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Effects of Inorganic Composition and Organic Ligands on Spin, Charge, and Thermal Transport
Properties of Semiconductor Nanocrystals

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Effects of Inorganic Composition and Organic Ligands on Spin, Charge, and Thermal Transport Properties of Semiconductor Nanocrystals

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Abstract

Semiconductor nanocrystals possess unique photophysical properties that make them desirable for many optoelectronic applications such as photovoltaics, LEDs, and quantum computing. When the size of a semiconductor is reduced to below the excitonic Bohr radius of the material, its carriers become quantum confined resulting in drastic changes to optical, electronic, phononic, and spintronic characteristics. Most notably these nanoscale systems exhibit absorption and emission tunable through size and shape in addition to composition. Their large surface-to-volume ratios and organic capping ligands also serve to set them apart from bulk semiconductors with ligand composition playing a key role in synthesis, crystal structure, and carrier dynamics/transfer. The tunability of these systems, from the inorganic core to the organic shell, coupled with solution processability, unique spin physics, and device incorporation make them a vibrant and critical area of research.

This dissertation studies fundamental physical properties of semiconductor nanocrystals, namely thermal, electronic, and spintronic, using ultrafast spectroscopy and analytical characterization. The effects of ligands on both intraparticle and interparticle dynamics are also examined in detail. After introducing the basics of semiconductor nanocrystals and the techniques used to study them in chapters one and two, six stories are discussed. The first two focus on thermal properties, covering the effects of heat generated by photoexcitation. Femtosecond stimulated Raman spectroscopy allows monitoring of optical phonon dynamics on femtosecond and

picosecond timescales. It is used in chapter three to study multiexciton recombination effects on longitudinal optical phonon dissipation in CdSe nanocrystals. As laser fluence is increased, and more excitons are generated, a phonon bottleneck limits particle cooling. A brief look into the interplay of optical phonon modes (transverse vs. longitudinal) in InP nanocrystals is also covered.

Chapter four utilizes a different technique to monitor thermal properties, time-resolved X-ray diffraction. Instead of phonons, perturbations to the crystalline lattice such as expansion and disordering are examined. Cooling lifetimes and melting thresholds in CuInSe₂ nanocrystals as a function of size and ligand composition (oleylamine vs. sulfide) are studied. It was found that exchange for a short anionic ligand such as sulfide does not affect the onset of melting but does allow more rapid cooling. Temperature dependent X-ray diffraction is also utilized to determine melting temperatures that are reduced from the bulk composition as well as calculate interfacial thermal conductivity.

CuInSe₂ nanocrystals are also the central focus of chapter five. Three different samples that were synthesized in the presence of different ligands (oleylamine, diphenylphosphine, and tributylphosphine) were examined and found to have lifetimes and quantum yields that vary by an order of magnitude. Investigations into the crystalline structure and surface compositions yield insight into a variety of defect states that limit photovoltaic device efficiency. CuInSe₂ nanocrystals capped with diphenylphosphine show substantial brightening after heating to 600K and TA, Raman, and XRD are utilized to examine subsequent differences in structure.

In chapter 6, intense photoexcitation and NMR is used to study the desorption of ligands (oleic acid) from the surface of CdSe nanocrystals. Both laser fluence and dosing time show strong effects on the percentage of ligand removed. For the sample with the highest absorbed photon dose, the nanocrystals begin to sinter together due to excessive ligand loss and photoluminescence

quantum yield drops substantially. Most samples retain their size and emission characteristics although two show brightening after exposure. All photoexcited samples exhibit oleic acid fragmentation into aldehydes, terminal alkenes, hydrogen and water.

The last two chapters (seven and eight) study spin-polarized electron transfer from CdSe/CdS core/shell nanocrystals to molecular acceptors. In the first, proof-of-concept is shown for a naphthalene diimide (NDI) acceptor coupled to three samples of varying shell thickness. Transient absorption confirms charge separation and recombination, while electron paramagnetic spectroscopy shows a spin-polarized NDI spectrum consistent with radical pair formation via the triplet mechanism. The second expands the work to include four other molecular acceptors as well as pulsed-EPR spectroscopy to determine T_2 lifetimes. Using varying ligand equivalents, the ratio of triplet/singlet character and the coherence lifetime is determined to be controlled in part by the rate of initial electron transfer.

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List of Abbreviations

AR – Auger recombination
CISe – CuInSe₂
CIS – CuInS₂
DPP – diphenylphosphine
EPR – electron paramagnetic resonance
FSRS – femtosecond stimulated Raman spectroscopy
FWHM – full-width half-maximum
HWHM – half-width half-maximum
LO – longitudinal optical
NC – nanocrystal
NDI – naphthalene diimide
NMR – nuclear magnetic resonance
OLAm – oleylamine
PI - pyromellitimide
PL – photoluminescence
PV – photovoltaic
QD – quantum dot
QIS – quantum information science
QY – quantum yield
SCRp – spin-correlated radical pair
TA – transient absorption
TBP – tributylphosphine
TCW – transient continuous wave
TM – triplet mechanism
TO – transverse optical
TRF – time-resolved fluorescence
TR-XRD – time-resolved X-ray diffraction
TCSPC – time-correlated single photon counting

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Chapter 1 : Introduction to Semiconductor Nanocrystals

1.1 Background

To start, it is necessary to understand the components of the phrase “semiconductor nanocrystals”. Semiconductors are materials whose properties lie between that of a conductor (such as metal) and an insulator (such as glass). Conductors possess a “sea” of electrons that are easily perturbed. They have high electrical and thermal conductivity, thus their name. Insulators are the opposite; their electrons are more confined into a valence band and it takes significant energy to move them into a conduction band where they can flow more freely. As their name implies, they do not transmit heat or electricity well. Semiconductors also contain a valence and conduction band, yet the energy that separates them is smaller such that wavelengths of light in the visible and near-infrared are enough to promote electrons from one to the other.¹ Silicon is a commonly used semiconductor and a good example of the important roles that this type of material plays in our lives, from solar cells to electronics.

Nanocrystals (NCs) are ordered (crystalline) materials with at least one dimension less than 100 nm.² When prepared as colloids (as opposed to within other solid materials) they have long fatty molecules that ensure stability in solution.³ These “ligands” coordinate to the surface of the NCs in a manner similar to inorganic complexes. Ligands passivate surface sites, a role that it is critical; due to their incredibly small size, a significant portion of atoms are present on the surface instead of completely encased in the crystalline lattice.⁴ At this length scale, many optical, electronic, thermal, spintronic, and mechanical properties become vastly different than those of the corresponding bulk materials. For example, catalytic behavior can increase substantially with a reduction in size⁵⁻⁷ while melting temperature may decrease,⁸⁻⁹ both due to higher surface area and energy. When the size of a semiconductor is reduced to a few nanometers, its carriers become

quantum confined; although they would prefer more space to move about, they are restrained within the volume of the particle.¹⁰⁻¹¹ This gives these materials the name “quantum dots”. Quantum confinement affects many properties, most notably the bandgap of the semiconductor, which in turn causes absorption and emission to be tunable with size and shape. Thus, semiconductor NCs exist as a different class of materials whose properties can differ substantially due to size, shape, and ligand. Through the next sections I will introduce some of the physical and chemical properties of these materials as well as potential applications and current challenges. Chapter 2 will provide further information on the techniques used to study semiconductor NCs.

1.2 Electronic Structure

If any dimension of a semiconductor NC is less than the excitonic Bohr radius of the material, then it is considered quantum confined in that direction.¹²⁻¹³ This can be thought of as the simple physical chemistry particle-in-a-box model; as the size of the nanocrystal is reduced, the energy gap between the valence and conduction band increases.¹⁴ This is summarized mathematically in the Brus equation (Eq. 1.1), which adjusts the bandgap of the bulk material ($E_{\text{bandgap,bulk}}$) by incorporating confinement energy ($E_{\text{confinement}}$) as well as a Coulombic term for the attraction between the electron and hole (E_{Coulomb}).¹⁵ Here, h is Planck’s constant, r is the radius of the NC, m_e^* and m_h^* are the effective masses of the electron and hole respectively, e is the elementary charge, ϵ_0 and ϵ_r are the vacuum and relative permittivity.

$$\text{Eq. 1.1} \quad E_{\text{Bandgap,NC}} = E_{\text{Bandgap,bulk}} + E_{\text{Confinement}} - E_{\text{Coulomb}}$$

$$E_{\text{Bandgap,NC}} = E_{\text{Bandgap,bulk}} + \frac{h^2}{8r^2} \left(\frac{1}{m_e^*} + \frac{1}{m_h^*} \right) - \frac{1.8e^2}{4\pi\epsilon_0\epsilon_r r^2}$$

As the dimensionality of the material is reduced to “zero” (0D, e.g. a spheroidal NC) the conduction and valence bands become discretized into electronic levels akin to molecular orbitals and the bandgap becomes inversely proportional to r^2 .¹² The effective mass of both electron and hole directly impacts the distribution of states with the heavier hole resulting in more concentrated density of states near the bandedge.¹⁶ 1D and 2D nanomaterials have band structures between that of the bulk and the discrete levels of a NC (Figure 1.1).¹⁷

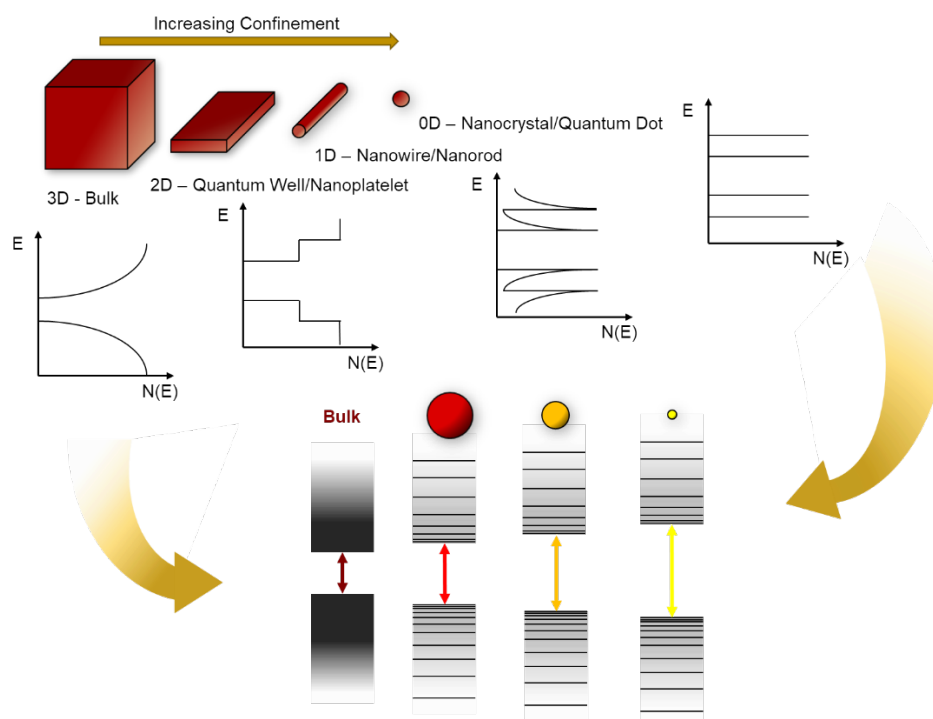


Figure 1.1: Effects of confinement on the electronic structure of semiconductors. As the dimension of semiconductors are reduced below the excitonic Bohr radius a transition from bands to discrete electronic levels occurs. Quantum-confined semiconductor NCs exhibit bandgaps that are tunable through size with smaller particles having larger bandgap energies.

An example of how the discrete electronic levels for a semiconductor NC, in this case CdSe, translate to the absorption spectrum is given in Figure 1.2. The electronic states can be described by S, P, or D, similar to molecular orbitals.¹⁸⁻¹⁹ Although not shown in this simplified example, ligands, surface traps, dopants, and intrinsic defects can introduce more electronic levels

both intragap and intergap.²⁰⁻²⁸ Shells are often grown to reduce non-radiative traps on the surface but are also important for engineering of unique electronic structures.²⁹⁻³⁰ Type I structures utilize a shell with a bandgap larger than that of the core resulting in localization of the carriers to the core, such as in the case of CdSe/ZnS.³¹ In Type II structures the core and shell have similar bandgap energies, but the conduction and valence levels of the shell are shifted higher or lower in energy.³² This separates out one carrier into the shell, while maintaining the other within the core. Quasi-Type II maintain a similar conduction or valence band energy across core and shell, while shifting the other band. The example shown in Figure 1.2d has a shell with a lower energy valence band that maintains the hole within the core of the material, however the conduction levels are similar for both core and shell allowing the electron to delocalize over both. An example of this is CdSe/CdS which is used in Chapters 7 and 8.³³

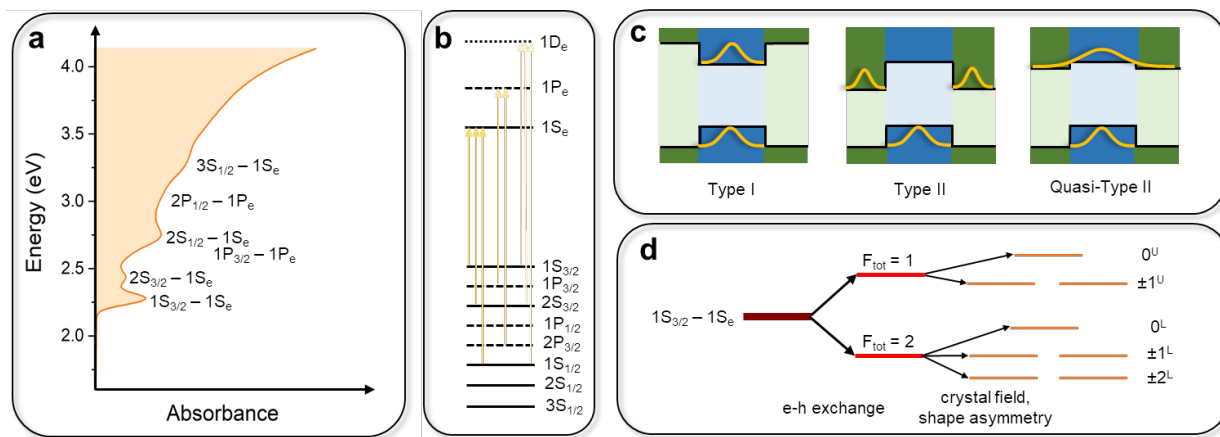


Figure 1.2: Electronic structure of CdSe NCs. (a) Absorption spectrum with transitions labeled. (b) Conduction and valence levels labeled with some transitions marked by arrows. (c) Examples of a few core/shell structures and how they affect electron and hole wavefunctions. (d) Exciton fine structure showing how levels split due to e-h exchange and crystal field/shape asymmetry.

1.3 Spin Properties

Semiconductors possess unique spin physics due to their optical selection rules.¹⁶ To conserve angular momentum, when circularly polarized light is absorbed, spin polarized electrons are excited (i.e. left or right handedness promotes a majority of spin-up or spin-down electrons).³⁴⁻
³⁶ In a related process, emission may be circularly polarized. Due to the heavy atoms of these materials, spin-orbit coupling causes mixing of spin states, thus they can be considered “singlet-like” and “triplet-like”, but not purely one or the other. These factors can be exploited for spin selective electron transfer from a NC to an acceptor.³⁷

In CdSe, within the lowest energy optical transition, is the exciton fine structure manifold.^{18,38} Here the electronic $1S_{3/2} - 1S_e$ state is split by the exchange interaction into a higher energy $F = 1$ and lower energy $F = 2$ state, dubbed the bright and dark exciton, respectively. The splitting between these states is small (1 – 25 meV) and therefore at room temperature, with no magnetic field to split the levels an equilibrium exists between these states.³⁹ These states are further split by crystal field anisotropy to give eight fine structure levels (Figure 1.2d).

1.4 Photophysical Processes

Absorption of a photon by a semiconductor NC generates an electron-hole pair, commonly referred to as an exciton (N) due to Coulombic attraction (binding energy) between the opposite charges. Semiconductors can absorb multiple photons resulting in multiple excitons being generated per NC. Here, all studies are on ensembles of NCs so instead of a specific number of N we consider a distribution as inhomogeneity between particles will result in absorption of different quantities of photons. $\langle N \rangle$ represents the average number of excitons in a sample of NCs and is described by a Poisson distribution,

Eq. 1.2
$$P = \frac{\langle N \rangle^N e^{-\langle N \rangle}}{N!}$$

where P is the proportion of NCs that have N excitons when the overall average number of excitons is $\langle N \rangle$ is known. $\langle N \rangle$ can be calculated easily when the absorption cross section (σ) and laser fluence (j) are known.

Eq. 1.3
$$\langle N \rangle = \sigma j$$

The equations below show how σ can be calculated from the absorption coefficient (α) or extinction coefficient (ε) where V is the volume of the NC and N_A is Avogadro's number.⁴⁰

Eq. 1.4
$$\sigma = V\alpha$$

Eq. 1.5
$$\varepsilon = \frac{N_A \sigma}{1000 \ln(10)}$$

Three specific cases will now be covered as examples to provide a brief overview of some of the processes that can occur. Figure 1.3 summarizes them as well.

