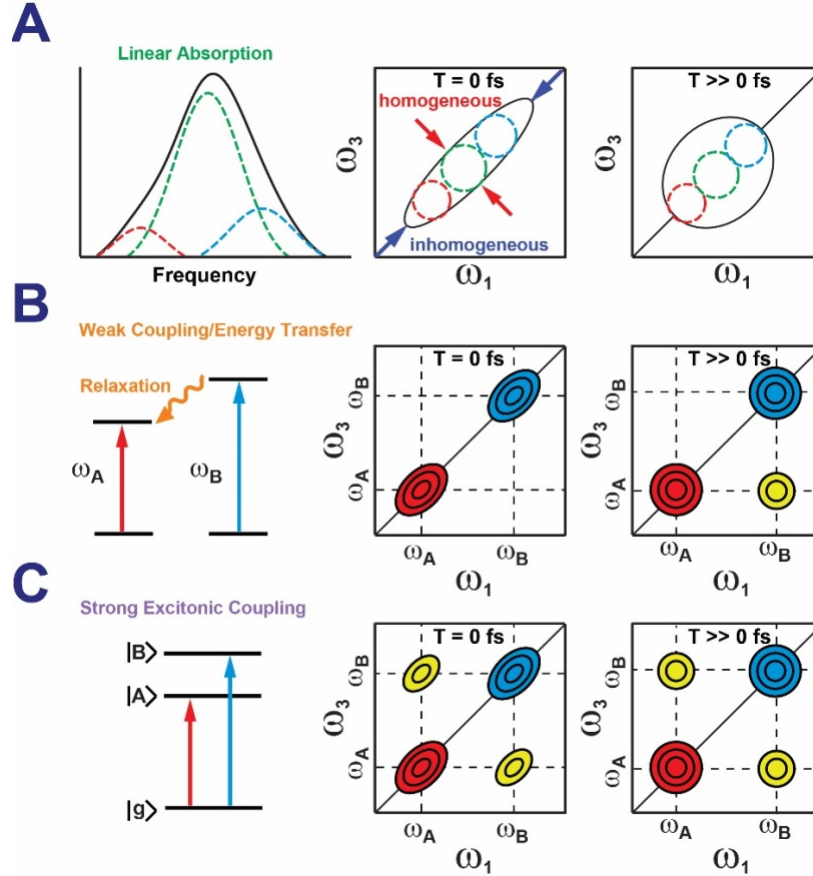


Figure 5.2: (A) Cartoon depicting the absorption lineshape of an inhomogeneously broadened system (left) and corresponding 2D spectra (right). The $T = 0$ fs spectrum shows the degree to which the linear absorption is inhomogeneously broadened while the $T \gg 0$ fs displays decorrelation of the excitation and detection frequencies due to spectral diffusion. (B) Energy level diagram (left) and 2D spectra (right) depicting energy transfer in a weakly-coupled system. The $T = 0$ fs spectrum shows no cross peaks while the $T \gg 0$ fs shows a cross peak below the diagonal, meaning that energy excited at ω_B has been detected at ω_A , indicating energy transfer between the two transitions. (C) Energy level diagram and 2D spectra for a strongly-coupled system in which the transitions share a common ground state, $|g\rangle$. This strong coupling is indicated by the appearance of symmetric cross peaks at $T = 0$ fs.

Additionally, the appearance of cross peaks, or broadened spectra, below the diagonal axis of a 2D spectrum can signal energy migration within the system as the frequency at which the system is initially excited, ω_B , is later detected at a lower energy, ω_A , indicating energy transfer (**Figure 5.2B**). One can also identify strongly-coupled states that share a common electronic state from the appearance of symmetric cross peaks about the diagonal axis of a 2D spectrum (**Figure 5.2C**).³⁴

Figure 5.3 shows a representative 2DES spectrum of colloidal oleate-terminated CdSe NCs (left) collected using our spectrometer, and a corresponding frequency-resolved pump-probe spectrum (right) at a time delay, T , of 25 ps. The result of a 2DES experiment is the same as a TA experiment, however with spectrally resolved information regarding the excitation axis. For example, if we take a slice along $\omega_{\text{pump}} = 2.30$ eV we obtain the TA spectrum highlighted in purple. This can be interpreted as the resulting TA spectrum if the sample was excited with a single frequency of $\omega_{\text{pump}} = 2.30$ eV at a time delay of $T = 25$ ps. In a traditional TA experiment the data obtained is an average over the ω_{pump} axis. This additional spectral dimension allows one to understand how frequencies across bandwidth of the excitation pulse evolve with time, allowing us to extract inhomogeneous and homogeneous linewidths, energy transfer, and electronic coupling which are obscured in TA. For the remainder of this work the analysis and discussion will focus on evolution of the B1 band, highlighted in **Figure 5.3** in the red box, as this feature reports on the average energy of excitations within the NCs in the sample.