Low Fluence, Bandedge Excitation: When photon density is kept low and $\langle N \rangle \ll 1$, most NCs will remain unexcited and those that do absorb light will only absorb one photon thus generating only one exciton. This is coined the single exciton regime. If the energy of light is also placed at the lowest end of the absorption spectrum then the single excitons generated will be only have enough energy to be excited to the bandedge. Here, few options are available for the carriers. The electron and hole may recombine and emit a photon, which will be lower in energy than the absorption by tens of meV due to Stokes shift^{12, 41} (although in some NCs the effective Stokes shift is much larger, upwards of hundreds of meV).⁴²⁻⁴³ This radiative recombination process tends to be on the order of nano- to microseconds in semiconductor NCs at room temperature.⁴⁴ Depending on the electronic structure it may be elongated at lower temperatures due relaxation into the lowest,

dark exciton state where recombination is spin-forbidden (this is the case for CdSe).³⁹ The electron and hole may also recombine via other pathways such as trapping at surface sites or intrinsic defects.⁴⁵⁻⁴⁶ Oftentimes this results in non-radiative recombination, although trap state emission is possible and generally results in broad PL at lower energies.⁴⁷⁻⁴⁸

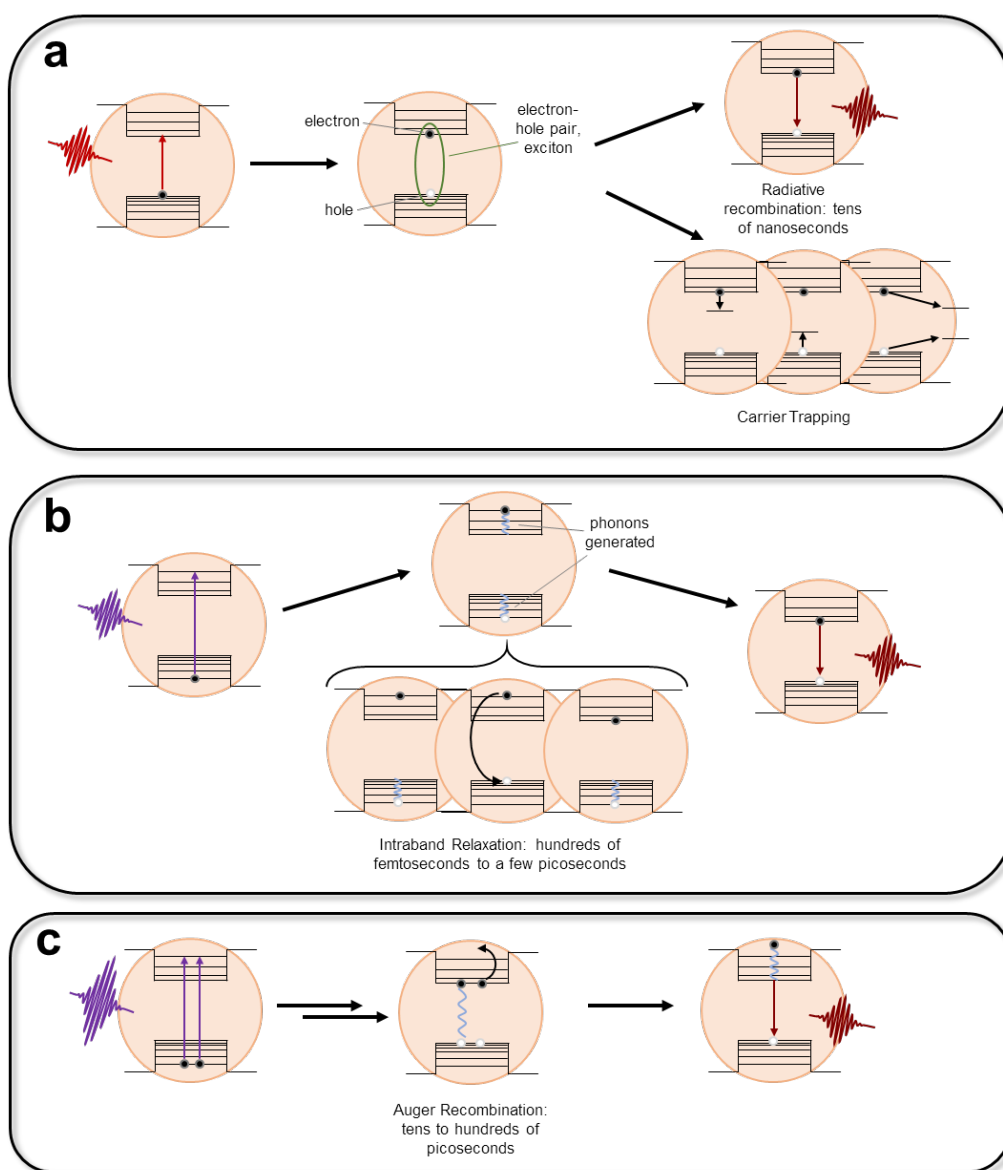


Figure 1.3: Photophysical processes in semiconductor NCs. (a) Low fluence, bandedge excitation. Radiative recombination and trapping can occur. (b) Low fluence, above-bandgap excitation. Carrier cooling occurs through phonon generation before recombination. Auger energy transfer allows electrons to cool through electronic states that exceed the energy of phonons. (c) High fluence, above-bandgap excitation. After cooling, Auger recombination transfer the energy of one exciton to the other.

Low Fluence, Above-Bandedge Excitation: If excitons are generated using higher energy light, then carriers need to relax to the bandedge before recombination can occur. To do so, electrons couple to phonons within the lattice and exchange excess energy. This process of intraband relaxation occurs rapidly, generally on the order of hundreds of femtoseconds to a few picoseconds.⁴⁹ The energy spacing in the conduction states are often larger than the highest phonon frequency, which would preclude cooling. In these cases, the hole can still relax given the density of states in the valence band is higher, then energy transfer from the electron to the hole may allow the remaining relaxation.⁵⁰⁻⁵¹ This Auger process is also very rapid (< 5 ps) and tends to be mostly independent of size.⁵²

High Fluence: If fluence is higher, a distribution of excitons will be generated in the ensemble of NCs and for some particles multiple excitons will be generated.⁵³ If the excitation wavelength is still larger than the bandgap then relaxation occurs as described above. Once carriers have relaxed to the bandedge any NC with multiexcitons may undergo a process known as Auger recombination.⁵⁴ This non-radiative process occurs when one exciton recombines by transferring its energy to another exciton. This results in a return to “hot” carriers that must once again relax to the bandedge. This process is difficult in bulk semiconductors, but accessible at the nanoscale due to momentum conservation being more easily satisfied.^{17, 55} Therefore, Auger processes are rapid, for example biexciton Auger recombination lifetimes are generally tens to hundreds of picoseconds in semiconductor nanocrystals and scale by volume (process is slower in larger NCs), far exceeding radiative recombination.⁵⁶ This process is not limited to biexcitons; triexciton and higher numbers of excitons undergo Auger recombination even more rapidly.¹⁹

Other Photophysical Processes: Most of the studies covered in this thesis can be understood in the framework of the cases presented above, but this does not mean that they represent all outcomes of photoexcitation. There are many more processes that can occur, e.g. Auger ionization, charge transfer, energy transfer, carrier multiplication, two-photon absorption, but these have been excluded in order to be succinct.

1.5 Thermal Properties

Heat is generated in the form of phonons during intraband relaxation, either from electrical carriers being excited above the bandgap or Auger recombination.⁵⁷ Non-radiative process such as surface trapping can also generate heat as carriers lose potential energy upon moving into the trap or through subsequent Auger processes.⁵⁸ In polar semiconductors, optical phonons chiefly couple to the carriers during cooling.⁵⁹ These then relax into acoustic phonons that can couple to ligand or solvent vibrations to dissipate the excess thermal energy into the surrounding medium.⁶⁰ With large quantities of excited carriers, these processes may bottleneck resulting in an inability of the particle to release heat to the surroundings.⁶¹ The large surface-to-volume ratio in these NCs has important consequences for heat dissipation. The confined space results in high carrier density and diffusion is limited. Ligands are critical for coupling to vibrations and allowing solvent molecules to interact with the surface.

Heat in semiconductor NCs can have a variety of effects, both positive and negative.⁵⁷ Increased temperature of NCs can result in reduced photoluminescence intensity and lifetime, which is detrimental for applications such as LEDs. Furthermore, heat in these materials may distort NC size and structure or disrupt crystallinity and surface passivation leading to trap states. Since NCs are heralded for size dependent properties this is not ideal. Small particle size

intrinsically reduces melting point as positive surface energy contributions counter internal lattice bonding,⁸ which raises the prospect of NCs presenting transient disordering upon intense excitation.⁶²⁻⁶⁵

In some cases, the photogeneration of heat is desired. For example, additive manufacturing and photonic curing relies on excess heat being generated after excitation causing sintering of NCs into bulk-like regions or continuous films.⁶⁶ In this way NC solutions can be applied as “inks” to form flexible, patterned devices before sintering into more bulk-like composition that is better for efficiency. This has shown success in CuInSe₂ NCs where photonic curing can replace high-temperature sintering that relies on Se gas to be present as well.

1.6 Synthesis of Semiconductor Nanocrystals

Since the first colloidal synthesis of semiconductor NCs, improvements to protocols has enabled rapid yet precise preparation across a wide range of sizes, shapes, and compositions. Despite variations in temperature and precursors, the synthesis of samples generally follows very similar processes. The reactions to generate the materials described within this thesis have been optimized in other work, so they will only be discussed briefly here.

Semiconductor NCs can be synthesized many ways however the studies covered in this thesis only rely on two: hot injection (e.g. CdSe) and heat-up methods (e.g. CuInSe₂).^{12, 67} Both use similar chemical processes of nucleation and growth to prepare NCs of specific sizes. In the first precursors are heated to high temperatures where upon injection of a reactant (generally the chalcogen) growth of NCs begins. The heat-up method is similar except temperature alone dictates the start of the reaction, generally by decomposition of precursors. In both methods nucleation and

growth is rapid, generally occurring within minutes. Size control is determined by temperature and the time it is maintained such that injection or rapid quenching can prevent further growth.

Shells are often added to NCs to modulate the electronic structure and increase photoluminescence quantum yield (PLQY, See Sections 1.3 and 1.4). In order to grow shells two main methods, exist, selective ion layer adsorption and reaction (SILAR) and continuous injection of precursors at high temperatures.¹² In the former anionic and cationic precursors are alternatively added to a solution of NCs thereby growing one layer at a time. The latter incorporates both precursors simultaneous, but over very slow injection rates using a syringe pump.

1.7 Surfaces and Ligands

One of the defining features of NCs are their large surface-to-volume ratios. In contrast to bulk materials, where surface processes are overwhelmed by those of the crystalline lattice, small NCs can have upwards of 50% of their atoms on the surface. This interface therefore can play a large role in electronic, phononic, and chemical processes. For example, they may impart trap states (see Section 1.4) or control thermal dissipation (see Section 1.5).

Organic ligands are oftentimes used in the synthesis of semiconductor NCs to serve as solvent and/or reactants.^{4, 68-70} They template the growth, coordinate reactive metal species, and ensure solubility of nuclei and NCs. Afterwards they maintain colloidal stability and serve to passivate the undercoordinated surface sites. As with inorganic complexes, ligands have a range of binding strengths and preferred coordinations.⁷¹⁻⁷² They may preferentially passivate certain facets, controlling the shape and anisotropy of the resulting particle. Their binding strength can change emission by passivating (or failing to passivate) surface sites that then serve as traps.

Binding strength can also dictate the ability to exchange the native ligands with other ligands. It can be difficult to exchange tightly bound phosphonic acid or thiol ligands for carboxylic acids, but easy to go the reverse direction. Ligand exchange is used for a variety of different reasons. Depending on the dipole and orbital wavefunction of the ligand it can alter the bandgap of the nanocrystal.⁷³ Exchange for short inorganic ions has been commonly used to increase charge transport in photovoltaic devices.⁷⁴⁻⁷⁵ With proper alignment of redox potentials ligands can serve as electron donors or acceptors.²⁴

1.8 Applications

Many, although not all, applications involving semiconductor NCs utilize their unique optoelectronic properties.¹² The tunability of emission makes them promising for LEDs, both in lighting and displays where color purity and stability is necessary.⁷⁶ In fact, multiple companies have now begun incorporating NCs into their televisions, oftentimes using InP. This intense emission is also key for biolabeling and sensing applications.⁷⁷⁻⁷⁸

The large absorption cross-sections of NCs has seen them built into photovoltaic devices with record efficiencies.⁷⁹ Here tunability of absorption through size is also important for maximizing the efficiency and the colloidal nature allows them to be used as inks for flexible, patterned devices. Catalysis using NCs is a very active area of research for NCs given the high surface area and reactivity, coupled with these absorption properties, photocatalysis using semiconductor NCs is promising.⁸⁰⁻⁸¹ The ability of semiconductor NCs to absorb multiple photons has also resulted in their study for lasing although Auger recombination can limit this.⁸² They also show promise for improving computing, both standard and quantum due to their nanoscale size and rich spin physics.⁸³

1.8 Challenges in Semiconductor Nanocrystals

Despite great progress in the synthesis, study, and commercialization of semiconductor NCs many fundamental questions remain unanswered. Each year, new compositions of NCs are made and new technologies are created; it is critical that fundamental studies of photophysical properties keep up.

Many of the challenges for semiconductor NCs remain in understanding how the nanoscale changes the properties of the material. Bulk semiconductors have been studied far longer than their nanoscale counterparts and their characteristics are well-understood in the framework of existing models. While semiconductor NCs are, at their core, still semiconductors, quantum confinement, large surface-to-volume ratios, and organic ligands change their behavior substantially.

Take, for example, the problem of intense excitation. Many applications rely upon generation of multiple carriers including LEDs, lasers, and photovoltaics. But what happens to a NC when it contains a multitude of carriers? Each exciton is going to generate heat as they relax, and Auger recombination will produce even more. In bulk materials this is less of a concern, the density of carriers remains low, Auger recombination is more difficult, and diffusion of both excitons and phonons aid in returning the system to equilibrium. It is not immediately clear how photoexcitation will affect NCs. Will thermal dissipation follow similar behavior as the bulk, i.e. optical phonons $\rightarrow$ acoustic phonons $\rightarrow$ surroundings, or will it bottleneck? How long does it take for NCs to return to equilibrium? How hot do NCs truly get upon photoexcitation? Temperature cannot be measured directly using standard methods so how do we determine this? NCs are also known to melt at lower temperatures than their corresponding bulk composition due to their high surface energy, but how much of a reduction does size cause in melting point? Do they return to their ordered state after some time? How does the NC behave after all this? Will its emission

diminish? Its structure change? Are the consequences of photogenerated heat the same as static heating?

Yet one must remember that it is more complicated than that, NCs are not just their semiconductor core, they are heavily impacted by the organic ligands on their surfaces. These passivate surface sites, provide colloidal stability, and can affect the electronic properties of the material. Synthesis of NCs with different ligands has become common and exchanging for molecules with different functionalities well-studied. However, many questions remain about the many roles the ligand plays. How does the ligand present on the NC affect all the questions above? Can it change rates of thermal dissipation? The onset of melting? What happens to the ligands themselves when the NC has been excited with intense illumination? Will they dissociate from the surface of the particles permanently? If so, what happens to the surface sites now left undercoordinated? How many can be removed before the NC loses stability? Is it possible for the NC to facilitate reactions at the surface, potentially altering the ligands themselves?

Ligands can also be chosen that purposefully affect optoelectronic properties, serving as electron donors and acceptors in conjunction with the NC. Study of these processes has allowed understanding of how electron transfer rates scale with size and driving force, but what about spin properties? Is it possible to transfer spin polarization from an inorganic material to an organic molecule or vice versa? The idea of spin-correlated radical pairs has been studied extensively for organic donor-acceptor complexes, but how does this change when a NC is involved? How long can coherence be maintained in such a system and what parameters impact it?

Even considering no excitation at all, the role of ligands is not necessarily complete. For many compositions, the ligand is present during the synthesis as well as afterwards, two distinct purposes that may alter the structural and photophysical properties separately. Ligands are known

to play a direct role in the appearance and passivation of surface sites that may serve as carrier traps, but what about internal defects? NCs are known to be more tolerant of defects and non-stoichiometric compositions, can the choice of ligand change the internal makeup of the material? What about syntheses that use two or more ligands with different functionalities? Will both be present on the surface afterwards? Will they bind to different sites?

Semiconductor NCs overall are remarkable materials that can improve numerous technologies. Before that though we need to truly understand their chemical, structural, and photophysical behaviors. Many of the questions and challenges outlined above are touched upon in the chapters of this thesis, but it is not a complete study. There are many areas that are not covered above or within. As we understand more about these tiny, significant structures, more questions will inevitably arise.

Chapter 2: Techniques to Study Semiconductor Nanocrystals

This thesis focuses on many fundamental properties of NC and as such a variety of analytical tools were utilized to characterize them fully. Many of these techniques are used by researchers in the NC community and therefore to aid both the reader and to give a broad overview they will each be covered briefly. Note that this is not a comprehensive list (for example many X-ray techniques are not covered) but should enable understanding of the work covered herein.

Static and time-resolved techniques are often used in conjunction to fully understand physical processes and properties. Timescales vary immensely depending on the process, for example, the photoexcitation of an electron is less than a femtosecond, vibrational motion and cooling is on the order of picoseconds, charge transfer can be nanoseconds, spin coherence can last microseconds, and photoluminescence can vary substantially, but extend up to milliseconds.⁸⁴⁻
⁸⁵ Figure 2.1 gives time-ranges of some processes in bulk semiconductors as an example of the orders of magnitude differences. Kinetics from a variety of techniques described below are fit to a sum of exponentials to produce rates (k) or lifetimes (τ) which are inversely related ($k = 1/\tau$) and that can be assigned to physical processes.

Eq. 2.1:

$$Signal = \sum_n A_n e^{-kt}$$

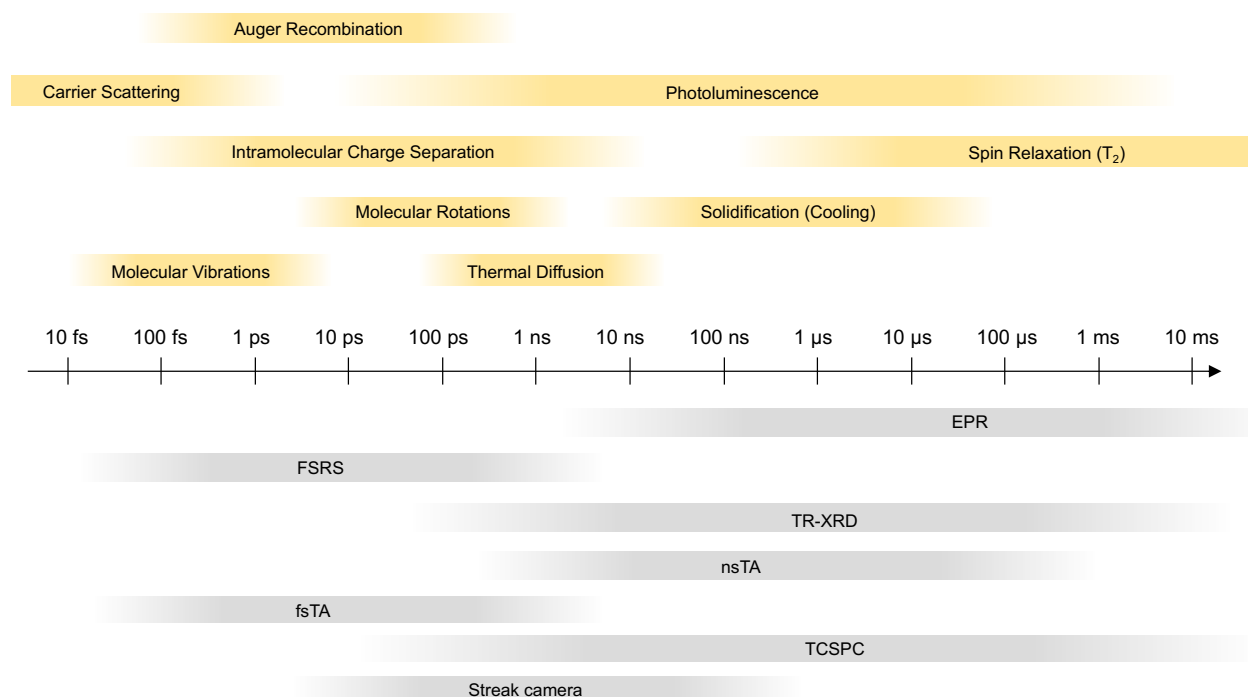


Figure 2.1: Timescales of processes in semiconductor nanocrystals (top, yellow) and spectroscopy techniques used to study them (bottom, grey).

Although some of the techniques covered herein require the use of low/high temperatures or magnetic fields, these parameters can also be considered as another dimension to others such as absorption or photoluminescence. Lower temperatures will sharpen transitions and reduce charge separation/recombination lifetimes.⁸⁶ If electronic states are close in energy it will reduce the thermalization of populations and force carriers into their lowest energy configurations. This can help determine the order of electronic structure when spin-forbidden and trap states are involved. Higher temperatures can be used to monitor degradation, annealing, and sintering effects as well as serve as calibrations for temperature sensing upon photoexcitation.⁸⁷⁻⁹¹ Magnetic fields can split degenerate levels such as triplets⁹²⁻⁹⁴ or the exciton fine structure in CdSe^{39, 95} to allow quantification of ordering and energy spacings.

2.1 Static and Transient Absorption

The absorption spectrum of semiconductor NCs is heavily impacted by the size of the particle with transitions shifting higher or lower in energy with decreased or increased radius, respectively. When very monodisperse samples are synthesized, some compositions such as CdSe exhibit distinct transitions that can be assigned.¹² Other compositions, such as CuInSe₂, exhibit broad linewidths that make clear identification more difficult.⁴² A lot of information can be garnered from an absorption spectrum such as the size of the NC, the homogeneity, and the concentration (if the extinction coefficient or absorption cross section is known).⁴⁰ Changes in the absorption spectrum of a sample upon shell growth, ligand exchange, or reduction/oxidation can be monitored to access completion of experiments.²⁹

Transient absorption (TA) is a pump-probe ultrafast spectroscopy technique wherein a laser pulse (pump) generates excitons in the sample and afterwards a white light probe pulse (either visible or NIR) arrives at a fixed time that is varied over the course of the measurement to build up a 3D map of absorption changes vs time-delay (Figure 2.2).⁹⁶ When the probe is concurrent with or subsequent to the pump pulse, it excites or depopulates transitions in the sample that appear as changes in the probe intensity. Differenced spectra with the pump on compared to with the pump off remove unexcited absorption signals (ΔA) and allow for small pump-induced changes in absorption to be discernable. Generally, three main features are observed in TA measurements on chromophores: (1) ground state bleach, (2) excited state absorption, and (3) stimulated emission. Ground state bleaches occur due to carriers blocking absorptive transitions resulting in reduction of probe photons able to excite that transition. This results in negative ΔA features that resemble inverted static absorption. Stimulated emission occurs when probe photons stimulate recombination resulting in fluorescence. This also produces negative ΔA features, this time

resembling the inverted photoluminescence spectrum. Excited state absorption (also known as induced absorption) is produced by absorption of probe photons from the excited state to a higher energy level. This gives a positive ΔA feature.

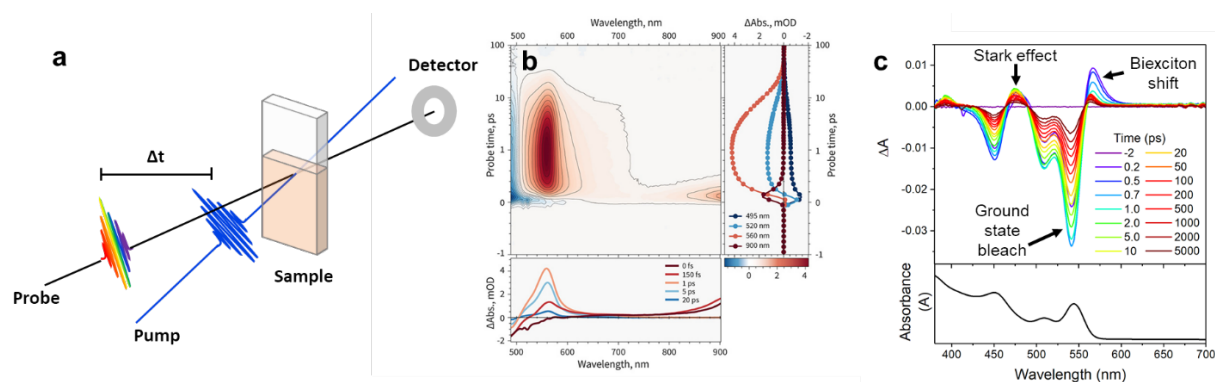


Figure 2.2: Transient absorption spectroscopy. (a) Schematic of the setup. (b) Example of a contour plot with kinetic and spectral traces shown on the respective axes.⁹⁷ (c) CdSe NCs transient and static absorption spectra with features labeled.

In semiconductor NCs, the interaction of excitons with the probe results in unique TA signals. For example, after generation of one exciton, the carriers induce local fields that result in optical transitions shifting in energy and intensity due to changes in optical selection rules. Upon differencing, this Stark effect causes TA features to become derivative-like in shape.⁹⁸ Hot carriers produce a similar derivative-like feature at the bandedge due to the biexciton effect (interaction of pump generated exciton and probe generated exciton), which decays with cooling lifetimes.⁵³ In semiconductor NCs the disparate effective masses of electrons and holes results in TA measurements predominately informing about electron transitions and behaviors due to the multitude of hole states readily accessible,^{49, 99-100} though this has recently come under debate.¹⁰¹ Rapid trapping of holes can also preclude their involvement in signals.¹⁰²

TA can also be a powerful tool for intersystem crossing in organic chromophores and for monitoring charge and energy transfer. In many organic systems intersystem crossing to a triplet can occur from the excited singlet or from recombination of triplet radical pair. They oftentimes live for microseconds when run in air-free cuvettes. Many organic species also have distinct optical transitions associated with their radical anion or cation allowing identification of where carriers have gone in molecular, NC, or hybrid QD-molecular donor-acceptors complexes.¹⁰³ NCs do not have as distinct of transitions due to the density of states, however decay or growth of bleach features can suggest that charge transfer has occurred.

2.2 Static and Time-resolved Photoluminescence

Absorption is not the only way to monitor electronic processes, photoluminescence spectroscopy is a convenient method of monitoring radiative recombination. In semiconductor NCs, emission, like absorption, is tunable through size, shape, and composition. Static PL measurements provide time-integrated emission signals, generally using a laser diode for excitation, and can provide information about the energy of the emissive transition as well as insight into the homogeneity of the sample as size distribution can broaden PL. Using an integrating sphere or a standard the PLQY of a sample can be calculated where PLQY is defined as

$$\text{Eq. 2.1} \quad \Phi = \frac{\text{number of photon emitted}}{\text{number of photons absorbed}} = \frac{k_r}{k_r + \sum k_{nr}}$$

where k_r is the rate of radiative recombination and $\sum k_{nr}$ is the sum of all non-radiative rates. For an integrating sphere measurement QY is calculated using Eq. 2.2, while calculating it in reference

to a standard is given in Eq. 2.3. The terms I , S , and A represent emission intensity, scatter intensity, and absorption respectfully.

$$\text{Eq. 2.2} \quad \Phi = \frac{I_{\text{sample}} - I_{\text{blank}}}{S_{\text{sample}} - S_{\text{blank}}}$$

$$\text{Eq. 2.3} \quad \Phi = \Phi_{\text{reference}} \frac{I_{\text{sample}}}{I_{\text{reference}}} * \frac{A_{\text{reference}}}{A_{\text{sample}}}$$

Many processes can compete with radiative recombination thereby reducing PLQY, for example charge transfer, energy transfer, Auger recombination, and carrier trapping. Inversely, ligand exchange, shell growth, and annealing can remove trap states and increase PLQY.^{19, 29, 49, 55}

Time-resolved fluorescence (TRF, also known as time-resolved PL) measurements provide another dimension to these measurements. Two of the most common TRF techniques are time-correlated single photon counting (TCSPC) and streak camera. TCSPC is, as the name implies, a photon counting technique where emission at a single wavelength is monitored and photons are “binned” in time to produce a kinetic trace. Oftentimes the wavelength of choice is that of the emission maximum. Streak camera data is resolved in both the time and spectral domain. Emitted photons are separated using a grating like TA before a cascading photoelectrode smears out the photon counts in time, thus giving this technique its name. Generally, streak camera data is binned in analysis to improve signal to noise (see Figure 2.3 for example data). Monitoring kinetics from either of these techniques can provide insight to the timescales of electronic processes beyond just spectral intensity, for example a reduction in lifetime may be a result of carrier transfer to another species thus that competes with radiative processes. Appearance of new features may be due to energy transfer from a photoexcited chromophore to an acceptor that is now emitting.

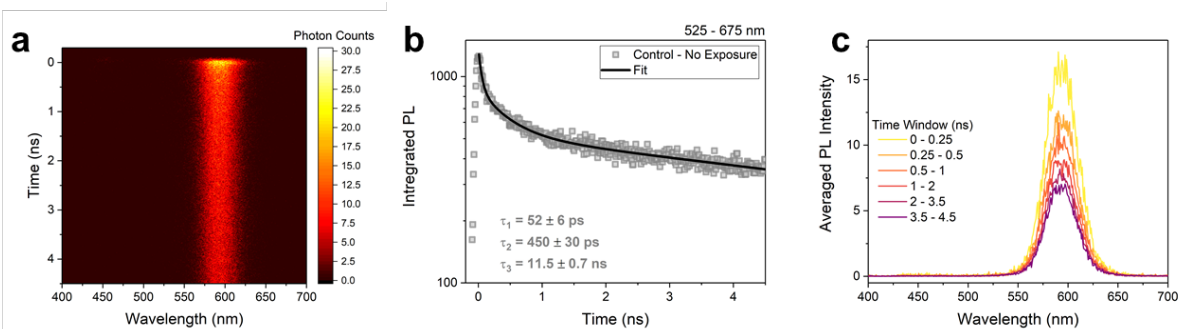


Figure 2.3: Streak camera measurements of CdSe NCs. (a) Contour plot showing the full time and spectral range. (b) Spectrally-integrated (525-625 nm) produces a kinetic that can be fit with three exponentials. (c) Temporally-binned data shows how the feature changes over time.

There are benefits to using time-resolved emission over absorption; it is a “background” free measurement, no differencing required as emission will only appear after photoexcitation. This also can make it simpler for interpretation with kinetics that are more easily fit. However, while scatter appears in TA measurements, emission signals are weaker and can be overwhelmed by photons from the light source. Furthermore, scatter in TA can be easily cropped post-experiment, but must be removed before detection in photoluminescence lest it damage sensitive optics. Lastly, while time-resolution in streak camera measurements have improved greatly they still are limited by detector response instead of laser pulse duration and therefore lack the higher time resolution of TA measurements. Fluorescence up-conversion does much better with regards to time-resolution, but requires a more complex setup.¹⁰⁴

2.3 Static Raman and Femtosecond Stimulated Raman Spectroscopy

Vibrational modes of semiconductor nanocrystals are usually very low in frequency due to the heavy mass of the atoms. As such, IR spectroscopy is limited to organic modes corresponding to ligands or intercalated molecules (e.g. methylammonium in perovskites).¹⁰⁵⁻¹⁰⁶ Raman spectroscopy, on the other hand, allows identification of these low-frequency modes and can

provide insight into crystallinity and defect structure.¹⁰⁷ At the nanoscale Raman modes may shift frequencies and broaden due to the small quantity of repeat unit cells; new features may also appear such as the surface optical mode in CdSe NCs.^{52, 108-111}

Time-resolved Raman is not as straightforward as many other ultrafast techniques. Simple pump-probe configurations lack high time resolution, high signal to noise, and may be complicated by intense fluorescence.¹¹²⁻¹¹³ Femtosecond stimulated Raman spectroscopy (FSRS) overcomes these downfalls by utilizing three pulses.¹¹⁴⁻¹¹⁵ Initially, a pump pulse like that from TA (here called the actinic pump) excites the sample. The probe consists of a broadband white light pulse that is overlapped temporally with another pulse called the Raman pump. The Raman pump is much longer temporally than the actinic pump, generally on the order of a few picoseconds, and very narrow spectrally. The combination of the probe and the Raman pump are critical and provide many benefits, (i) the long time range of the Raman pump allows the frequency of the Raman modes to be well-defined while (ii) the short time of the probe allows ultrafast detection of their dynamics (tens to hundreds of femtoseconds), and (iii) the narrow bandwidth of the Raman pump ensures separation of Rayleigh and Raman scattering. FSRS is also not spontaneous, but stimulated Raman so the signal appears in tandem with the white light probe instead of spreading radially. Because of this it is much more intense than most Raman techniques and relatively free of scattered light. This does result in large backgrounds in FSRS due to the white light, which may show transient behavior as it interacts with the actinic pump.

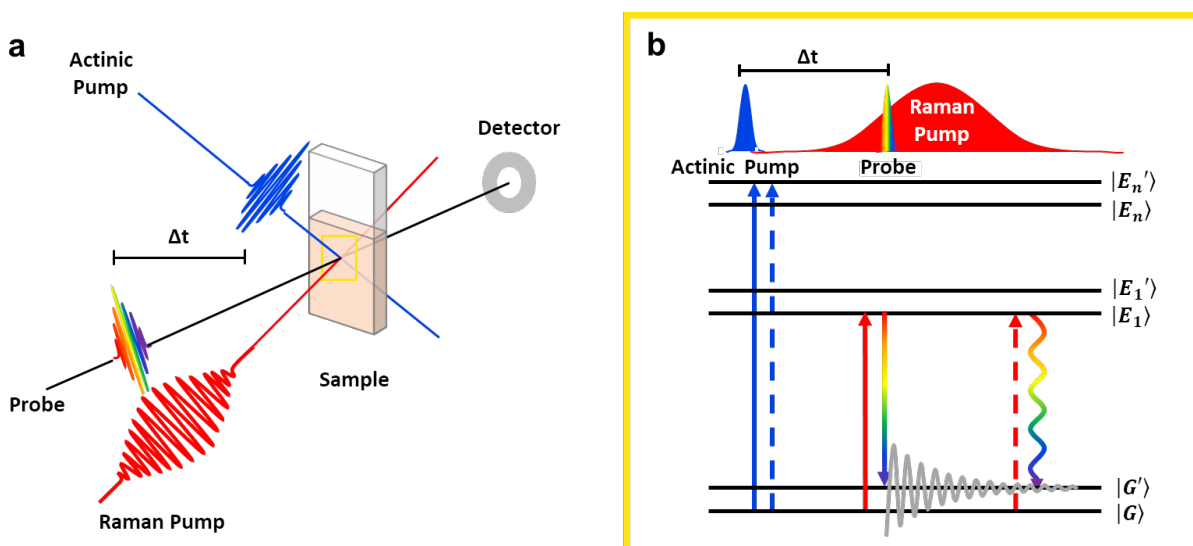


Figure 2.4: Femtosecond stimulate Raman spectroscopy. (a) Schematic of laser pulses. (b) Feynman diagram showing the interaction of all three laser pulses.

Data analysis for FSRS can be complicated due to the large background described above as well as smaller signals than TA. In the case of organic molecules the Raman pump wavelength is chosen specifically to ensure monitoring of excited state features that form upon interaction of the sample with the actinic pump. For semiconductor NCs, most of these features are overlapped with static absorption features resulting in convolution of ground and excited state Raman signals. Depletion of Raman gain (I) depends on the exponential of the inverse of the phonon occupation number (n) (Eq 2.4) such that loss in Raman intensity upon photoexcitation in semiconductors corresponds to an increase in phonon population.⁵²

Eq. 2.4

$$I = I_0 e^{\frac{c}{n+1}}$$

2.4 Static and Time-resolved X-ray diffraction

X-ray diffraction provides information about the crystallinity of a sample by measuring the elastic scattering of X-rays off the periodic arrays of atoms within the sample. The diffraction follows Braggs law:

$$\text{Eq. 2.1} \quad n\lambda = 2d\sin\theta$$

where n is an integer, λ is the wavelength of (X-ray) light, d is the spacing between crystal lattice planes and θ is the angle of incident irradiation. For a single crystal, distinct diffraction patterns can be measured and the crystal structure (i.e. unit cell, space group) can be reconstructed. NCs are too small to produce such patterns and therefore measurements of solutions or films gives powder diffraction spectra. If the composition of the NC is already known, say CdSe, then these powder patterns can inform on the crystallinity and polymorph (e.g. wurtzite vs. zincblende). The latter of these two is particularly important for NCs as they may form structures and compositions not common in macroscopic crystals.¹¹⁶⁻¹¹⁷ Fitting the peak lineshape can provide insight into the size of the particles using the Scherrer equation (Eq. 2.2).¹¹⁸ Here, τ is the size of the crystalline domain and K is a dimensionless shape factor.

$$\text{Eq. 2.2} \quad \tau = \frac{K\lambda}{\beta\cos\theta}$$

Time-resolved X-ray diffraction (TR-XRD) is a pump-probe technique that utilizes a visible light pump to excite the sample and X-ray probe to monitor changes in diffraction. This experiment is carried out using a high energy X-ray source (in this case, Argonne National Laboratory's Advanced Photon Source) where colloidal samples are heavily concentrated and flowed using a jet. Similar to TA or FSRS, the pump fluence can be changed as well as the time delay between pump and probe. The diffracted X-rays are collected as a powder pattern and

azimuthally integrated. Due to the small portion of NCs that absorb photons, changes in the diffraction intensity are small. To aid in identifying transient behavior the data is differenced similar to TA (pump on minus pump off).