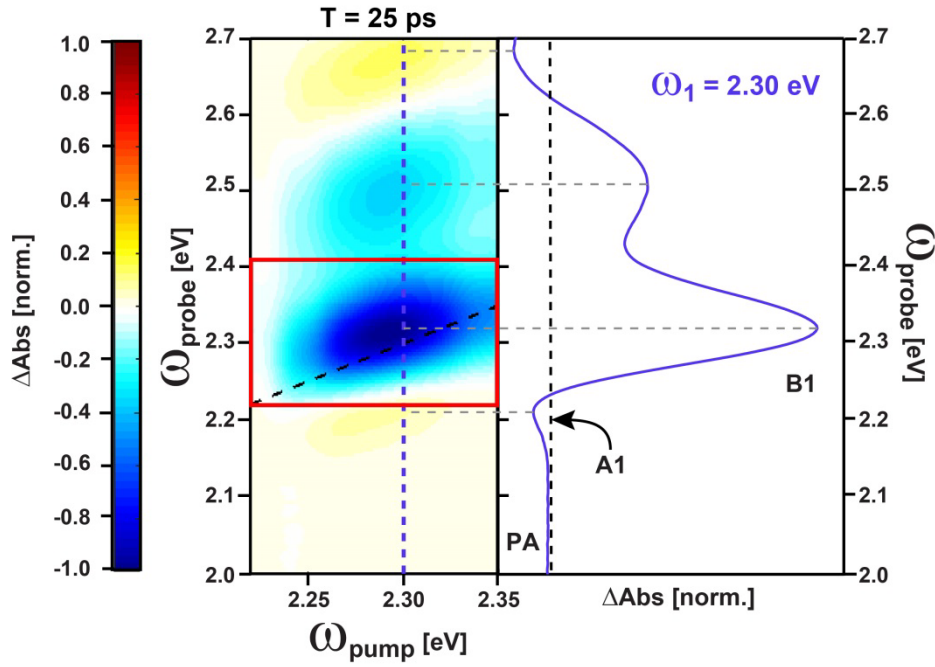


Figure 5.3: 2DES spectrum of CdSe NCs terminated with oleate ligands (left). B1 band used for analysis is highlighted (red box). Slice shown at $\omega_{\text{pump}} = 2.30$ eV (dashed purple) and corresponding frequency resolved pump-probe spectrum (solid purple, right).

Experimentally, we have implemented 2DES using a home-built noncollinear optical parametric amplifier (NOPA), described elsewhere (**Section 3.2**), and an acousto-optic programmable dispersive filter (AOPDF) based-pulse shaper (Fastlite Dazzler). The pulse shaper is used to create the phase-locked excitation pulse pair that allows for execution of the 2DES experiment by applying RF waveforms to a TeO_2 crystal to create a programmable diffraction grating. This gives the user precise control over the frequency, bandwidth, amplitude, and phase of the pulse pair used to excite the sample. This precise control allows us to implement a number of signal-enhancing detection schemes such as phase cycling,⁴³ which improves the signal-to-noise ratio by eliminating

spurious background signals, and rotating frame detection, which improves data collection efficiency by allowing for undersampling of the detected signal by multiplying it by a known reference frequency.⁴³ Using these techniques, we integrated a functioning 2DES spectrometer into our existing TA setup with relative ease.

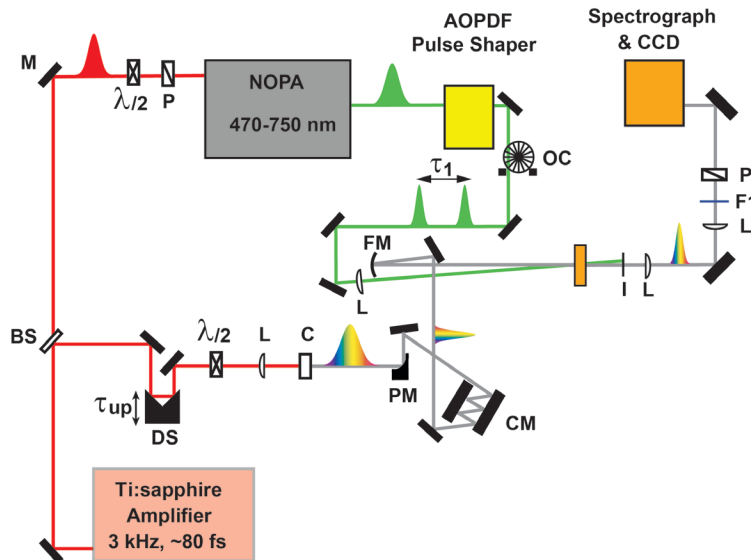


Figure 5.4: Setup depicting our 2DES spectrometer employing a pump-probe geometry. Abbreviations are as follows (BS) beam splitter, (M) mirror, (DS) delay stage, ($\lambda/2$) half-wave plate, (L) lens ($f=15, 25$ cm), (C) c-cut sapphire, (PM) parabolic mirror, (CM) chirped mirror compressor, (FM) focusing mirror ($f = 25$ cm), (I) iris, (F1) 0° angle of incidence 800nm HR mirror, (P) polarizer, (OC) optical chopper.

Figure 5.4 displays a representative diagram of our 2D spectrometer. Briefly, a femtosecond Ti:sapphire regenerative amplifier (Coherent Legend Duo Elite, 3 kHz, 4.5 mJ) generated ~ 90 fs pulses centered at 804 nm with a bandwidth of 160 cm^{-1} (FWHM). A small portion of the amplifier output ($\sim 1 \text{ } \mu\text{J}$) was focused into a 3 mm thick c-cut sapphire window to produce broadband probe pulses (470 - 780 nm) via self-phase modulation. The probe pulse was temporally compressed from 480 - 640 nm using a pair of chirped mirrors (LAYERTEC chirped mirror pair 109811) to a FWHM of less than 60

fs across the shaped spectral range. Tunable pump pulses (535 - 547 nm center wavelength) were generated using a home-built NOPA. Broadband pulses produced by the NOPA were temporally compressed to less than 20 fs, as measured via frequency resolved optical gating (FROG), and spectrally narrowed to ~ 40 nm bandwidth (FWHM) about the center wavelength using a Fastlite Dazzler AOPDF Pulse Shaper. The Dazzler was also used to produce the excitation pulse pair using Labview controlled software. For the spectra displayed in **Figure 5.6, 5.7, and 5.8** the τ_1 delay was scanned from 0 to 150 fs in 2 fs steps, and signals with 0, $2\pi/3$, and $4\pi/3$ relative phases were collected under a rotating frame where $\omega_{\text{rot}} = 2500 \text{ cm}^{-1}$. For colloidal solutions, all samples were diluted in a 1 mm path length cuvette and stirred vigorously throughout data collection. Wavelength dependent instrument response functions (IRFs) for each scan were obtained using a 1 mm path length cuvette filled with DCM. Collection of frequency-dependent IRFs allowed for chirp correction of the supercontinuum probe pulse. A rotation mount (Thorlabs KPRM1E) was used to continuously rotate NC films at a rate of 25 degrees/s throughout data collection to prevent charging effects. Frequency dependent instrument response functions for each scan were obtained using a cleaned SiO_2 substrate. Collection of frequency-dependent IRFs allowed for chirp correction of the supercontinuum probe pulse.