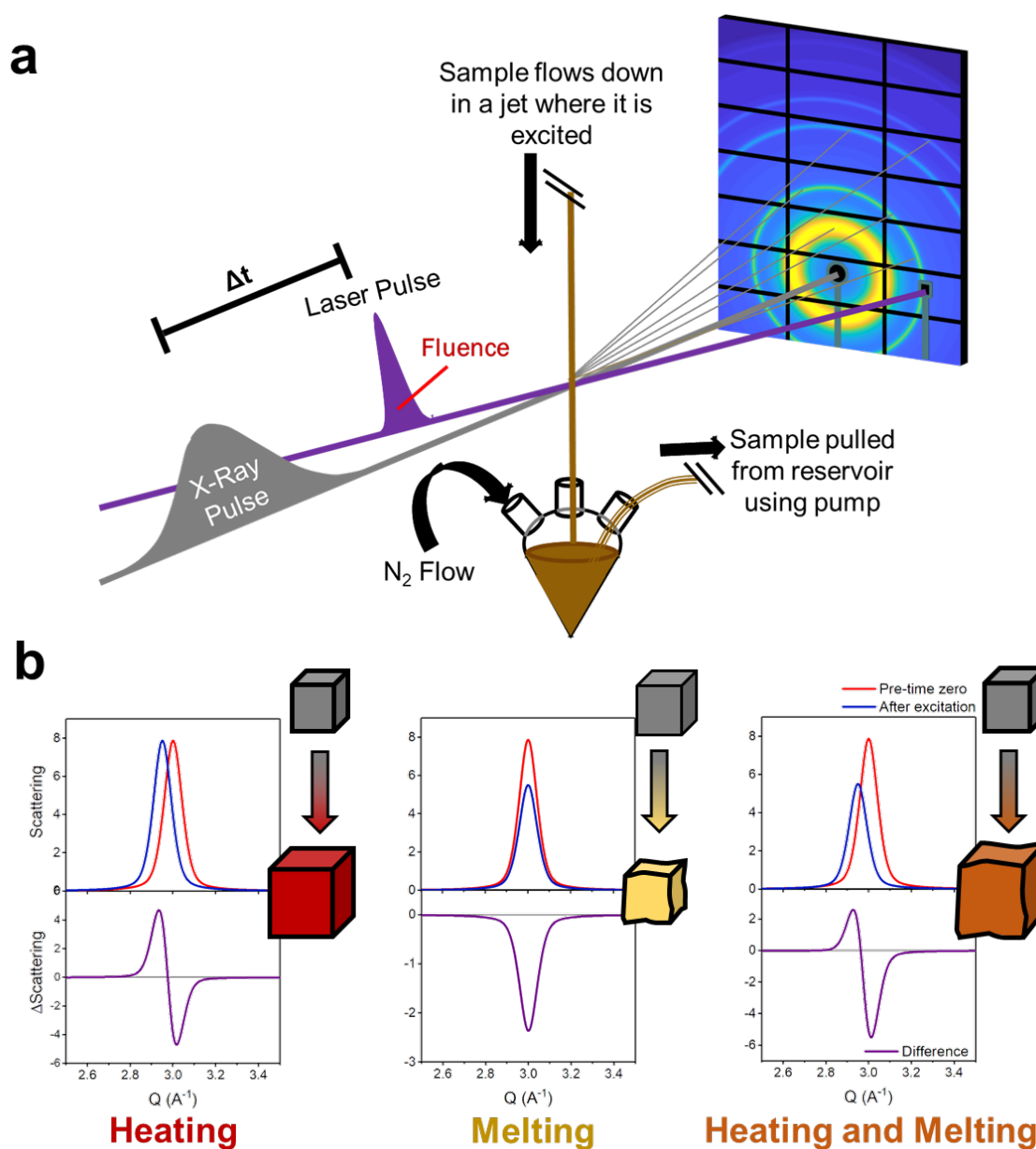


Figure 2.5: Time-resolved X-ray diffraction. (a) Experimental setup. (b) Effects of heating and melting on X-ray diffraction patterns as measured and after differencing.

Photoexcitation may induce several changes to the diffraction patterns (Figure 2.5b). Heating of the NCs causes expansion of the lattice which is seen as a shift to lower Q . After differencing this behavior produces a derivative lineshape. At incredibly high fluences the NCs may become disordered or melt resulting in a loss of diffraction intensity, upon subtraction this is seen as a negative feature. These two cases are not necessarily independent and a combination of a derivative and negative feature may occur as well.

2.5 Electron Microscopy

Electron microscopy is a powerful tool for imaging NCs. Given their incredibly small size transmission electron microscopy (TEM) is often required to image the materials as opposed to scanning electron microscopy (SEM). A subset of TEM, scanning transmission electron microscopy (STEM) allows rastering of the beam across samples, which can provide dark field imaging that may allow better visualization. Both SEM and STEM may be used for energy dispersive X-ray spectroscopy (EDX or EDS) and electron energy loss spectroscopy (EELS) to allow elemental analysis. SEM can be utilized for lithography of and imaging of ordered/assembled NCs. High-resolution TEM (HR-TEM) may permit imaging of lattice fringes, defects, and twinning with the crystal. Electron diffraction can confirm the atomic composition.

Samples are commonly diluted, dropcast onto copper grids (TEM) or silicon wafers (SEM), and allowed to dry. Post-imaging measurements and analysis can provide size distribution as well as morphology. Many new developments in electron microscopy technology have expanded these instruments beyond analytical tools into complex and remarkable experiments. For example, in-situ synthesis¹¹⁹, melting^{8, 120}, and optical experiments¹²¹ are just a few avenues where electron microscopy has proven incredibly useful.

2.6 Nuclear Magnetic Resonance

Nuclear magnetic resonance (NMR) has long been used as an analytical tool for identification of molecular species. For semiconductor NCs it can serve not only as a means of identifying organic ligands, but also their binding status, dissociation, and solvation.¹²² When covalently attached to the surface of the particle, resonances associated with molecular species are broadened and shifted downfield. Integration of these features can be used to identify the quantity of ligands present in the sample when a standard is added (e.g. ferrocene, CH_2Br_2). Furthermore, changes in these resonances has been utilized during ligand exchange to understand binding strengths and ratios of exchanged molecular species. Using isotope labeling can relate whether species on the surfaces of NCs are in constant equilibrium between those in solution or tightly attached.

More complicated 2D NMR techniques such as DOESY or NOESY can help differentiate bound vs. free species as well as diffusion coefficients.¹²² Incorporating different pulse sequences such as those used in dynamic nuclear polarization can provide more detailed information about the complicated surface chemistry of these materials.¹²³⁻¹²⁴ NMR is also not limited to protons and recently the study of other nuclei such as ^{113}Cd and ^{31}P NMR has been utilized to probe the inorganic atoms of semiconductor NCs.¹²⁵⁻¹²⁶ Solid state NMR¹²⁷, variable temperature NMR¹²⁸, and in-situ synthesis¹²⁹ are rapidly expanding uses of this technique.

2.7 Electron Paramagnetic Resonance

Electron paramagnetic resonance spectroscopy (EPR) is analogous to NMR in many ways. Instead of nuclear transitions, EPR uses microwaves to probe electron spin transitions. There are different microwave frequencies commonly used in EPR, such as X band (10 GHz), Q band (35

GHz), and W band (95GHz). In continuous wave (CW) EPR the wavelength of microwave radiation is kept constant while a magnetic field is swept. The magnetic field causes splitting of electron levels due to the Zeeman effect. When this splitting causes transition energies to be resonant with the microwave radiation an increase (absorptive) or decrease (emissive) signal is detected. Hyperfine splitting on top of EPR spectra can provide insight into nearby nuclei. CW EPR spectra are recorded as derivative spectra, thus an absorptive feature would transform into a derivative lineshape.

Transient CW (TCW), also commonly called time-resolved EPR (TREPR), utilizes a similar process with the inclusion of a pulsed laser. Microwave irradiation remains continuous but data is collected as a function of laser time delay and magnetic field allowing monitoring of light-induced spin processes. Notably these spectra are not given as derivatives, thus absorptive and emissive features are in fact due to their respective spin transition directions. While TCW EPR is a powerful technique for many systems, it is particularly enlightening for donor-acceptor spin-correlated radical pairs. TCW spectra can provide insight to into the coupling (J and D) in radical pairs, as well as the lower limit for charge separation lifetimes. Recombination of the radical pair to a triplet state can be differentiated from spin-orbit intersystem crossing as their spectral structure varies.

Pulsed EPR techniques use microwave pulses to manipulate spin states. They can be coupled to a laser to monitor photoinduced processes although this is not strictly necessary. Pulsed EPR allows direct measurement of spin processes without constant microwave irradiation mixing spin states. For the work covered here the Hahn echo sequence is the only type of pulsed-EPR experiment that needs explanation. It is comprised of a laser flash followed by a $\pi/2 - \tau - \pi - \tau - \text{echo}$ sequence where $\pi/2$ and π represent microwave pulse lengths, τ is the waiting time,

and the echo is recorded. Maintaining the magnetic field at one frequency and sweeping tau produces an ESEEM that when fit gives T_2 , spin coherence lifetimes.

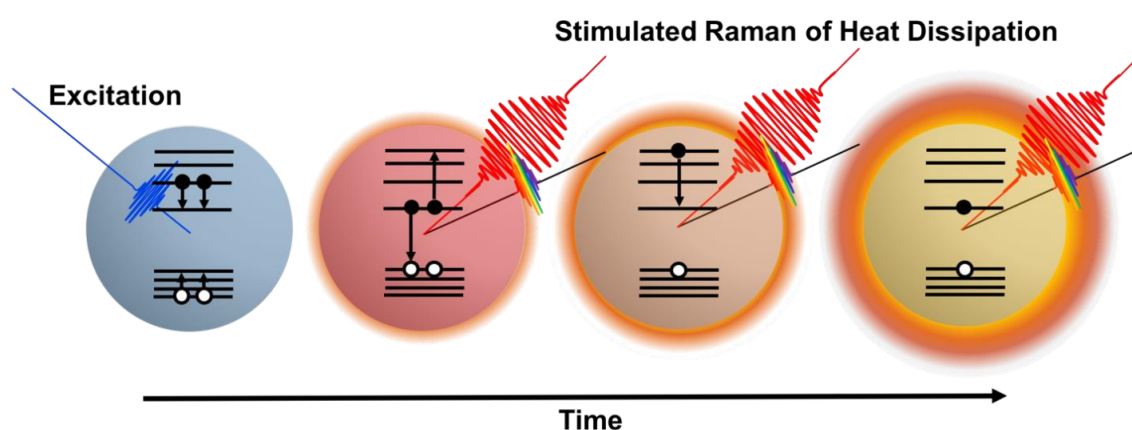
While EPR, both theory and experiment, are well understood and optimized for organic and inorganic compounds, nanoscale semiconductors are an area of research that has not been fleshed out as much. One of the few areas where EPR is used frequently is for identifying the oxidation state of metals in some NCs⁴² (e.g. Cu^+ vs. Cu^{2+}) as well as dopants¹³⁰⁻¹³¹ (e.g. Mn in CdSe). Occasionally parameters such as g-values can be determined in NCs.¹³² Studies of spin in NCs as part of donor-acceptor systems is sparse compared to work on photophysics and use of EPR as a technique to understand spin is an even narrower subset. Work on electron transfer from a molecular species to the QD has been studied by monitoring the EPR spectrum of the donor previously¹³³, but this thesis shows (potentially) the first instance of spin-polarized electron transfer from a QD to a molecule through EPR.³⁷

2.9 Thermogravimetric Analysis and Inductively Coupled Plasma Techniques

Thermogravimetric analysis (TGA) and inductively coupled plasma (ICP) spectroscopy are destructive techniques that can provide insight into the chemical structure of semiconductor NCs and their ligands. TGA uses a microbalance within a furnace to detect changes in mass that occur upon burning of a sample. For semiconductor NCs this is generally the organic ligands burning off, providing information about the relative ratio of organic to inorganic species. When coupled to a gas chromatography-mass spectrometry (GC-MS) instrument, further identification of the organic fragments can be studied. TGA may also provide insight to exothermic or endothermic processes such as phase changes.

For ICP, semiconductor nanocrystals are digested using an acidic solution and burned in a plasma. Using either mass spectrometry (MS) or optical emission spectroscopy (OES) the identity of the inorganic ions, their quantity, and relative ratio can be determined.

Chapter 3: Optical Phonon Processes Measured Using Femtosecond Stimulated Raman Spectroscopy



This chapter is adapted from:

Harvey, S. M.; Phelan, B. T.; Hannah, D. C.; Brown, K. E.; Young, R. M.; Kirschner, M. S.; Wasielewski, M. R.; Schaller, R. D., Auger Heating and Thermal Dissipation in Zero-Dimensional CdSe Nanocrystals Examined Using Femtosecond Stimulated Raman Spectroscopy. *The Journal of Physical Chemistry Letters* **2018**, 9 (16), 4481-4487, with additional unpublished components on InP NCs.

3.1 Introduction

NCs exhibit unique phononic properties that fundamentally alter the behavior of both charge carriers and lattice excitations relative to higher dimensional materials.¹³⁴ Whereas the fundamental behaviors of charge carriers for several NC compositions have been investigated using transient electronic spectroscopy and terahertz conductivity,¹³⁵⁻¹³⁶ less is known regarding the lattice response to electronic excitation. In general, thermal processes and the transfer of heat out of NCs is not well-understood owing to a lack of probes, despite significant influence of thermal energy on optoelectronic properties.^{90, 137-139} For materials with a continuous density of states, such as one- and two-dimensional semiconductor NCs, transient absorption and time-resolved photoluminescence spectroscopies can convey information about electronic and lattice temperatures due to higher-energy lineshape components observed in transient spectra that obey defined functional forms.^{61, 140-141} However, discrete electronic energy levels prevent these observables in zero-dimensional NCs and as such, comparable studies are unavailable. Other investigations on zero-dimensional materials monitor time-averaged behavior, or were performed at cryogenic temperatures.^{65, 142-143} Therefore, lattice relaxation measurements currently present an experimental challenge.

In this study, we investigate lattice dynamics of semiconductor NCs following controlled fluence optical (electronic) pumping. Such excitation produces thermal energy via two main processes. Following creation of above-gap, hot carriers, intraband carrier cooling occurs, which imparts into the lattice any energy in excess of the band-edge.^{49, 99, 144} For electron-hole pairs (excitons) in many semiconductor NC compositions this process occurs on sub-picosecond timescales.¹⁴⁴⁻¹⁴⁵ At elevated intensity, an additional process of Auger recombination (AR) can occur, where one exciton recombines via non-radiative transfer of energy to an additional charge

carrier that subsequently relaxes to the band-edge. AR lifetimes of biexcitons range from tens to hundreds of picoseconds with a well-known linear dependence on particle volume for CdSe,^{56, 146-149} and even faster lifetimes of a few picoseconds for InP.¹⁵⁰ Multiexciton AR rates strongly outcompete radiative recombination of 15-50 ns (298 K) for these compositions.^{44, 150}

Frohlich electron-phonon scattering, the dominant form of carrier cooling in polar semiconductors, is understood to initially generate longitudinal optical (LO) phonons that then scatter into lower energy acoustic modes, producing a quasi-equilibrium within the particle.^{59-60, 151} In CdSe NCs, LO phonons are the only optical mode, though a lower energy shoulder attributed to surface optical (SO) phonons is present that is not observed in the bulk.¹¹¹ InP NCs have two optical phonon modes, a lower frequency transverse optical (TO) mode is present alongside the LO.¹¹⁰ These phonons eventually equilibrate with surrounding media through surface terminations, organic ligands, and solvent.¹⁵²⁻¹⁵³ While femtosecond infrared spectroscopy has seen significant success in monitoring vibrational dynamics,¹⁵⁴⁻¹⁵⁵ the low frequency modes of inorganic NCs prevent application of this technique.¹⁵⁶ Terahertz spectroscopy can probe these low frequency modes; however, the signals are often convoluted with carrier dynamics.¹⁵⁷ Raman scattering can resolve such modes without carrier dynamics affecting signal and with the benefit of using visible light. Hannah *et. al.* showed the potential of using femtosecond stimulated Raman spectroscopy (FSRS) on CdSe NCs to monitor the lattice dynamics following generation of single excitons.⁵² Although FSRS is more commonly used for small organic molecules or bulk crystals, its fluorescence rejection, along with high temporal and spectral resolution make it a promising technique for study of fundamental vibrational processes in NCs.¹¹⁴⁻¹¹⁵

Herein, through pump-fluence-dependent examinations of multiple sizes of CdSe NCs, we observe delayed recovery of LO phonon stimulated Raman gain at elevated fluence. We attribute

this to Auger heating of the lattice due to multiexcitons and, furthermore, reveal that resultant LO phonons recover more slowly than electronic AR, which we suggest corresponds to the timescale of NC cooling owing to the prominence of an acoustic phonon thermalization bottleneck on lattice relaxation via a highly impedance mismatched NC-organic interface. Lastly, we study the interplay of TO and LO phonons in InP NCs upon photoexcitation and find that the TO mode is generated first followed by conversion to LO. Similar to CdSe NCs, increasing power lengthens the cooling rate suggesting Auger heating and a potential phonon bottleneck.

3.2 Auger Heating in CdSe Nanocrystals

Figure 3.1a shows a schematic for a typical FSRS experiment, the details of which have been described previously.¹⁵⁸ A ~ 50 fs actinic pump at 3.1 eV creates a Poisson distribution of hot single excitons or multiexcitons depending on the fluence, where the average number of generated excitons per NC relates to cross-section and fluence, $\langle N \rangle = \sigma j$. Stimulated Raman spectra are then acquired at set time delays by a temporally overlapped ~ 1.5 -2 ps Raman pump and a chirped broadband fs probe pulse. Since the actinic pump is tuned to an energy higher than the band gap, a hot exciton is generated. The interaction of the sample with the probe and leading edge of the Raman pump produces a vibrational coherence. A second interaction with the trailing edge of the Raman pump then stimulates emission of the Raman signal in the direction of the probe. Although not given here, Feynman and energy level diagrams of all resonant FSRS processes have been determined.¹⁵⁹⁻¹⁶² Due to the nature of the Raman pump and probe pulses (the first being much longer than the second) a broad background is produced due to electronic excitation and cross correlation even at negative time delays where there is no actinic pump excitation. Note that only NCs excited by the actinic pump evolve in time.

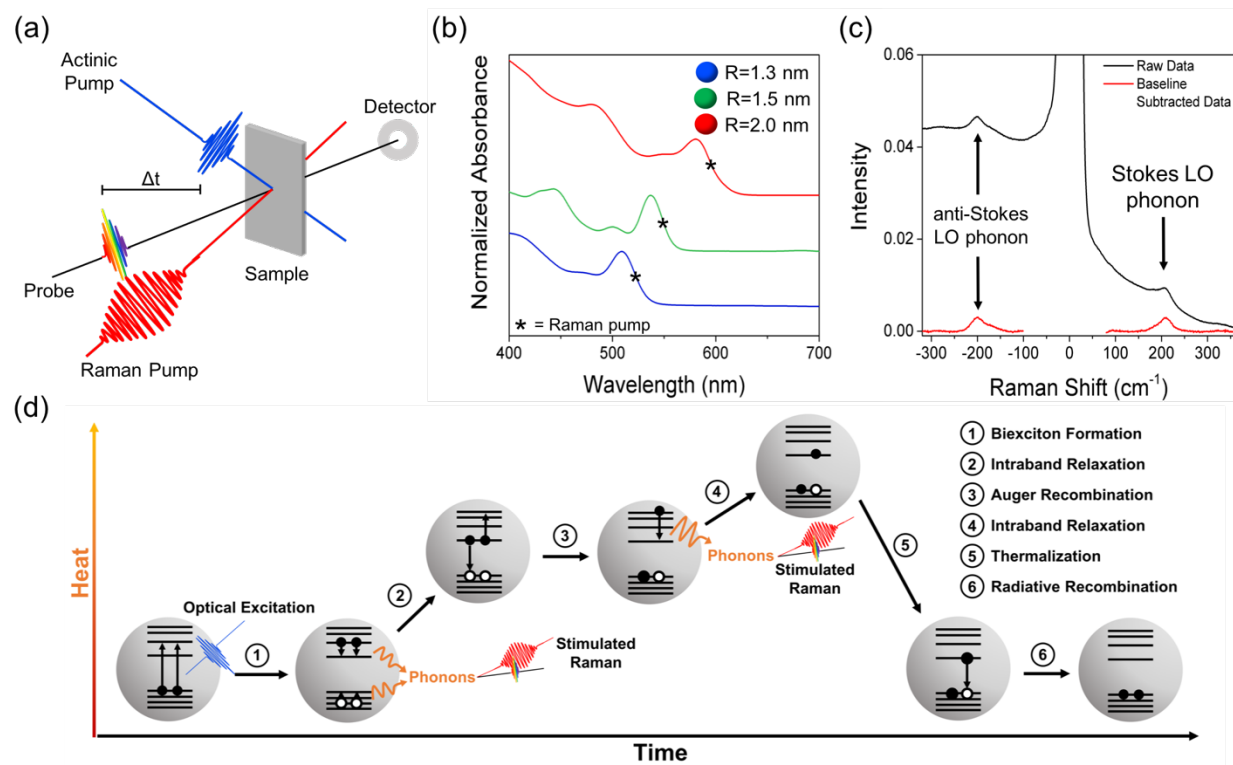


Figure 3.1: (a) Schematic of time-resolved FSRS experiment where the sample is first excited by a femtosecond actinic pump of controlled fluence followed by a pair of pulses at set time delays (Raman pump on the order of picoseconds and a femtosecond chirped broadband probe) that produce stimulated Raman signal. (b) Absorption spectra of the three sample of CdSe nanocrystals. Raman pump wavelength is given as a (*) for each sample. (c) Example of a static FSRS spectrum for $R = 1.3$ nm CdSe. The LO phonon Raman features evident at approximately $\pm 210 \text{ cm}^{-1}$ sit atop a broad background along with the Rayleigh scattering (black line). This background is subtracted before data analysis (red line). (d) Schematic showing the optical excitation of a NC resulting in the creation of two excitons followed by subsequent relaxation and recombination. During intraband relaxation cooling of hot carriers can generate LO phonons causing the NC lattice to become heated. The combination of Raman pump and probe allow stimulated Raman monitoring of these phonons.