5.3 ELECTRONIC STRUCTURE OF LIGAND EXCHANGED NANOCRYSTALS

In this section we use 2DES to compare the electronic structure of NCs before and after PDTC ligand exchange. NCs were synthesized using previously described methods

to yield high-quality size and shape uniform NCs.⁴ These high-quality NCs aid in the formation of long-range ordered solids, as shown previously.^{26,42,44} This is important as the close proximity of these NCs can impact inter-NC coupling of electronic states when compared to NCs in solution, where both insulating ligands and solvent molecules can prevent this coupling. This inter-NC coupling can aid in exciton transport within the film and serve as the basis for mini-band formation.²⁶

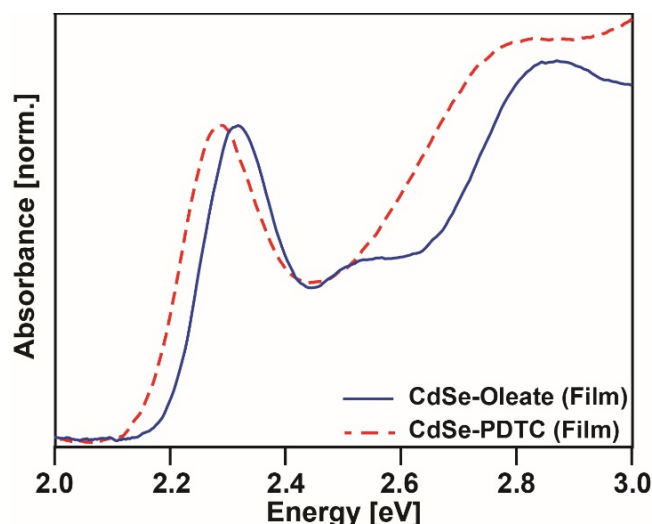


Figure 5.5: Normalized absorption spectra of CdSe-oleate (blue) and CdSe-PDTC (dashed red) film.

Figure 5.5 plots absorption spectra of representative oleate-capped and PDTC exchanged NCs used for this study. There are observable differences in the steady-state absorption spectra including a ~ 35 meV redshift, and broadening of the X1 band of the PDTC-exchanged film relative to the oleate-capped case. This indicates changes in the electronic structure of these samples due to the presence of the PDTC ligand. As described previously, these spectral changes can likely be attributed to a combination of relaxation of quantum confinement and formation of new states formed between NCs due

to increased electronic coupling, which we have shown previously in the form of improved transport (see Chapter 4).⁴⁴ We note that relative to ligand exchanges shown in Chapter 4, the redshift upon PDTC treatment is smaller. We attribute this effect to the use of NCs with larger diameters (2.3 vs 2.8 nm) for this study. As the size of the NC increases, the energetic gap between the VB states and PDTC HOMO increases, which in turn decreases the amount of energetic overlap between them.⁴⁵ Thus, the confinement energy of larger NCs is not impacted as strongly as smaller particles.

2DES Analysis of Colloidal Nanocrystal Solutions

We use 2DES to visualize changes in the electronic structure of our NCs and to test our hypothesis regarding how ligand exchange with PDTC impacts inhomogeneous and homogeneous contributions to the system's absorption lineshape, as separating these contributions is not possible using ground-state absorption spectra alone. Shown in **Figure 5.6A** are 2D spectra displaying the X1 band of oleate-capped and PDTC-exchanged NC suspensions at $T = 25$ ps. Looking at the two spectra we notice several differences. First, the inhomogeneous linewidth along the diagonal is broader for the PDTC-exchanged solution than the CdSe-oleate solution. This is consistent with our prediction that ligand exchange with PDTC introduces energetic disorder into the system based on the distribution of these ligands throughout the NC ensemble. More interestingly, however, we notice that the antidiagonal linewidth is also larger in the ligand-exchanged case, corresponding to an increase in the contribution from homogeneous broadening of about 30 meV (**Figure 5.6B**). There are several different effects that could account for this broadening: (1) alteration of exciton-fine structure due

to hybrid orbital formation between NC VB states and PDTC's HOMO; (2) increased exciton-phonon coupling due to changes in the phonon modes of the NC upon binding of PDTC; or (3) spectral diffusion due to bandgap energy fluctuations from ligand motions on the NC surface.