Three samples of wurtzite CdSe NCs dispersed in hexanes were studied as a function of fluence with radii ranging from 1.3 to 2.0 nm. For each, the Raman pump was tuned to the low-energy side of the absorption full-width half-maximum (FWHM) to ensure resonance and minimize absorption of the Raman pump as shown in the absorption spectra in Figure 3.1b. Such placement yields resonance enhancement of both ground and excited state phonon modes.

However, since unexcited NCs do not evolve in time, and negligible population decays on sub-nanosecond timescales, we monitor excited state dynamics. Figure 3.1c shows how the Rayleigh scattered and stimulated Raman features sit atop the aforementioned broad background. The Stokes and anti-Stokes peaks near positive and negative 210 cm^{-1} respectively, correspond to LO phonons with a surface optical (SO) phonon as a second peak around 180 cm^{-1} .^{156, 163} LO phonons are dipole-changing, out-of-phase vibrations of atoms within the unit cell while SO phonons are believed to arise owing to dangling bonds at the NC surface, though this is an area of debate.^{111, 156} It has been previously reported that the dynamics of the LO and SO phonons are indistinguishable and therefore we focus on LO phonons in this study.⁵² In order to analyze the dynamics of these features, the peaks and background were simultaneously fit to a sum of Gaussians and a polynomial, respectively, allowing separation of Raman and background. Throughout this chapter, peak intensity and peak position/shift correspond to the LO phonon modes with the former being represented by the peak area of the Gaussian fit and the latter by the maximum. In Figure 3.1d we summarize the processes occurring upon creation of a biexciton. Unlike single excitons, which only undergo one excitonic intraband relaxation, the creation of biexcitons causes each of two excitons to relax to the band edge and, following AR, undergo intraband relaxation yet again upon creation of a single hot exciton. LO phonons are produced during each of these relaxation steps, which we are able to monitor using the stimulated Raman signal described above.

As previously reported, stimulated Raman scattering intensity depends exponentially on the inverse of the LO phonon occupation number.⁵² Upon low fluence actinic excitation corresponding to formation of single excitons in the NCs, the intensity of the Stokes and anti-Stokes LO phonon Raman features deplete on a sub-picosecond timescale during intraband cooling

to the band edge, as known from reports using electronic spectroscopy.^{49, 99, 144} This initial FSRS depletion conveys lattice excitation specifically arising from generation of LO phonons. After depletion, stimulated Raman signals show recovery as the LO phonon population decreases via scattering into lower energy acoustic phonons until a quasi-equilibrium is reached. This collection of phonons then thermalizes with the surrounding media such as ligands and solvent.^{52, 142}

Increasing actinic pump fluence results in formation of more than one exciton in some NCs. As $\langle N \rangle$ is increased, the amplitude of the peak depletes more until it eventually disappears as shown in Figure 3.2a where Stokes and anti-Stokes features are given at 100 fs and compared to negative time delays. We see the complete disappearance of the LO phonon mode at sufficiently elevated pump intensity, meaning loss of Raman gain which suggests large LO and acoustic populations. In addition, the recovery for NCs that contain more than one exciton takes notably longer to return to the initial intensity than for the population excited with single excitons, as shown in Figure 3.2b, where the intensity of the Stokes peak for the $R = 2.0$ nm CdSe NCs is plotted as a function of time. Note, the signal is normalized at negative time delays to allow comparison. Here, the increased number of excitons causes additional heat generation upon relaxation to the band edge both before and after AR, which in turn causes the NCs to take longer to reach equilibrium.

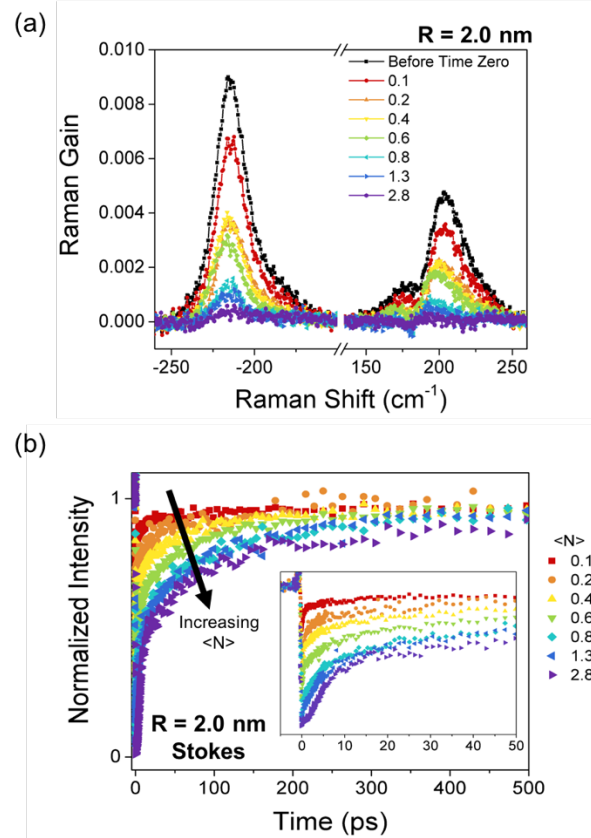


Figure 3.2 (a) Baseline-subtracted data for the R = 2.0 nm CdSe NCs at $t = 100$ fs as a function of $\langle N \rangle$. (b) Dynamics of the Stokes LO phonon for the R = 2.0 nm CdSe NCs normalized at negative time delays. As $\langle N \rangle$ is increased the signal depletes and recovery is slowed. Inset shows the same dynamics at early time delays.

In order to evaluate the effects of elevated fluence on LO phonon dynamics, the single exciton dynamics were subtracted from data acquired using higher pump fluences. This was accomplished by fitting each dataset with both the single exciton fit determined from low fluence data (where relative amplitudes and time constants were fixed, but allowed to float collectively in amplitude) and one or two more exponentials for multiexciton components. Figure 3.3a shows differenced data for the Stokes feature of the R = 2.0 nm CdSe NCs where the single exciton component has been subtracted. Here, the data are inverted to facilitate visualization. As the population of multiexcitons in the NC sample increases, a ~ 100 ps recovery time component

builds in along with an additional, less prominent, faster component (<10 ps) at very high fluence. Similar measurements exhibit a clear size dependent trend as shown in Figure 3.3b where the differenced data for each CdSe NC sample is shown, here for $\langle N \rangle$ in the range of 1.0 to 1.3. Similar to AR, as the size of the NC increases, the lifetime becomes longer, from about ~ 15 ps for the smallest NC to ~ 100 ps for the largest. This signal is attributed to Auger heating where the resultant hot exciton produced upon biexciton annihilation generates additional LO phonons upon cooling, but with the following additional observable.

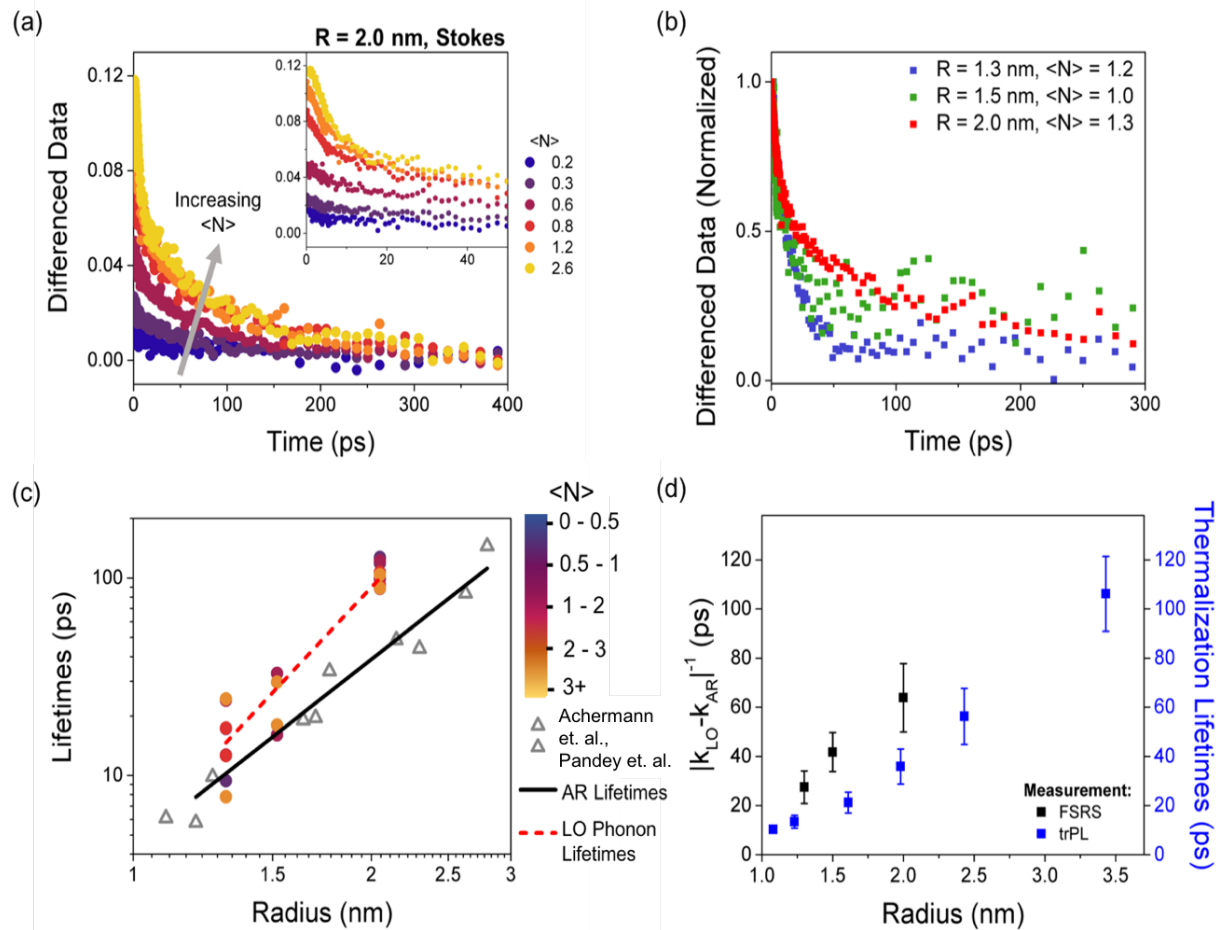


Figure 3.3 (a) Differenced data for the Stokes feature of the $R = 2.0$ nm CdSe NCs. Single exciton dynamics have been subtracted to show effects due to multiexcitons. Early time delays are given in the inset. (b)

Multiexciton dynamics for the three samples with $\langle N \rangle$ between 1.0 and 1.3. Larger NCs show longer decay lifetimes similar to trends for AR. (c) Comparison of AR lifetimes¹⁴⁷⁻¹⁴⁸ with those found in this study plotted on a log-log scale. FSRS recovery lifetimes are appreciably longer than electronic AR for all three sizes of NCs. Included are fits from multiple $\langle N \rangle$ given as different colors to represent a spread in data. Solid black represents a fit to AR lifetimes from the literature, while the dashed line is a guide to the eye for the LO Phonon lifetimes. (d) Thermalization lifetimes determined from comparison of electronic Auger recombination lifetimes and FSRS lifetimes compared to an indirect evaluation of thermalization based on transient photoluminescence (trPL) at cryogenic temperatures.¹⁴²

After fitting the FSRS recovery dynamics in this regime of elevated fluence, where Auger recombination should occur, we compared dynamics to literature AR time constants measured by electronic transient absorption, which we stress exhibit sensitivity to the electronic, charge carrier populations and not lattice response (Figure 3.3c). Even with some spread in observed lifetimes measured for varied values of $\langle N \rangle$ relating multiexciton populations, our multiexciton-derived FSRS recovery time constants clearly exhibit longer lifetimes than those reported for electronic relaxation processes. We attribute this increase in lifetimes to a phonon buildup in NCs where a quasi-equilibrium of LO phonons and acoustic phonons are produced as a consequence of Auger heating of the lattice. With the NC achieving an elevated temperature quasi-equilibrium, LO phonon populations decay more slowly, slowing FSRS signal recovery to yield a lifetime that exceeds that of the biexciton. We attribute this slow decay to impedance mismatch between the inorganic lattice and the organic interface, which doesn't allow acoustic phonons to transfer to ligand or solvent efficiently. Importantly, this delayed recovery appears because thermalization occurs following electronic AR with a finite lifetime. We evaluate the apparent thermalization rates for different samples via comparison of elevated-fluence FSRS data and those of Auger recombination,²⁶⁻²⁸ recognizing that observed recovery dynamics in FSRS arise from a convolution of AR heating, which generates LO phonons, and subsequent thermalization (Figure 3.3d). These thermalization lifetimes are sensitive to size of the NC and increase with the NC

radius, though we are not certain of the functional form. Interestingly, the observed rates, here measured for NCs in liquid dispersion near ambient temperature, correspond approximately with rather different thermalization measurements based on instantaneous radiative rate at cryogenic temperatures in a solid alkane dispersion that we reported previously.¹⁴² It is important to point out however that multiple temperature dependent variables including particle and medium heat capacities, linear thermal conductivity, and an unknown interfacial thermal conductivity, make this similarity only incidental, yet comparable in terms of size-dependent trend and timescale magnitude.¹⁶⁴

We also consider the fast component observed at higher $\langle N \rangle$ for each sample. While initially thought to relate to triexciton decay, when plotted against lifetimes the literature data does not correlate well (Figure 3.4).¹⁴⁶ Notably our lifetimes seem to be less size dependent and also faster than the triexciton lifetimes, suggesting a different source. We rule out Auger ionization, which we expect would exhibit longer timescales,⁵⁴ as well as charged multicarrier recombination due to rapid stirring of the sample. Further studies may elucidate the processes contributing to this effect. We believe that any triexciton or higher-order exciton decay would contribute to the acoustic phonon thermalization bottleneck instead of resolving as another feature. Slowed rates of thermalization have been discussed in the literature for the onset of electron-hole plasma generation that effectively screens charges.^{140, 165} We do note that there did not appear to be a clear trend in lifetime with $\langle N \rangle$ however.

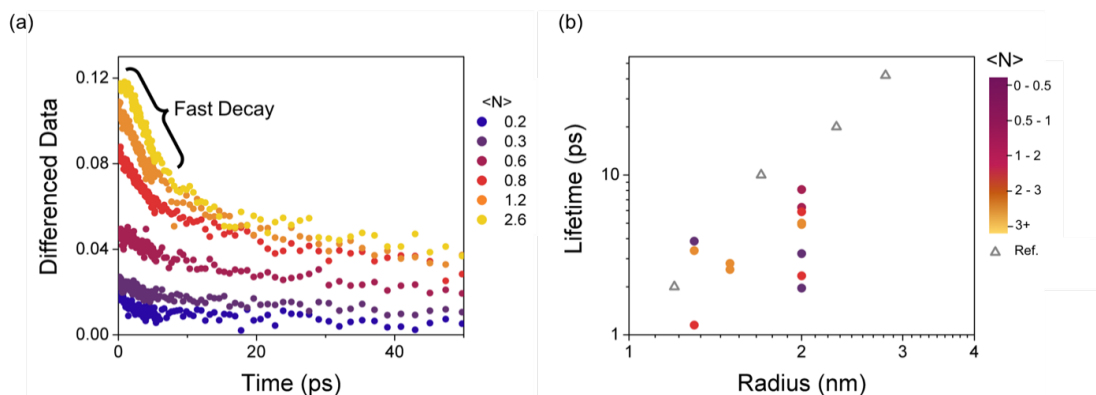


Figure 3.4. (a) Reprint of the inset from Figure 3.3a ($R = 2.0$ nm CdSe, Stokes) highlighting the fast decay. (b) Lifetimes of fast decay component compared to triexciton lifetimes from the literature¹⁴⁶ on a log-log plot. Multiple excitation fluences for a given particle radius relate some variability in fitting of lifetimes.

In addition to trends in the magnitude of the LO phonon modes, we evaluated the fitted LO phonon peak position vs excitation fluence. This is shown in Figure 3.5 for the Stokes LO phonon feature of $R = 2.0$ nm. Upon optical excitation, the peak shifts to lower frequencies before recovering. The shift clearly depends on fluence, shifting beyond 5 cm^{-1} for the highest examined values of $\langle N \rangle$. We attribute this to increasing mode softening in the NCs as more disorder arises in the particles upon increasing phonon generation that, for sufficient fluences, leads to loss of crystalline order and, e.g. reduced X-ray diffraction.⁶⁵

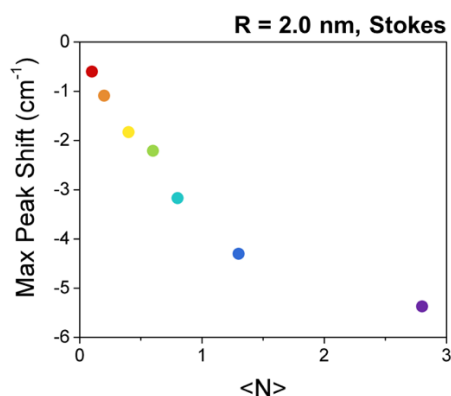


Figure 3.5 Max peak shift at ~ 100 fs for as a function of $\langle N \rangle$. As $\langle N \rangle$ increases the peak shifts to lower frequencies (more negative). Colors denote the same $\langle N \rangle$ as given in Figure 3.2.