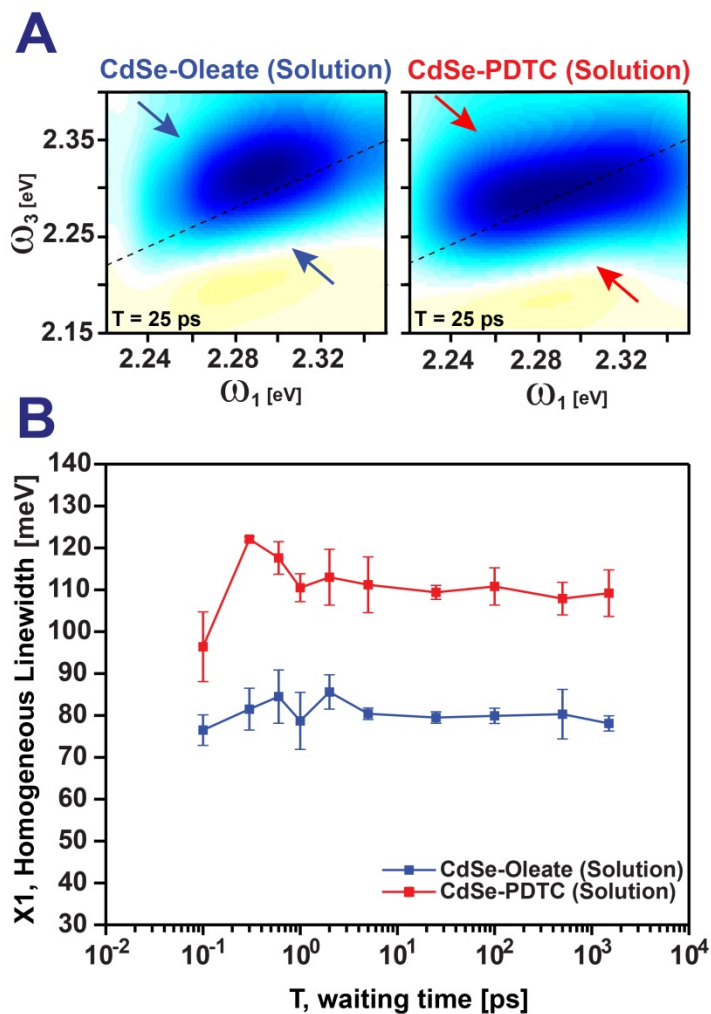


Figure 5.6: (A) Normalized 2DES spectra of the X1 band of CdSe-oleate (left) and CdSe-PDTC (right) solutions at $T = 25$ ps highlighting changes in the antidiagonal linewidth. (B) FWHM values for a Lorentzian fit to the antidiagonal linewidth of CdSe-oleate (blue squares) and CdSe-PDTC (red squares) solutions as a function of waiting time, T .

While the first two scenarios should maintain a relatively constant contribution to the homogeneous linewidth, contributions from spectral diffusion should display time-dependence over the short timescales of ligand motion as the ligands re-equilibrate following excitation and sample the available conformational space available at equilibrium. Looking at the antidiagonal linewidth as a function of T for each sample in **Figure 5.6B** we see that while the CdSe-oleate solution's linewidth doesn't appear to change over the lifetime of the experiment, the antidiagonal of the CdSe-PDTC solution initially broadens rapidly, from 95 meV to 120 meV, over 300 fs, followed by a 10 meV narrowing over 1 ps. CPMD simulations have shown that oleate ligands bound to CdSe remain relatively immobile and largely bind to the NC surface in a bidentate bridging geometry.³ In contrast, these simulations show PDTC exhibits fluxional behavior on NC surfaces, shifting from a primarily bidentate bridging geometry to a mixture of bidentate bridging, chelating, and chelating-tilted.³ These motions between different equilibrium binding geometries lead to corresponding shifts in the band gap of CdSe.³ Similar conclusions regarding the fluxional nature of PDTC were reached in a DFT study.⁴⁶ While spectral diffusion doesn't appear to play a role in homogeneously broadening the linewidth of CdSe-oleate, our data, together with these simulation results, suggests PDTC ligand motion homogeneously broadens the measured PDTC linewidth at over time. Therefore, while changes in the exciton fine structure and increased exciton-phonon coupling contribute to the *static* homogeneous linewidth of PDTC ligand-exchanged NCs we attribute the additional broadening relative to oleate-capped NC films, that grows with increasing T, to spectral diffusion due to PDTC ligand motion on the NC surface.

2DES Analysis of NC Films

While we now have an understanding of electronic structure in isolated colloidal NCs, processing them into a solid-state film can drastically alter their electronic structure. For example, both ligand vibrations and the NC phonon spectrum can be altered by constraining range of motion accessible to these degrees of freedom.⁴⁷ This should limit the amount of broadening due to spectral diffusion if ligand motion has been sterically hindered by the surrounding NC matrix. However, in a solid-state architecture we also open new mechanisms to alter NC electronic structure through both NC-NC coupling interactions and energy transfer pathways that are unavailable in solution. In particular, based on our prior work we expect ligand exchange with PDTC in a CdSe film to allow efficient energy transfer *between* NCs as evidenced by a time-depedent redshift of the photo-bleach of CdSe's lowest energy exciton absorption band.⁴⁴

Displayed in **Figure 5.7A** are 2D spectra comparing the X1 band of CdSe-oleate and CdSe-PDTC films at $T = 100$ ps. While the 2D spectrum of the CdSe-oleate film largely resembles the solution spectrum, we see distinct differences in the shape of the PDTC-exchanged film relative to the CdSe-PDTC solution spectrum. The lineshape of the X1 band in the PDTC-exchanged film is asymmetrically skewed towards lower energy about the diagonal axis, broadening the antidiagonal linewidth. This shape difference between solution and film indicates a change in the mechanism for this broadening.

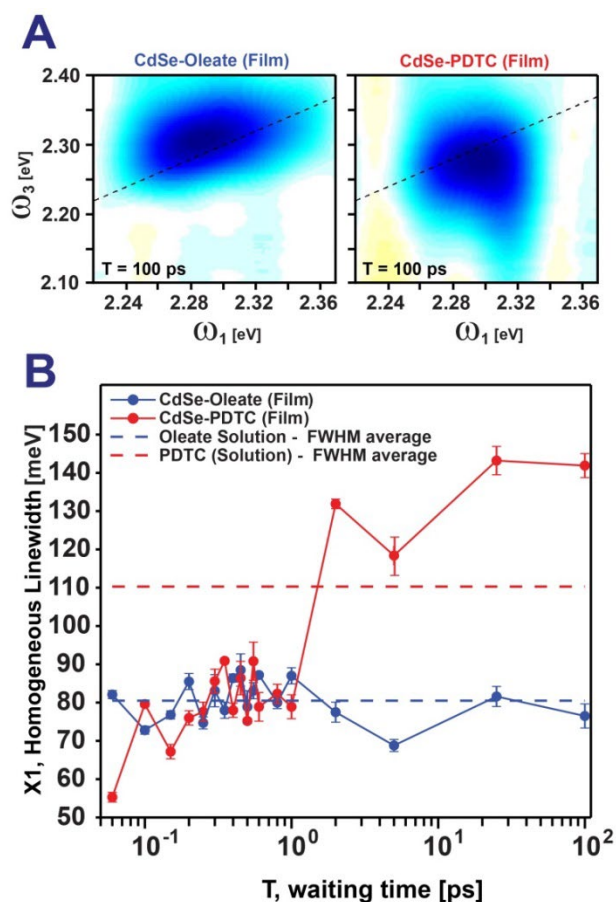


Figure 5.7: (A) Normalized 2DES spectra of the X1 band of CdSe-oleate (left) and CdSe-PDTC (right) films at $T = 100$ ps, highlighting changes in the antidiagonal linewidth. (B) FWHM values for a Lorentzian fit to the antidiagonal linewidth of CdSe-oleate (blue circles) and CdSe-PDTC (red circles) films as a function of waiting time, T . Average homogeneous linewidths for both CdSe-oleate (blue, dashed) and CdSe-PDTC (red, dashed) solutions are plotted for reference.