Up until this point, focus has been on the Stokes features as they were the most easily distinguishable and were studied in the previous FSRS work. While the magnitude of peak depletion and peak shift were nearly identical for both Stokes and anti-Stokes features their lifetimes differed substantially. Figure 3.6a-b show peak shift as a function of time for the Stokes and anti-Stokes LO phonon mode respectively. Both show an increase in peak shift as fluence is increased, however the anti-Stokes feature recovers almost instantly compared to the Stokes. Peak intensity for the two features after photoexcitation is much more similar, yet even these are not identical. Consistently the anti-Stokes recovered faster than the Stokes as seen in Figure 3.6c. The reasoning behind these behaviors remains elusive, yet may potentially point to differences in carrier distribution that may provide insight to effective temperature.¹⁶⁶

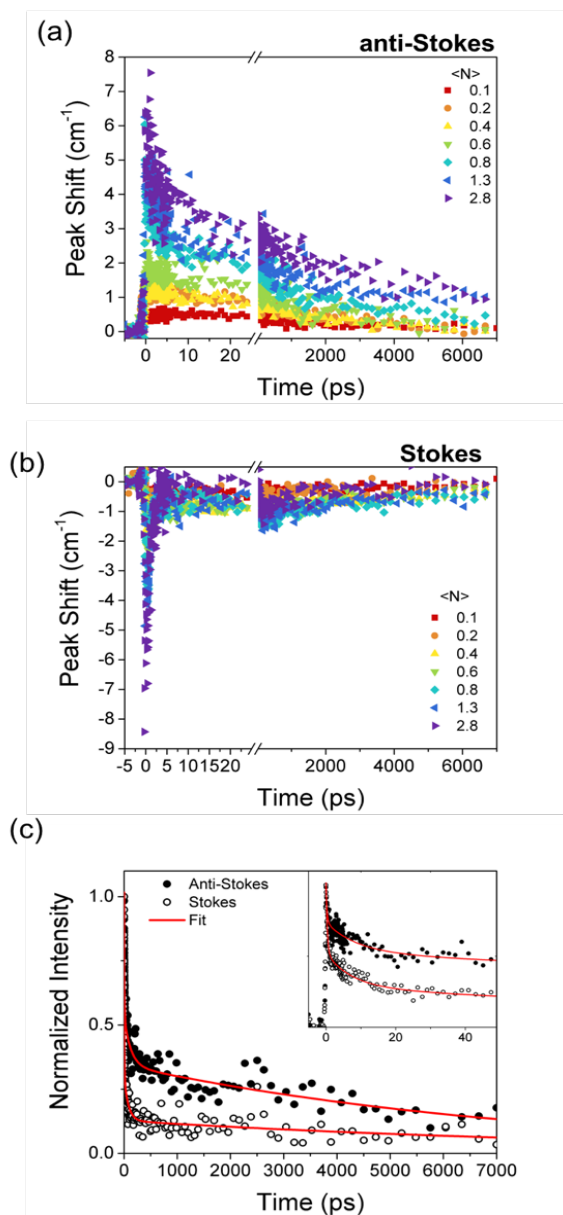


Figure 3.6 CdSe NC with $R = 2.0$ nm, (a) and (b) peak shift for the anti-Stokes and Stokes LO phonon mode respectively as a function of $\langle N \rangle$, (c) comparison of Stokes and anti-Stokes single exciton LO phonon dynamics with fits.

3.3 Transverse and Longitudinal Optical Phonons in InP

InP NCs have garnered interest as a potential replacement for more toxic Cd-based semiconductors. With tunability across similar wavelength ranges as CdSe they are a very active area of research and have seen commercial success in QLED TVs. However, many of their

photophysical properties remain unstudied and work on thermal properties mostly non-existent. Unlike CdSe NCs, InP has two optical modes, a transverse mode around 307 cm^{-1} and a longitudinal mode around 344 cm^{-1} .¹⁶⁷ Static Raman spectra of InP NCs has shown that the intensity of these modes depends on the size of the particle, but no studies have been undertaken to understand how photoexcited carriers couple to these modes. Here, preliminary work on using FSRS to monitor the dynamics of both the LO and TO phonon in a sample of InP NCs is shown.

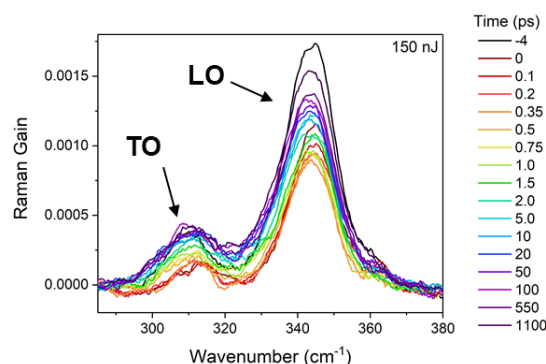


Figure 3.7: Transverse optical (TO) and longitudinal optical (LO) phonon modes in InP from -4 ps before excitation to ~1 ns after. Depletion of FSRS signal indicates generation of phonons.

InP NCs capped with myristic acid and a lowest energy absorption of 600 nm were studied. The actinic pump was kept at 400 nm for both FSRS and TA experiments, while the Raman pump was placed at 640 nm. An example of the Stokes Raman spectrum is given in Figure 3.7 where the TO and LO phonon modes labeled at 311 and 344 cm^{-1} respectively. Upon photoexcitation depletion of the features signifies generation of phonons from intraband relaxation, with both peaks depleting rapidly. Recovery is slow with the TO mode returning to pre-time zero intensity in about 50 ps and the LO showing reduced intensity past 1 ns.

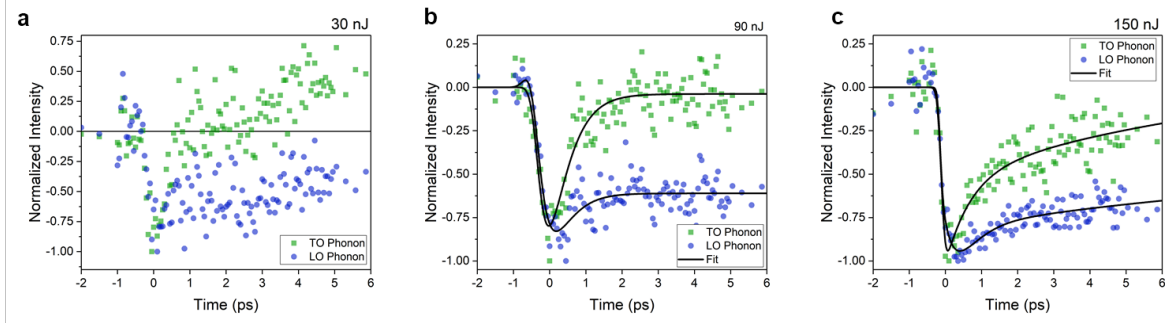


Figure 3.8: Peak intensity as a function of time for (a) 30 nJ, $\langle N \rangle = 0.6$, (b) 90 nJ, $\langle N \rangle = 1.8$, and (c) 150 nJ, $\langle N \rangle = 3.1$.

To more carefully monitor the early time dynamics the peaks were fit to two Gaussians functions using the same procedure as CdSe NCs analysis. Normalized peak intensity as a function of time for three different powers (30 nJ, 90 nJ, 150 nJ) is given in Figure 3.8. These correspond to $\langle N \rangle$ values of 0.6, 1.8, and 3.1 respectively, (while single exciton regime dynamics are preferred, the low signal to noise precluded collection). For all three powers, depletion of the TO mode occurs first followed by the LO mode shortly after. Fits in the two higher powers are provided to serve as guides to the eye given the noise and minimal difference in time. It is unusual that the lower energy mode seems to transfer its energy to a higher energy, although the difference between them is only a few meV. Potentially, the TO mode couples better to electrons, while the LO mode couples to acoustic phonons. As $\langle N \rangle$ is increased the lifetimes of both phonon features lengthen, likely due to increased Auger recombination. The short lifetime for Auger in InP (a few picoseconds) is much shorter though than the lifetimes seen here suggesting that a phonon bottleneck is occurring in this material as well.

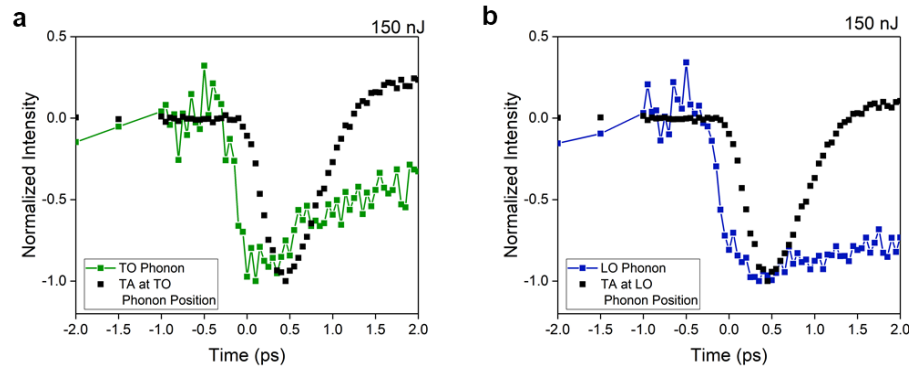


Figure 3.9: TO (a) and LO (b) phonon peak intensity compared to TA signals at the same white light spectral position.

As a last check TA measurements were performed using the same spectral window as FSRS; the results of this are shown in Figure 3.9. Phonon generation occurs as soon as photoexcitation of the sample occurs. Importantly the TA dynamics are identical at the two spectral positions where the Raman modes are present. Given the nature of FSRS, Raman signals appear in conjunction with the white light probe and therefore temporal chirp does exist. However the very short spectral difference between the area of white light where the TO and LO phonons are monitored means that chirp is not a concern and any differences in timing for depletion are real.

3.4 Conclusion

In conclusion, we have shown, for the first time, the effects of Auger heating due to AR on lattice dynamics for zero-dimensional semiconductor NCs, here of CdSe, using FSRS to monitor LO phonon populations. The process of Auger recombination generates a significant population of LO phonons within the NC core. FSRS signals related to the Auger heating phonons decay more slowly than electronic Auger recombination, which we relate to a quasi-equilibrium and an acoustic phonon bottleneck that dictates thermalization and net heat outflow, causing decay lifetimes that exceed reported Auger recombination lifetimes. By analyzing three sizes of CdSe

NCs, we determined lifetimes of thermalization that increase with particle size. Furthermore, we note peak shift and therefore disorder in the crystal increases with $\langle N \rangle$. InP NCs exhibit two optical phonon modes, a lower energy TO mode and a higher energy LO mode. Upon photoexcitation, generation of TO phonons occurs immediately before they couple to LO modes. Recovery of FSRS signal, and therefore thermal dissipation lifetimes increase with higher power similar to CdSe. FSRS signals persist for longer than Auger recombination suggesting a phonon bottleneck in this material as well.

3.5 Outlook

As it stands, FSRS is still a vastly underutilized technique for monitoring generation and dissipation of heat in semiconductor NCs, likely due to a combination of scarcity and difficulty. It is further complicated by some inorganic systems showing little to no FSRS signal even with clear spontaneous Raman. Despite this, there is much to be studied here as there is so little known. Many groups have worked on improving this technique and expanding it in interesting directions (e.g. incorporating microscopy with FSRS for spatial resolution,¹⁶⁸⁻¹⁶⁹ higher rep rate lasers to improve signal to noise,¹⁷⁰ different setup configurations¹⁷¹⁻¹⁷²).

Even within systems such as CdSe, many parameters can be changed, optimized, and exploited. What effects do wavelength (both AP and RP) have on signal? One would assume that exciting at the bandedge with very low fluences ($\langle N \rangle \ll 1$) would result in hardly any phonon generation as intraband relaxation and Auger recombination are shut off, but is a noticeable difference observed as the AP is moved from 400 nm closer to the bandedge? The Raman pump is consistently placed on the red side of the lowest energy absorption, yet it just needs to be resonant with an electronic transition. Can it be placed higher in energy with similar results?

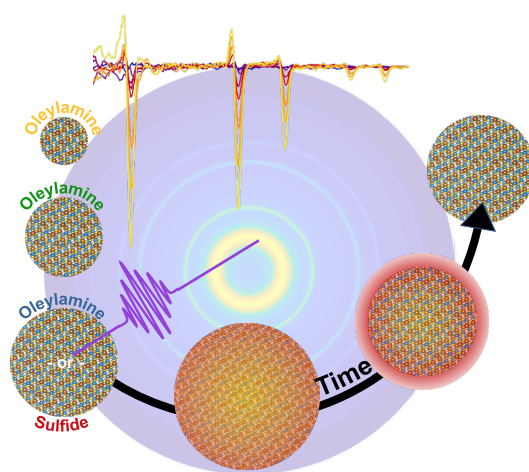
What other Raman features besides optical phonons can be explored? With high enough resolution and careful reduction of scattering can low-frequency acoustic phonons be monitored? What about vibrations due to organic species such as ligands or intercalated molecules (e.g. methylammonium in perovskites)?

Given the importance of solvent and ligand vibrations to cooling in semiconductor NCs, can the rates of phonon dissipation be modulated by exchanging native ligands and solvent? Would small inorganic ions allow faster cooling as was seen in CuInSe₂ TR-XRD?⁶⁴ Does the bulkiness of the solvent affect its ability to interact with ligands and the surface?

And finally, but perhaps most attainable, what can we learn about other compositions? The field of semiconductor NCs has allowed a variety of compositions beyond CdSe to be readily synthesized. Expansion of II-VI compositions and the III-V, I-III-VI₂, and perovskite semiconductors are all ripe for study using FSRS and there is much to be learned about their phononic properties.

Ideally FSRS would join other complicated spectroscopies such as impulsive stimulated Raman spectroscopy, 2D electronic spectroscopy, 2D infrared spectroscopy, and pump-pump/two pump/pump-dump transient absorption spectroscopy as an important tool for understanding photophysical processes in semiconductor NCs.

Chapter 4: Thermal Properties of CuInSe₂ Examined using TR-XRD



This chapter is adapted from:

Harvey, S. M.; Houck, D. W.; Kirschner, M. S.; Flanders, N. C.; Brumberg, A.; Leonard, A. A.; Watkins, N. E.; Chen, L. X.; Dichtel, W. R.; Zhang, X.; Korgel, B. A.; Wasielewski, M. R.; Schaller, R. D., Transient Lattice Response upon Photoexcitation in CuInSe₂ Nanocrystals with Organic or Inorganic Surface Passivation. *ACS Nano* 2020, *14* (10), 13548-13556.

4.1 Introduction

Colloidally synthesized semiconductor nanocrystals (NCs) offer the prospect of electronically tailorable inks, which can be deposited as thin films for light-emitting diodes¹⁷³ or photovoltaics.¹⁷⁴ Significant interest exists in passive or active patterning of these materials to obtain superlattices¹⁷⁵⁻¹⁷⁶ or printed electronics.¹⁷⁷⁻¹⁷⁸ Due to quantum confinement of electron-hole pairs (often referred to as excitons regardless of binding energy), NCs can exhibit optoelectronic properties that differ substantially from bulk counterparts and are electronically tunable through size and shape.^{12, 55} At the same time, reducing particle size to the nanoscale also impacts thermal behavior and elevates the importance of interfacial phenomena. For instance, NCs exhibit highly active surfaces and substantial melting point depression compared to the bulk owing to high surface energy.^{8, 179-181} Thus, particles can, desirably or undesirably, sinter together into more spatially extended, bulk-like solids under temperature elevation or local methods such as pulsed laser annealing.^{66, 182-185} In the latter of these approaches, above-bandgap optical excitation produces intraband-relaxation induced heating as electronic carriers cool *via* phonon scattering,^{49, 144} and, for excitation regimes that produce multiple excitons per particle, Auger recombination annihilates excitons to produce hot carriers that subsequently impart thermal energy into the lattice.^{54, 146} Investigations into the effects of heating in NCs significantly lags research on their synthesis and optoelectronic properties. Namely, the correlation of excitation fluence, effective lattice temperature, and rates of cooling remain poorly characterized.^{57, 61, 186} With improved understanding of these behaviors, the physical response of NCs can be better predicted and controlled.

CuInSe₂ NCs in particular are of interest for their solution processability and a bulk-phase near-infrared bandgap (1.02 eV at 298K) comparable to that of silicon (1.1 eV).¹⁸⁷⁻¹⁹⁰ Additionally

this composition is a less toxic alternative to common semiconductor NCs such as CdSe or $\text{CH}_3\text{NH}_3\text{PbI}_3$.¹⁹¹ These properties have led to their incorporation into thin film solar cells. CuInSe₂ NCs can be drop casted¹⁹²⁻¹⁹⁵ or sintered to produce uniform, highly conductive, bulk-like thin film photovoltaics,¹⁹⁶⁻¹⁹⁷ with record efficiencies up to 15% for bulk¹⁹⁸ and 7% for NCs.^{189, 199-200} Sintering is often performed either under sustained elevated temperatures in the presence of selenium vapor or by rapid photonic curing,^{66, 197, 201} where the latter offers the prospect of retaining quantum confinement while increasing conductivity. Another broadly researched method for improving devices is substitution of the highly insulating, synthetic ligands for small inorganic ions that improve carrier mobility between the NC cores by reducing spatial separation thus facilitating charge transport.^{75, 202-204}

Here, we examine structural responses to photo-induced thermal effects in CuInSe₂ NCs as a function of particle size as well as the impacts of altering surface chemistry from the insulating organic ligand, oleylamine (OLAm), to a short inorganic ligand, S^{2-} . Time-resolved X-ray diffraction (TR-XRD) allows us directly to monitor the effects of optical excitation on the crystalline lattice as functions of both laser fluence and time delay between excitation and X-ray pulses. From this technique, we can monitor the effects of rapid deposition of thermal energy upon intraband relaxation and Auger recombination.^{61, 63, 65, 186} We find size-dependent melting thresholds and recrystallization dynamics where larger NCs require higher numbers of absorbed photons (and, thus, excitons) to melt and longer timescales to return to equilibrium. Exchange to S^{2-} ligands does not appreciably impact melting threshold, however the sulfide-capped NCs recover much more quickly than the OLAm counterparts. Fitted cooling times relate order-of-magnitude higher interfacial thermal conductivity for the S^{2-} ligand. Finally, we perform

temperature-dependent, static X-ray diffraction calibrations to quantify transient lattice expansion as well as to determine effective lattice melting temperature.

4.2 Experimental Methods

Synthesis of CuInSe₂ Nanocrystals

5 mmol CuCl (0.49 g), 5 mmol InCl₃ (1.11 g), 10 mmol Se (0.79 g), and 40 mL oleylamine was loaded into a 100 ml 3-neck flask in a nitrogen filled glovebox. The flask was sealed and transferred onto a Schlenk line. The reaction mixture was held under vacuum (< 200 mtorr) at 110 °C for 12 h to degas and allow precursor complexes to form. The flask was then filled with nitrogen and heated to a reaction temperature of 200 °C, 220 °C, or 240 °C for 10 min, with higher reaction temperatures yielding larger nanocrystals (NCs). The heating mantle was then removed, and the reaction mixture was allowed to cool below 60 °C.

Next, the NCs were purified with two precipitative isolation steps. The crude reaction solution was transferred into centrifuge tubes and 40 mL of ethanol was added to precipitate the NCs. The solution was centrifuged at 2600 rcf for 10 min and the clear supernatant was discarded. The precipitated NCs were redispersed in 10 ml of toluene and centrifuged again at 2600 rcf for 10 min. The well dispersed NCs in the supernatant were transferred to another centrifuge tube and 10 mL of ethanol was added. The solution was centrifuged again at 2600 rcf for 10 min and the clear supernatant was discarded. The purified NCs were dispersed once more in 5 mL of toluene and centrifuged a final time at 2600 rcf to remove any poorly capped particles. The nanocrystal solution was then dried by rotary evaporation, weighed, and transferred to a nitrogen filled glovebox. Finally, the NCs were dissolved in anhydrous toluene at a concentration of 100 mg/mL. In this state, the NCs retain colloidal stability for months to years. For X-ray diffraction experiments NCs were dried under nitrogen and dispersed in dodecane.

Na₂S Ligand Exchange

In a nitrogen filled glovebox, 260 mg (3.33 mmol) Na₂S was dissolved in 3 mL of formamine. 3 ml of CuInSe₂ NCs dissolved in toluene at a concentration of 100 mg/mL was then added to the Na₂S solution, which formed a biphasic mixture. The solution was stirred for 2 hrs, during which time the NCs transfer from the toluene phase to the formamine phase. The clear toluene phase is then decanted. Clean toluene was then added, the solution was shaken, and the toluene was decanted again to remove any residual oleylamine ligand. This toluene rinse was repeated 2 more times. Next, the solution was centrifuged at 2600 rcf for 5 min. The clear supernatant was discarded, and the NCs were dispersed in 5 mL of methanol. 5 mL of toluene was then added to precipitate the NCs and the solution was centrifuged again at 2600 rcf for 5 min. The clear supernatant was discarded and the methanol/toluene precipitation procedure was repeated 2 more times, for a total of 3 precipitative isolation steps. The purified S²⁻ capped NCs were then transferred into a nitrogen filled glovebox and dispersed in anhydrous methanol where they retained colloidal stability for months to years. The NCs were dried and dispersed in DMF prior to X-ray diffraction experiments. FTIR experiments confirmed complete ligand exchange from oleylamine to S²⁻.

4.3 Results and Discussion

We synthesized three CuInSe₂ NC ensembles with average diameters of 3.4, 5.4, and 10.8 nm, herein referred to as small, medium, and large particles, using published methods.^{189, 205} The surfaces of these NCs were passivated during synthesis with OLAm ligands and dispersed in dodecane for XRD experiments. As described in the Experimental Methods Section (4.2), a portion of the large NCs were separately ligand-exchanged using Na₂S to replace the surface

functionalization with sulfide anions (S^{2-}), a common inorganic capping agent,²⁰³ and dispersed as a stable colloidal solution in more polar dimethylformamide (DMF). FTIR in the the samples before and after ligand exchange confirm complete replacement of OLAm by S^{2-} (Figure 4.1b). The static XRD patterns of all four samples appear in Figure 4.1a and match calculated reflections of the chalcopyrite crystal structure.²⁰⁶ As the NCs decrease in size, diffraction features increase in width owing to Scherrer broadening (Figures 4.1, 4.3). Both large NC samples exhibit similar diffraction peak linewidths, with a slight increase of full-width half-maximum (FWHM) for the S^{2-} sample indicating that the ligand exchange caused minimal reduction in size. Transmission electron microscopy (TEM) evaluation of particle size (Figure 4.2) also shows an average diameter of 10.2 nm for the large, S^{2-} sample compared to 10.8 for the OLAm sample with overall shape unchanged. Figure 4.2 displays images of all NC samples, which are approximately spherical though they tend to aggregate when dried on a grid. Steady-state absorption spectra of the samples in Figure 4.1c show broad band-edge absorption, characteristic of this material composition, with an onset in the near-infrared that extends through the visible. The lowest-energy transition for each sample is marked with a circle, as well as the laser excitation wavelength (400 nm, grey bar) used in TR-XRD experiments. We note that the transition for the large S^{2-} is bluer than that of the OLAm sample due to the difference in size.

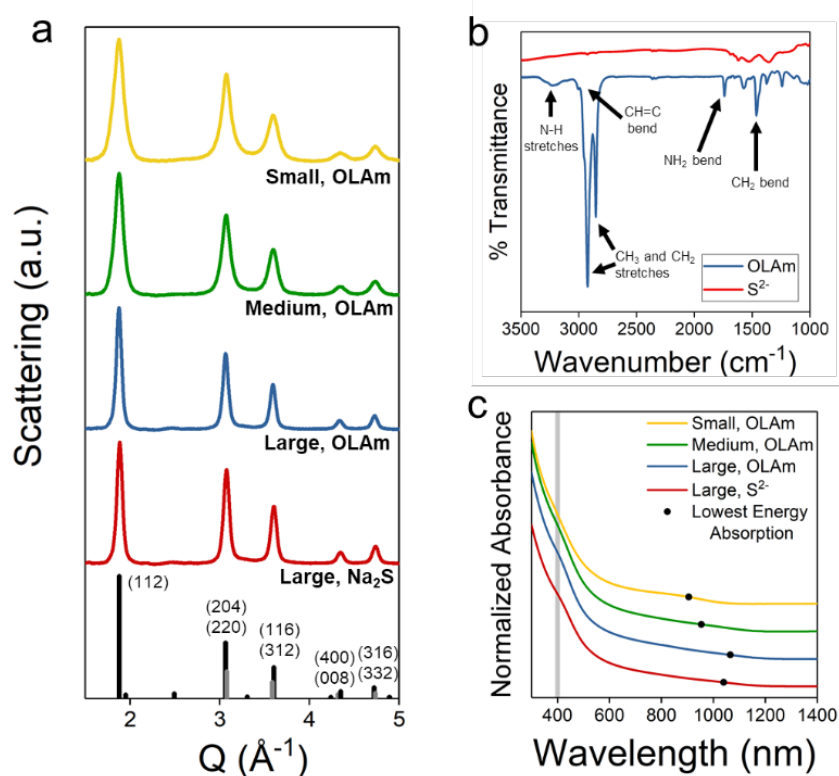


Figure 4.1: Static characterization of CuInSe₂ NCs: (a) Static X-ray diffraction patterns of the four studied samples showing the chalcopyrite diffraction peaks as labeled. (b) FTIR spectra of the large samples showing the loss of OLAm features upon ligand exchange (c) Normalized and offset steady-state absorption spectra with marker denoting the lowest-energy absorption peak and grey vertical bar indicating optical pump excitation wavelength for the TR-XRD experiments (400 nm).

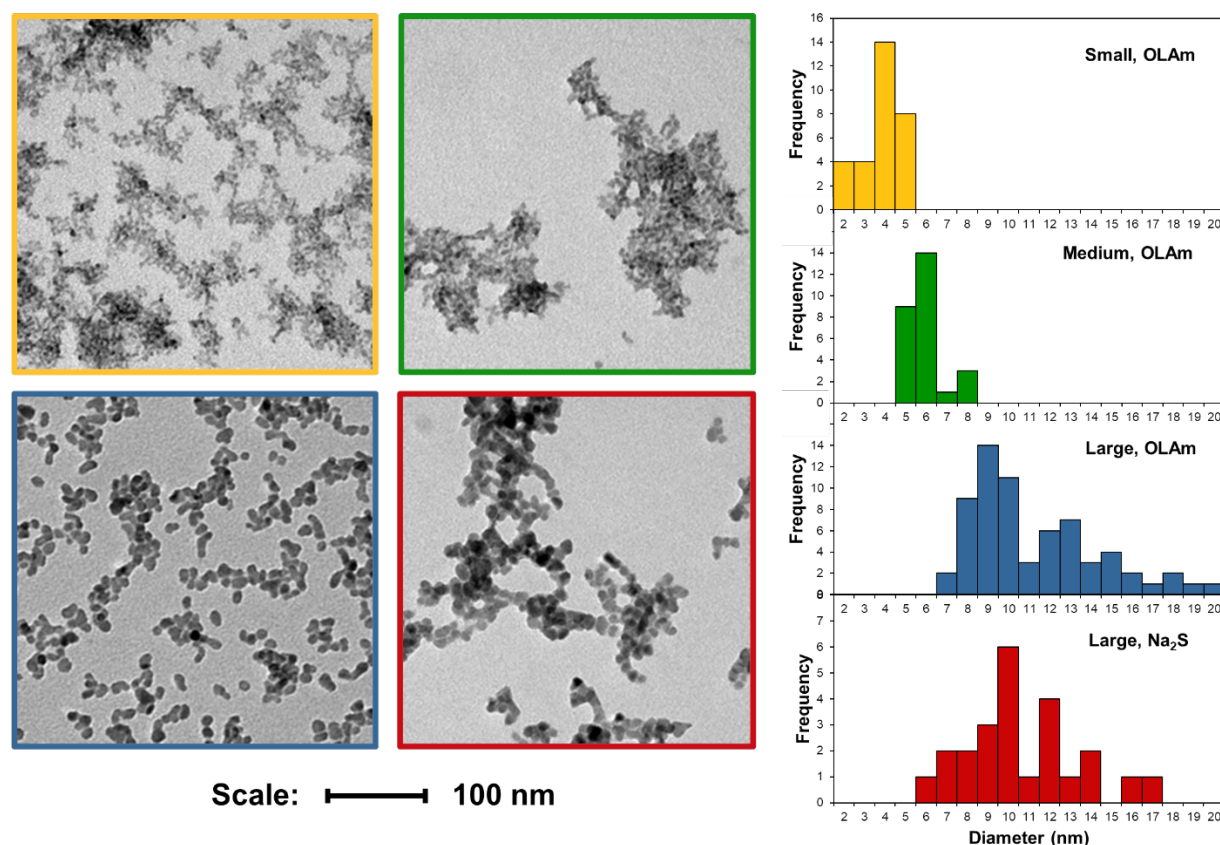


Figure 4.2: Transmission Electron Microscopy (TEM) images with histograms of NC diameters for (a) small, OLAm, 3.4 ± 0.9 nm (yellow), (b) medium, OLAm, 5.4 ± 0.9 nm (green), (c) large, OLAm, 10.8 ± 3.1 nm (blue), and (d) large, Na₂S, 10.2 ± 2.7 nm (red). Due to aggregation of the samples on the TEM grids, only a limited number of NCs could be measured for each sample (24 to 66 NCs). TEM-derived particle sizes were consistent with Scherrer-broadened full-width at half maximum (FWHM) of XRD signals (Figure 4.3 below). Measurements of particle size were performed using ImageJ software.

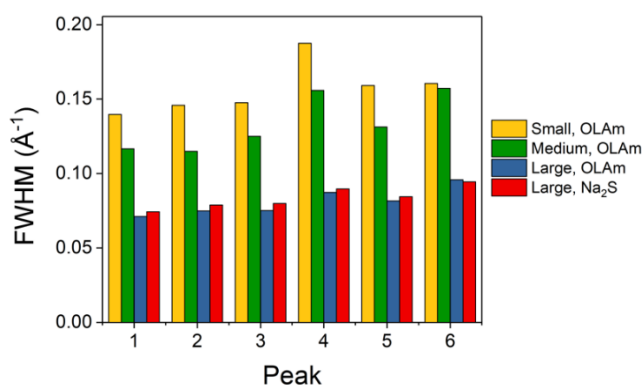


Figure 4.3: Full width half maximum (FWHM) of the static X-ray diffraction peaks in Figure 1a. As the nanocrystals decrease in size so does the FWHM of the X-ray diffraction due to Scherrer broadening:

We performed TR-XRD using 1.6-ps, 400-nm pump pulses from the frequency doubled output of an amplified Ti:sapphire laser and 11.7 keV X-ray probe pulses at Beamline 11-ID-D of the Advanced Photon Source (Argonne National Laboratory). The combined instrument response function was 79 ps. NCs suspended in dodecane (DMF for S²⁻-exchanged particles) were rapidly flowed through a degassed, recirculating liquid jet. Upon controlled-fluence optical excitation, lattice heating and expansion of the NCs can produce symmetric derivate-like features in the differenced XRD patterns as peaks shift to lower Q values, whereas transient disordering or melting results in negative features due to reduced diffraction intensity in comparison to static XRD.^{63, 65} (See the Section 2.4 for more experimental information and differenced diffraction pattern examples.) With increasing laser fluence, j , the average number of photogenerated electron-hole pairs per excited NC, $\langle N \rangle = \sigma j$, increases in accord with the size-dependent absorption cross-section, σ , which results in both single-picosecond intraband relaxation-derived heating of initially hot excitons as well as tens-of-picosecond, non-radiative, multiexciton Auger recombination-derived heating.^{49, 196}

For each of the three OLAm NC samples, we measured fluence-dependent TR-XRD signals, which appear in Figure 4.4a for the largest NC sample at a pump-probe time delay of 40 ps (Figure 4.5 shows data for small and medium NCs). At lower laser fluences, symmetric derivative lineshapes appear, with increased scattering at lower Q, relating NC lattice expansion. As j increases, the peaks become asymmetric with a larger amplitude negative component, consistent with the onset of transient disordering or melting. We presume that melting occurs over the volume of the nanocrystal and not solely at the surface from the lineshape as surface melting would result in substantial Scherrer broadening from the smaller crystalline core of the NC. Weak trends associated with Debye-Waller effects that relate larger diffraction losses in higher Q features

are observed (Figure 4.6).²⁰⁷ Integration in Q-space of the (204)/(220) and (116)/(312) peaks, shown in Figure 4.4b as a function of $\langle N \rangle$, effectively nullifies the symmetric derivative (lattice expansion) features and therefore conveys transient disordering (melting) behavior of these materials. Presented data is normalized to allow easier comparison. For all three samples, the melted fraction increases with $\langle N \rangle$. Table 4.1 provides melting threshold values. Still higher powers caused irreversible degradation of the samples. Figure 4.4c plots the melting threshold of the three OLAm samples versus radius on a log-log scale showing the shift in threshold to higher $\langle N \rangle$ ranges as size increases. Similar to previous studies of CdSe NCs,⁶⁵ we observe that a larger number of photogenerated excitons per particle are needed to achieve transient disordering in larger CuInSe₂ NCs. This trend, which already incorporates effects of absorption cross-section, relates to the higher specific heat of larger NCs as well as changing fractional surface energy.^{142,}

¹⁸¹ When corrected for volume, the average number of excitons needed to melt is fairly consistent across the three samples (Table 4.1), further evidence that melting is occurring throughout the NC and not just at the surface.

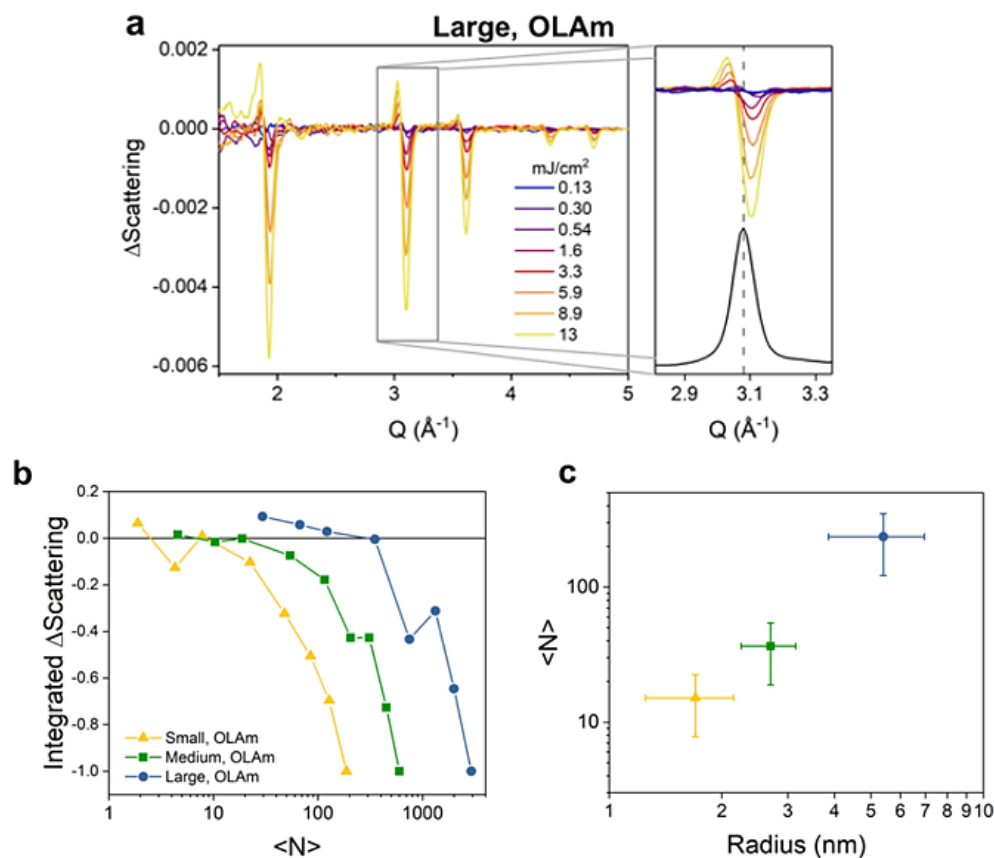


Figure 4.4: Fluence-dependent TR-XRD data measured 40 ps after excitation. (a) Pump-on vs pump-off differences in diffraction for the large, OLAm NCs show lineshapes that become asymmetric at higher indicated fluences, indicative of both heating and melting. To the right is a zoomed in view of the (220)/(204) feature with the static XRD (black). The grey dashed line corresponds to the peak position prior to excitation. (b) Integration in Q-space of the (220)/(204) and (116)/(312) peaks relates net reduced diffraction and loss of crystallinity (melting). (c) Comparison of radius to melting threshold for the three sizes.