Plotting the antidiagonal linewidth versus waiting time (**Figure 5.7B**) gives us additional insight into the mechanism of line broadening in PDTC films, and how it differs from solution. To aid with comparing the antidiagonal linewidth for solution and film samples, we have added to **Figure 5.7B** the average antidiagonal FWHM values measured for solution samples as dashed lines. Looking at the data for CdSe-oleate, we see that the film behavior largely matches that of the colloidal sample, maintaining a

constant antidiagonal linewidth of about 80 meV as the waiting period is increased from 60 fs to 100 ps. In contrast, while both the solution-exchanged and solid-state CdSe-PDTC samples display a broadening of the antidiagonal, the timescale over which this broadening occurs is very different. Rather than being broadened from early waiting times, in films the antidiagonal of CdSe-PDTC maintains a linewidth similar to that of CdSe-oleate until a waiting time of 1 ps, after which it broadens beyond that of the solution FWHM. An explanation for the lack of broadening in PDTC films at early times is outlined above. When NCs are processed into a film changes PDTC vibrational motions that homogeneously broaden the measured line shape are altered. By creating a solid film these motions are damped due to a reduction in the range of motion which affects the homogeneously broadened linewidth.

At waiting times longer than 1 ps, where CdSe-PDTC films show significant antidiagonal broadening, it is useful to refer back to the 2D spectrum plotted in **Figure 5.7A**. The appearance of a new, asymmetric feature around $\omega_1 = 2.32$ eV and $\omega_3 = 2.15$ eV is captured in the extracted FWHM value, yet has a very different line shape than the antidiagonal of the solution spectrum. This feature is consistent with a peak arising due to energy transfer, akin what is shown in **Figure 5.2B**, where energy transfer manifests as a peak below the diagonal axis of the 2D spectrum because the absorption transition is detected at a lower energy than it was initially excited. While our cartoon depiction showed this phenomenon as a distinct, well-separated cross peak, in practice, due to heterogeneity in the NC film's energetic landscape, this process appears as an asymmetric broadening of the antidiagonal linewidth below the spectrum's diagonal axis.

Based on our prior experiments in which we observed exciton migration in PDTC-treated NC films from high to low-energy NC sites, we assign this antidiagonal broadening to similar exciton migration within the film. In **Section 5.4** we will attempt to characterize the dynamics of this energy transfer and also determine its dependence on the energy of the photons used to excite the NC film.

5.4 ENERGY DEPENDENCE OF EXCITON DYNAMICS IN PDTC-EXCHANGED NANOCRYSTAL FILMS

While understanding how ligand-exchange with PDTC impacts NC electronic structure aids our interpretation of the energetic heterogeneity in both colloidal NCs and NC films, we ultimately are interested in how these factors impact dynamics in these materials. To measure exciton dynamics in the NC films, we use a combination of TA and 2DES to understand the impact of PDTC exchange on their dynamics, but also how the initial energy of the excitations produced in these systems impacts exciton mobility as this can alter the character of the states being excited. For example, states that are highly mixed between NC and ligand-based character should exhibit more delocalizing behavior than those that are primarily NC-centered. By varying the energy of our excitation pulse we can access different initial excited states, and use the magnitude of the shift of the NC lowest energy exciton band to assess the degree to which these states exhibit mixed NC-ligand character. We predict states that display the fastest time-dependent changes in the lowest exciton band would exhibit the most hybrid character due to the ability to access more delocalized ligand states, enhancing excitonic migration.

First, we use 2DES to monitor energetic migration in both CdSe-oleate and CdSe-PDTC films when excited near the band edge exciton (X1). Based on the calculated band structures for oleate- and PDTC-capped CdSe we would expect the ligand-exchanged NC films to exhibit greater ligand contributions to the band edge states due to the proximity of PDTC's HOMO to the $1S_{3/2(h)}$ VB state.³ This enhanced ligand character of the band edge states predicted for PDTC-exchanged NCs should result an increase in energetic migration.

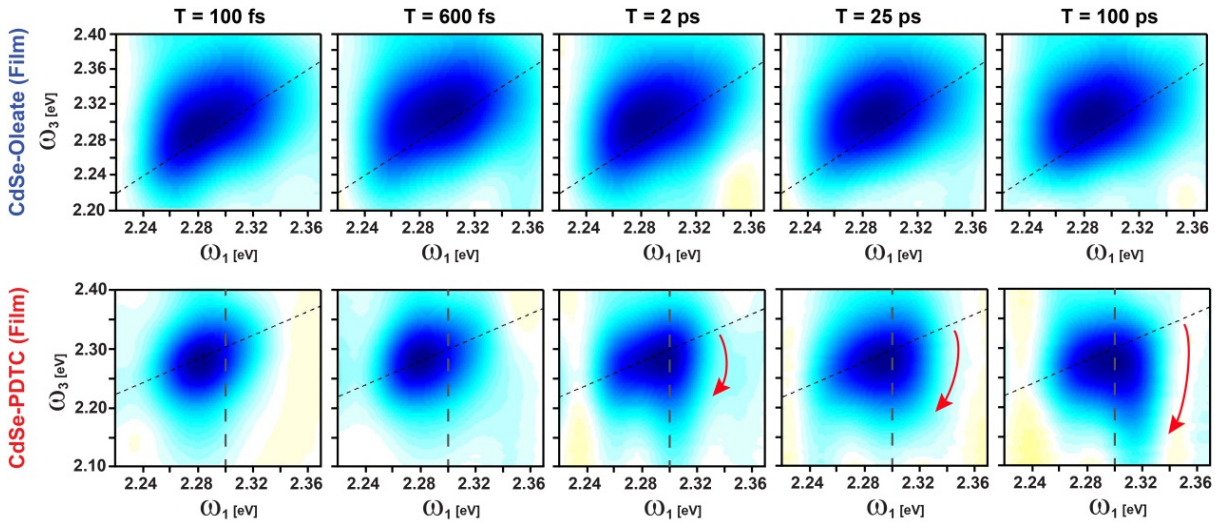


Figure 5.8: Normalized 2DES spectra of the X1 band of CdSe-oleate (top) and CdSe-PDTC (bottom) films for waiting times ranging from $T = 100$ fs to $T = 100$ ps. Red arrows highlighting changes in the antidiagonal linewidth attributed to exciton migration to low energy sites.

Figure 5.8 plots 2DES spectra of oleate-capped and PDTC-exchanged NC films as a function of the waiting time, T . Looking at the 2D spectra for the oleate-capped films in **Figure 5.8**, we see there is relatively little evolution of the lowest exciton band when the waiting period is scanned from 100 fs to 100 ps. The constant homogeneous

linewidth (**Figure 5.7B**) and the minimal change in shape of the X1 peak indicate the primary deactivation pathways for excitons in this material are a combination of charge trapping and emissive recombination of carriers as these processes should only effect the overall amplitude of the peak and not the lineshape. While the former is a non-radiative pathway and the latter radiative, they similarly contribute to a decrease in the overall bleach amplitude, as this feature reports on population of the X1 state,^{48,49} while having minimal effect on the peak positions and line shape.

Conversely, 2D spectra for PDTC-exchanged NC films show distinct changes as T is increased (**Figure 5.8, bottom**). First, we notice that the X1 peak is less diagonally elongated relative to CdSe-oleate solutions and films, as well as colloidal CdSe-PDTC samples. This lack of diagonal elongation displays the degree to which the frequencies excited in the system are correlated, or retain memory of their initial excitation energy. For example, if a system is excited at frequency " ω_A ", and detected at ω_A at some time much later, those frequencies have remained correlated, and the system is said to have a high degree of frequency memory. One can imagine a system where no external factors influence the energy of the absorbing state would retain this diagonal elongation for long periods. However, systems where the excitation can exchange energy with the bath, or experience spectral diffusion due to frequency fluctuations from vibrations or other external factors, experience decorrelation leading to a change in peak shape. In this scenario an excitation at ω_A would be detected some time later at a different frequency, ω_B due to these factors.

Analyzing the peak shape for our CdSe-PDTC spectra (**Figure 5.8, bottom**) we see that as the waiting time is increased the peak shape shifts from slightly diagonally elongated to much more round. This indicates the frequencies excited in the CdSe-PDTC film undergo rapid decorrelation. Since the amount of diagonal elongation reports on the degree of static heterogeneity in the system, we conclude that some new effect introduces *dynamic* disorder into the system. To provide insight as to a possible mechanism, it is useful to look at the symmetry of the peak shape as a function of time, which indicates growth of an asymmetric cross peak below the diagonal as T increases (**Figure 5.8, bottom**). As discussed above in **Section 5.3**, we attribute the appearance of this cross peak at $\omega_1 = 2.30$ eV and $\omega_3 = 2.15$ to exciton migration along a downhill energy gradient. Here we examine time-dependence of this energy transfer process by plotting the energy of the lowest exciton band for different sets of frequencies along the ω_1 axis as a function of the waiting period, T . This is akin to measuring the B1 band position in transient absorption spectra produced for different initial excitation frequencies (ω_1). We then perform a similar analysis to find the X1 band minimum as was used in Chapter 4 for each excitation (ω_1) value. As the energy of this feature reports on the average energy of excitons, we can use shifting of this peak to track exciton migration in the film as a function of the energy initially imparted to an exciton.

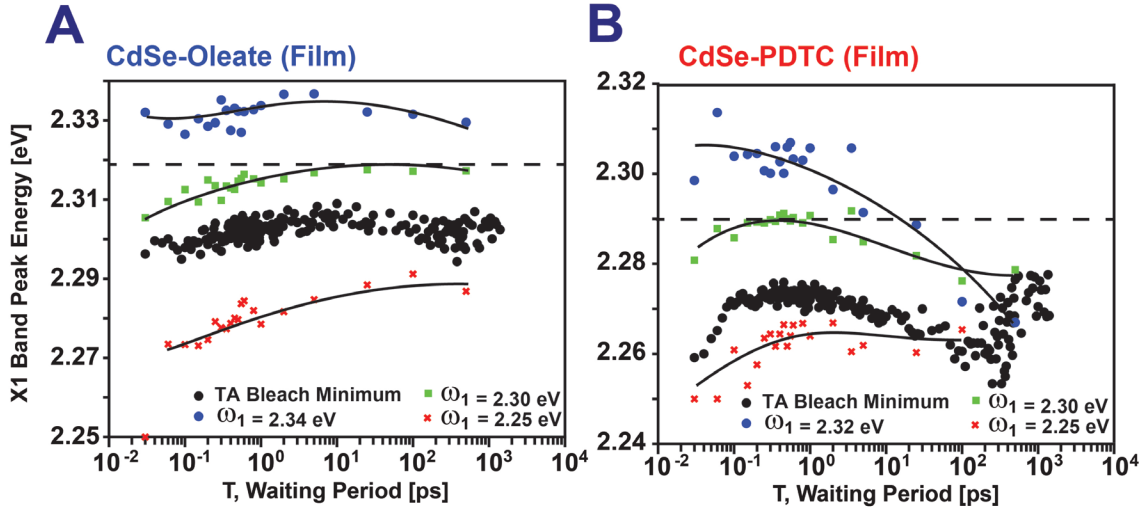


Figure 5.9: X1 band shifting data from 2DES (colored shapes) and TA spectra (black circles) for (A) CdSe-oleate and (B) CdSe-PDTC films as a function of time delay. X1 absorption max for each sample shown in black dashed.

Since the corresponding TA experiment essentially averages over the excitation-resolved information contained in the 2DES spectrum, we can compare the bleach shifting data from the two experiments and find which frequencies contribute to the overall peak shifts measured by TA. **Figure 5.9** plots the X1 band center position as a function of time delay for various ω_1 frequencies from the 2D spectra as well as TA spectra for both X1-pumped CdSe-oleate and CdSe-PDTC films. As TA spectra cannot easily resolve dynamics from specific excitation frequencies they report the average behavior of the full NC ensemble following X1 photoexcitation

In the CdSe-oleate case (**Figure 5.9A**), we see two time-dependent changes in the center position of the X1 band. First, we see a subtle blue shift of ~ 7 meV over ~ 10 ps that we previously attributed to a loss of stimulated emission that contributes to the low-energy side of the bleach line shape.⁴⁴ At longer delay times (~ 100 ps) we see a slight red

shift which we have attributed to downhill exciton migration within CdSe-oleate films over longer time scales.⁴⁴

Looking at X1 dynamics measured at specific ω_1 frequencies with 2DES, we find they reveal static heterogeneity in the ensemble that is average over in the TA spectra. The $\omega_1 = 2.25$ eV data on the red side of the X1 peak displays a blue shift with increasing T that is consistent with the loss of stimulated emission predicted by TA. As the low energy side of the line shape has the most overlap with the emission spectrum of the NC ensemble it should be most influenced by changes in the amplitude of the stimulated emission. The ω_1 frequencies on the high energy side of the bleach ($\omega_1 = 2.30$ eV and $\omega_1 = 2.34$ eV) also display a slight blue shift due to the loss of stimulated emission, however at long times they display the red shift that is in agreement with higher energy excitations of smaller NCs in the ensemble, migrating towards lower energy sites in the lattice, as we have predicted. Importantly our data shows that the amount of migration that has occurred by 500 ps, the longest T value we have measured, is minimal as dynamics initiated at different initial frequencies have not relaxed to band center.

The X1 bleach dynamics captured by TA for the CdSe-PDTC film (**Figure 5.9B, black**) display many similar features seen in the CdSe-oleate data. However the timescales and magnitudes of the X1 time-dependent shift have changed. The initial blue shift, signaling the loss of stimulated emission, is much faster relative to CdSe-oleate, which is consistent with both decreased fluorescence lifetimes⁵⁰ and quantum yields^{44,50} upon treatment with PDTC due to the formation of trap states induced by ligand exchange. The redshift seen in the CdSe-oleate data is also seen in the ligand-exchanged

film. However, the rate and magnitude of the shift have increased. This is consistent with previous predictions that (1) the ligand exchange increases energetic heterogeneity⁴⁴ and (2) the band edge states of the CdSe-PDTC film experience enhanced spatial delocalization relative to CdSe-oleate due to their mixed NC-ligand character, facilitating inter-NC exciton transfer.^{3,44,50,51} The increased heterogeneity leads to a larger magnitude of the X1 bleach shift by increasing the distribution of the average energy of X1 states in the NC ensemble, while the partial hybridization of the NC and PDTC ligand states leads to an increase in the exciton migration rate by decreasing the energetic barrier for inter-NC exciton transfer at the NC-ligand interface. Finally, the X1 blue shift at $T > 100$ ps has been observed previously⁴⁴ and was discussed in Chapter 4. Briefly, highly PDTC-substituted lattice sites with lower X1 energies experience enhanced exciton decay rates^{44,50,52} due to an increase in the density of states near their band edge relative to CdSe-oleate. Therefore the average X1 energy at long times increases as less-substituted PDTC sites dominate transient spectra as they represent the largest fraction of the surviving excitations.

Moving to the X1 bleach minimum plots of the ω_1 slices from 2DES spectra, we again see that ω_1 frequencies to the red ($\omega_1 = 2.25$ eV) of the NC ensemble average display a blue shift at early times corresponding to a fast loss of stimulated emission. On the high-energy side of the TA bleach ($\omega_1 = 2.30$ eV and $\omega_1 = 2.34$ eV) we observe a red shift of the X1 energy as the higher-energy excitations in the ensemble funnel to lower energy sites within the film. While the energetic red shifts in the CdSe-oleate film were relatively small (< 10 meV) and occurred over hundreds of picoseconds, we see much

faster downhill shifting over a larger energetic scale in the ligand-exchanged films. At the highest energy ω_1 frequency plotted ($\omega_1 = 2.32$ eV), we see a downhill shift of nearly 40 meV within 100 ps, while lower the energy excitation ($\omega_1 = 2.30$ eV) leads to a more moderate shift, ~ 20 meV, over the same timescale.

While this data provides support for our hypothesis that exciton mobility in PDTC-exchanged films depends on the initial energy of the excitation, we can more rigorously test this theory by further varying the energy of the pump pulse. Calculations have predicted that PDTC affects not only VB states near the band edge, but also higher-energy CB states further from the NC bandedge.³ Excitation into these high-energy states would create potential for enhanced spatial delocalization of both the electron *and* hole, speeding transfer.

While limitations of our pulse shaper's spectral range prevents us from using 3.1 eV (400 nm) excitation pulses as the pump in 2DES experiments, we can compare the results of our X1-pumped 2DES experiments to TA experiments performed with a 3.1 eV pump to understand the pump energy dependence of exciton mobility in CdSe-PDTC films. By exciting with 3.1 eV pulses, well above the NC band edge, we attempt to characterize the degree of mixed character of these highly excited states through their impact on the mobility of excitons and use this information as a benchmark against calculations of CdSe-PDTC's electronic structure.

Figure 5.10 shows bleach shifting plots for PDTC films excited at 3.1 eV and at the band edge at $\omega_1 = 2.32$ eV from 2DES (X1). For this analysis we have chosen to focus on the red shift portion of the plots as this represents the downhill migration of

excitons. To highlight changes in the timescale of this migration we have elected to plot our data analogous to a time-dependent Stokes shift^{53–55}:

$$S(t) = \frac{B(t) - B(\infty)}{B(0) - B(\infty)} \quad (5-1)$$

Where $B(t)$ represents the center energy of the X1 bleach. Thus, the normalized shift, $S(t)$, starts at 1 and decays to zero. Comparing the plots for X1 and 3.1 eV excitation we find differences in the rate of the X1 bleach shift. In the X1 pumped data (**Figure 5.10, black circles**) we see that the X1 shift can be well fit with an exponential decay with a time constant of ~ 30 ps.

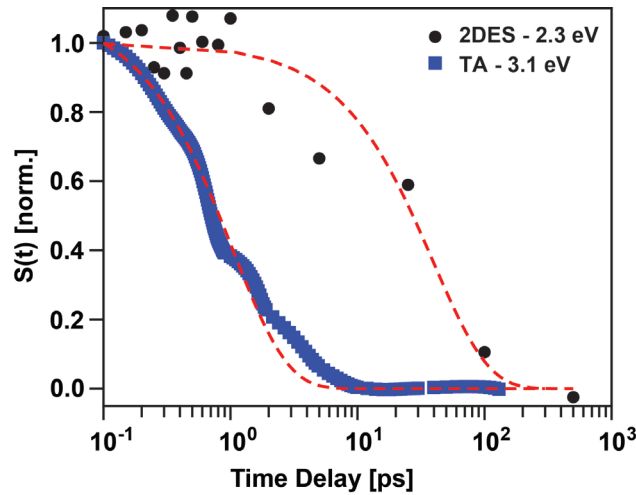


Figure 5.10: X1 bleach shifting data from X1 pumped 2DES data ($\omega_1 = 2.32$ eV, black circles) and 3.1 eV pumped (blue squares) CdSe-PDTC films.

In contrast, when the same film is excited at 3.1 eV this shift occurs $30\times$ faster, with a time constant of ~ 1 ps (**Figure 5.10, blue squares**). This picture is consistent with a scenario where the higher energy exciton is more delocalized due to a greater amount of PDTC LUMO character in the CB.³ While the band edge excited hole is the

predominantly delocalized species when X1 is pumped, the high energy excitation provides both the hole and electron access to highly delocalized states, leading to downhill energetic migration at a faster rate. While the energetic landscape that the excitations can sample is the same, the character of the states impacts the rate at which the carriers are able to access these more delocalized states.

Though preliminary, these results confirm some of the predictions made by theory, particularly when taken in context with the results in Chapter 4. In Chapter 4 we studied smaller NCs (2.3 nm diameter) than the NCs used here (2.8 nm diameter) and we saw a larger impact on the rate of the bleach shift. We attribute these differences to larger reduction in the hole confinement energy upon PDTC substitution as the smaller NCs experience more quantum confinement. Another effect contributing to these differences is the alignment of the PDTC HOMO and NC VB states. As previously reported the redox properties of electronic states of CdSe NCs change with NC size, which can change their energetic position relative to the HOMO and LUMO states of PDTC.^{3,45,51,52,56,57} This change in energetic resonance of the NC and ligand-based states serves to further tune the spatial extent of hybrid NC-PDTC states as discussed in Chapter 2. A study of the bleach energy migration as a function of NC size would serve to further validate these predictions about the nature of NC-ligand coupling in this system.

5.5 CONCLUSIONS

This study has provided deeper insight into the electronic structure of PDTC-exchanged NC films and the nature of the hybrid states formed due to NC ligand coupling using a combination of TA and 2DES. In our study of NC electronic structure we find additional homogeneous broadening, relative to the CdSe-oleate solution, contributes to the measured linewidth of dispersed CdSe-PDTC NCs in solution. We attribute this broadening to spectral diffusion stemming from PDTC ligand motion as such motion has been shown via CPMD simulations to modulate the bandgap of CdSe NCs.³ Moving to NC films, we find that at early times the homogeneous linewidths of CdSe-PDTC and CdSe-oleate films are similar. This narrowing of the homogeneous linewidth in ligand-exchanged films, relative to solutions of CdSe-PDTC NCs, is due to steric hindrance of ligand motions in the solid-state. At long waiting times, we see a unique broadening of the homogeneous linewidth of CdSe-PDTC films that we attribute to the growth of an asymmetric cross peak, indicating exciton transfer to lower energy lattice sites within the film.

Next we compared X1 bleach shifting data from NC films excited near the band edge with both TA and 2DES data, and find it is both consistent with previously assignments and highlights heterogeneity present in both CdSe-oleate and CdSe-PDTC.⁴⁴ In general, frequencies to the red of the average X1 energy tend to blue shift due to a loss of stimulated emission, while frequencies to the blue of the average tend to red shift, which we assign to higher energy excitations migrating to lower energy NCs within the ensemble. Both of the rates of magnitudes of the downhill migration are strongly

enhanced in CdSe-PDTC films due to a combination of decreased fluorescence in these samples,^{50,52} and a larger degree of electronic heterogeneity in these samples.⁴⁴

Finally, to understand the character of the CB and VB states of the NC ensemble in films upon PDTC ligand exchange, we compare the downhill energy migration dynamics of these films excited near the NC band edge (X1) and following 3.1 eV excitation. Consistent with predictions from theory,³ we find our results support a picture where higher energy states excited at 3.1 eV tend to show more delocalized behavior as both the excited electron and hole states are of mixed PDTC-NC character, compared to the samples excited near the band edge where only hole states are predicted to be delocalized. The result of this work is a deeper understanding of the interaction between NCs and their surface ligands, and how this interaction impacts the dynamics of excited carriers in both individual NCs and NC solids.

5.6 REFERENCES

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Vita

Michael S. Azzaro was born and raised in Schenectady, New York. He attended the State University of New York at Geneseo in Geneseo, New York where he earned his Bachelor of Science in Chemistry with Honors. While at SUNY Geneseo he completed research projects with Dr. Jeffrey Peterson synthesizing PbSe nanocrystals and studying their exciton fine structure using low-temperature photoluminescence spectroscopy, and with Dr. David K. Johnson studying the mechanism of inhibition of reactive oxygen production by apocynin. In the Fall of 2013 he enrolled in graduate school at the University of Texas at Austin where he joined the research group of Dr. Sean T. Roberts. Here he built and developed ultrafast spectroscopic experiments to study the interactions of nanocrystals and strongly interacting exciton-delocalizing ligands. Following completion of his PhD he has accepted a position with Intel Corporation in Hillsboro, Oregon.

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