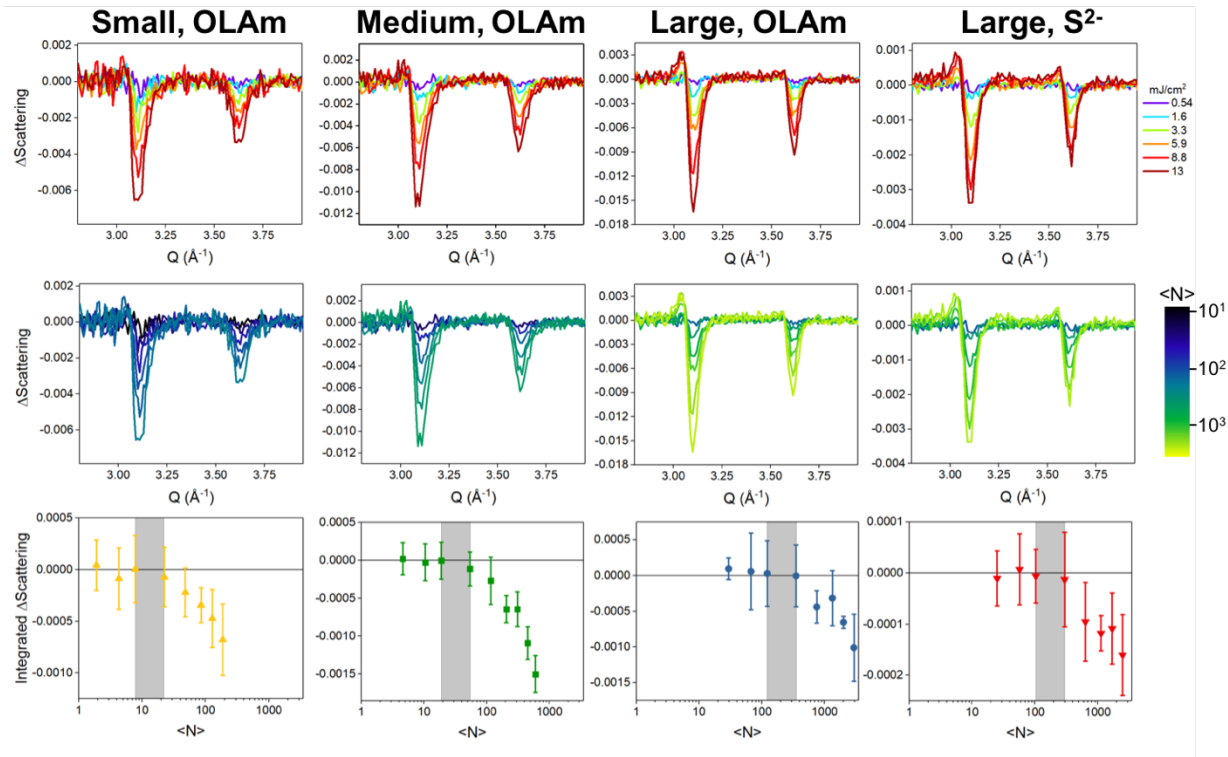


Figure 4.5: Differenced X-ray diffraction patterns as a function of pump laser fluence for the four samples each probed at 40 ps pump-probe time delay. (Top row) $\Delta\text{Scattering}$ as a function of laser power, (middle row) $\Delta\text{Scattering}$ as a function of $\langle N \rangle$, (bottom row) integrated $\Delta\text{Scattering}$ showing increased melting at higher $\langle N \rangle$ as size increases as well as melting threshold ranges given in grey.

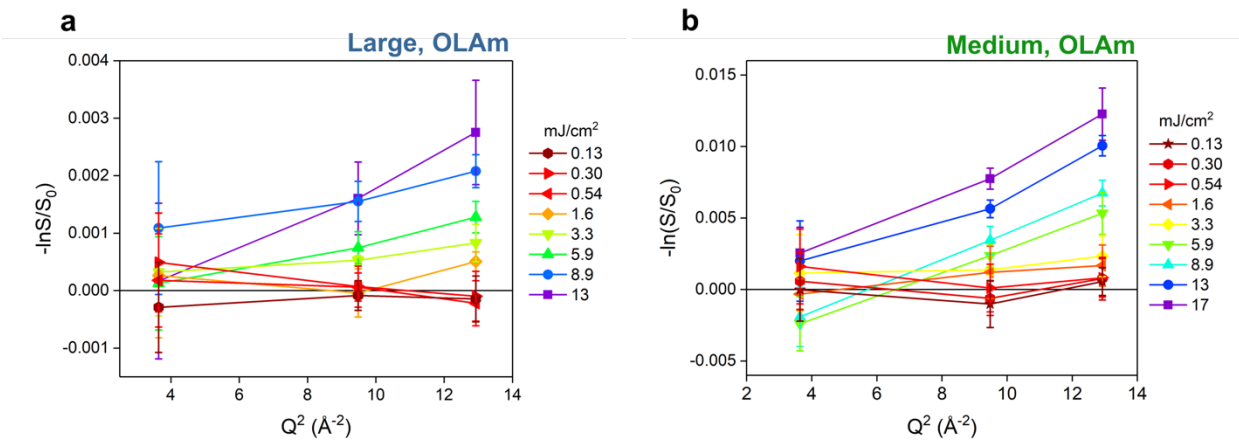


Figure 4.6: Debye-Waller effects for (a) Large, OLAm NCs and (b) Medium, OLAm NCs. Diffraction peaks at higher Q attenuate more strongly upon heating. Here we have plotted the $-\log$ of the static scattering intensity at 40 ps (S) over the static scattering intensity at -5 ns (S_0) as a function of Q^2 .

We analyzed picosecond to microsecond dynamics of TR-XRD signals for the three particle sizes to determine thermal dissipation rates. In this comparison, samples were excited above the melting threshold and differenced diffraction patterns for the samples at several time delays appear in Figures 4.7a-c. Similar to the power dependence at high flux, the early time points exhibit asymmetric peak shapes, suggesting a mixture of heated and melted NCs. In order to analyze the dynamics, we integrated only the negative transient signals of the (204)/(220) and the (116)/(312) peaks, shown in Figure 4.7d, as integration of the entire transient feature increased noise in the analysis. Such evaluation does not separate the melting *vs* lattice-expansion component. Though the instrument lacks sufficient time-resolution to evaluate the melting process, two distinct recovery regions are apparent in these integrated dynamics and necessitate biexponential fitting (τ_1 and τ_2). The more rapid τ_1 region corresponds to both NC recrystallization and cooling that is on the order of hundreds of picoseconds and shows a size-dependent trend among the three samples with faster recovery for the smaller particles.^{52, 142, 186} The slower τ_2 region is marked by continued NC cooling and lattice reversion back toward the original volume. This occurs on a nanosecond time scale in the range of ~ 2 ns.^{52, 142, 186} While a slight size dependent trend is evident, the reduced signal level at late times does not allow us substantial additional insights, but local heating of ligands and proximal solvent could slow apparent cooling. Further support for two regimes derives most clearly from the dynamics of the large NCs in Figure 4.7c, where the asymmetric line shape at early times transforms into a more symmetric derivative with time that then continues to decay in intensity.

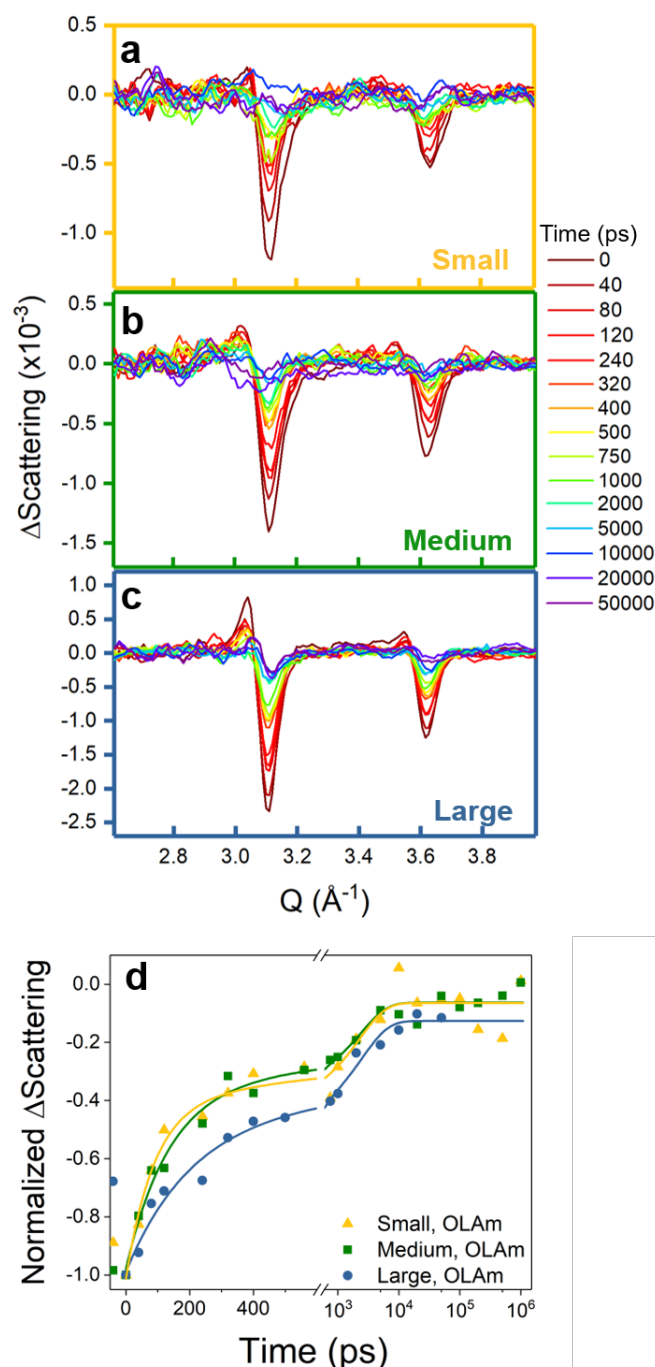


Figure 4.7: TR-XRD dynamics at 5.9 mJ/cm². (a-c) Differenced spectra for the large, medium, and small OLAm NCs as a function of time delay showing the region around the (220)/(204) and (116)/(312) peaks. (d) Integration of the negative component of the (220)/(204) and (116)/(312) peaks for the three different size OLAm-capped NCs. Dynamics are a convolution of both recrystallization and cooling that cause a biexponential recovery. Early times show a clear size dependent trend to recrystallization within the first several hundred picosecond time window. Late times (note axis break) are characterized by continued cooling of the NCs which occurs on the nanosecond timescale.

In order to discern transient changes in effective lattice temperature in time-resolved signals, we performed static X-ray diffraction for equilibrium sample temperatures ranging from 25 to 170°C. As seen in Figure 4.8a-b for the largest NCs, diffraction peaks shifted to lower Q as expected upon static temperature elevation, though changes are small ($<0.01 \text{ \AA}^{-1}$ upon changing from 25 to 170 °C). After baseline subtraction, the peaks were fit to pseudo-Voigt lineshapes, which are commonly implemented for XRD patterns.²⁰⁸ We were able to determine the change in lattice parameters (a and c) as well as particle volume (Figure 4.8c) for the medium and large NC samples. Reliable fitting of the smallest NCs was imprecise due to broad and asymmetric lineshapes. We find that NC lattices of the large and medium sizes expand more than the bulk over the probed temperature range.²⁰⁹ Bulk CuInSe₂ has nonlinear thermal expansion, but by 160°C we find that the medium and large samples had expanded by 0.57% and 0.44%, respectively, compared to the bulk expansion of 0.13%. Similarly, the medium NCs expanded more than the large, likely related to increased surface energy per particle.²¹⁰⁻²¹² While we were unable to measure thermal expansion for the smallest sample we anticipate that it would have an even larger percentage of expansion than the medium NCs.

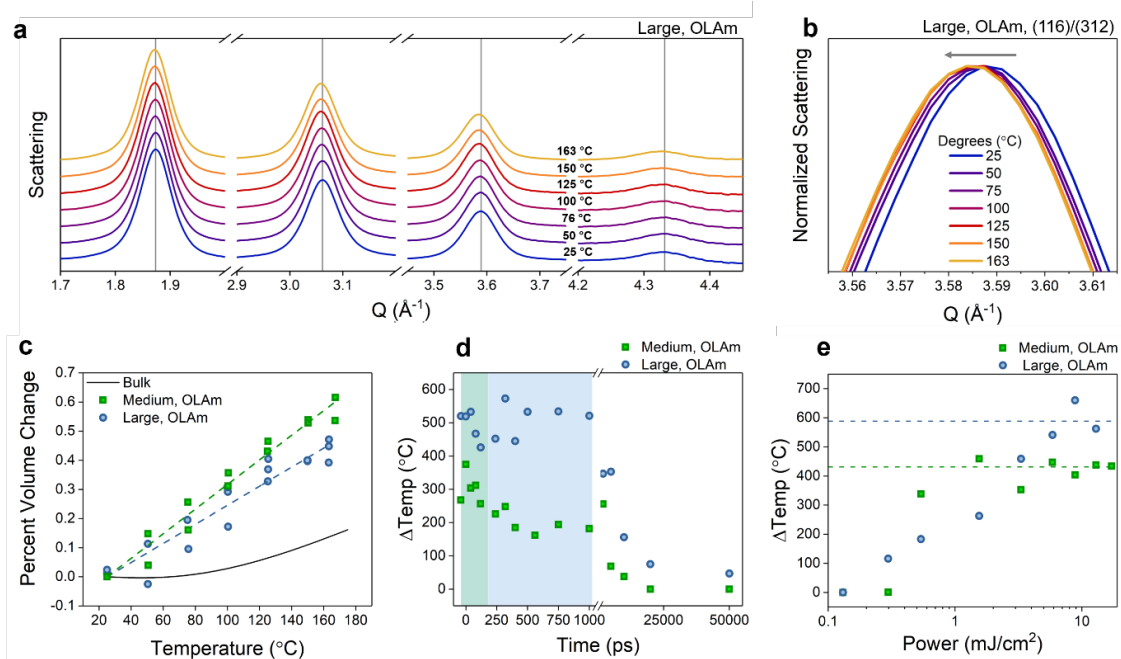


Figure 4.8: Temperature-dependent static XRD. (a) Large, OLAm NC XRD as a function of temperature shows shifts to lower Q values. (b) Normalized, zoomed in, XRD of the (116)/(312) diffraction peak showing shift with temperature. (c) Fits of these peaks relate the change in lattice volume as a function of temperature for large and small OLAm NCs. Dashed lines shown are meant to guide the eye. The thermal expansion of bulk CuInSe_2 is plotted in black for comparison. (d) Time-dependent (at $j = 5.9 \text{ mJ/cm}^2$) and (e) fluence-dependent (at $t = 40 \text{ ps}$) changes in temperature derived from TR-XRD for the large and medium, OLAm NCs. Data were fit using parameters from static temperature dependent XRD to correlate peak shift with temperature. At early times in (d) the temperature remains fairly constant over τ_1 lifetimes suggesting recrystallization processes. Shaded areas represent constant temperature. In (e), transient signals at larger fluences lack systematic increase of effective temperature with fluence, suggesting the NCs undergo disordering (cease diffracting strongly) in this range.

Table 4.1: Dynamics lifetimes, melting thresholds, and melting temperatures

Sample (Diameter, Capping Ligand)	τ_1 (ps)	τ_2 (ns)	Melting Threshold ($\langle N \rangle$)	Melting Threshold per Volume ($\langle N \rangle/\text{nm}^3$)	Melting Point from Power Dependence ($^\circ\text{C}$)	Melting Point from Dynamics ($^\circ\text{C}$)
Small (3.4 nm, OLAm)	90 ± 27	2.3 ± 1.3	7.8 – 22	0.4 – 1.1	-	-
Medium (5.4 nm, OLAm)	136 ± 29	2.4 ± 1.1	19 – 54	0.2 – 0.7	455 ± 20	325 ± 50
Large (10.8 nm, OLAm)	201 ± 57	2.5 ± 1.2	122 – 350	0.2 – 0.5	615 ± 60	525 ± 50
Large (10.2 nm, S^{2-})	207 ± 42	-	103 – 297	0.2 – 0.5	-	-

Based upon the temperature-dependent XRD measurements, we estimate changes in effective lattice temperature as a function of pump-probe time delay (Figure 4.8d) and laser fluence (Figure 4.8e) for the large and medium OLAm NC samples. The effective lattice temperatures derived from the kinetics show fairly constant temperatures at early times after excitation, commensurate with the τ_1 time component. As discrete NCs are recrystallizing during this time window, we suggest that lattice heat of fusion partially negates cooling as the lattice orders, consistent with a phase transition. There is then a more pronounced decrease in temperature at later times corresponding solely to heat dissipation. Averaged temperatures at early times appear in Table 4.1. Fluence-dependent data at high powers (Figure 4.8e) show similar plateaus in effective lattice temperature. Here, proximity to the apparent melting threshold results in leveling-off of temperature increase with fluence, in particular since only the fractional population of remaining crystalline lattices continue to strongly diffract. From the highest fluences examined we estimate a non-equilibrium melting temperature of $\sim 455 (\pm 20)^\circ\text{C}$ for the medium NCs and $\sim 615 (\pm 60)^\circ\text{C}$ for the large NCs. While higher than those found from the dynamics, both analyses show the same trend. Similar to other NC compositions, these melting points are size dependent and appreciably lower than the equilibrium bulk-phase melting point (987°C).^{8, 188}

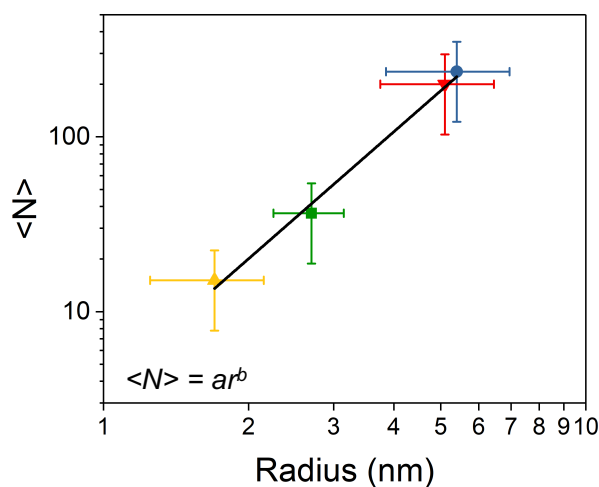


Figure 4.9: Plot of $\langle N \rangle$ versus radius on a log-log scale shows that the reduction in melting threshold for the S^{2-} sample can be attributed to size effects as ligand exchange caused a reduction in particle diameter.

Lastly, we exchanged the native OLAm ligand on the largest NCs for S^{2-} (using Na_2S) and repeated the measurements noted above. Figure 4.5 shows that the melting threshold of the S^{2-} sample is nearly unchanged from the OLAm sample, with a very slight reduction. Seeing as the TEM images and static X-ray diffraction showed a slight decrease in the diameter of the NC after ligand exchange, we attribute the subtle difference to a size effect although surface energy will also differ for the different ligands. We plot the melting threshold vs radius in Figure 4.9. When fitting the OLAm samples to a power law, we find that the S^{2-} sample agrees reasonably with the fit confirming that the change in ligand identity in this instance does not distinctly affect the melting threshold.

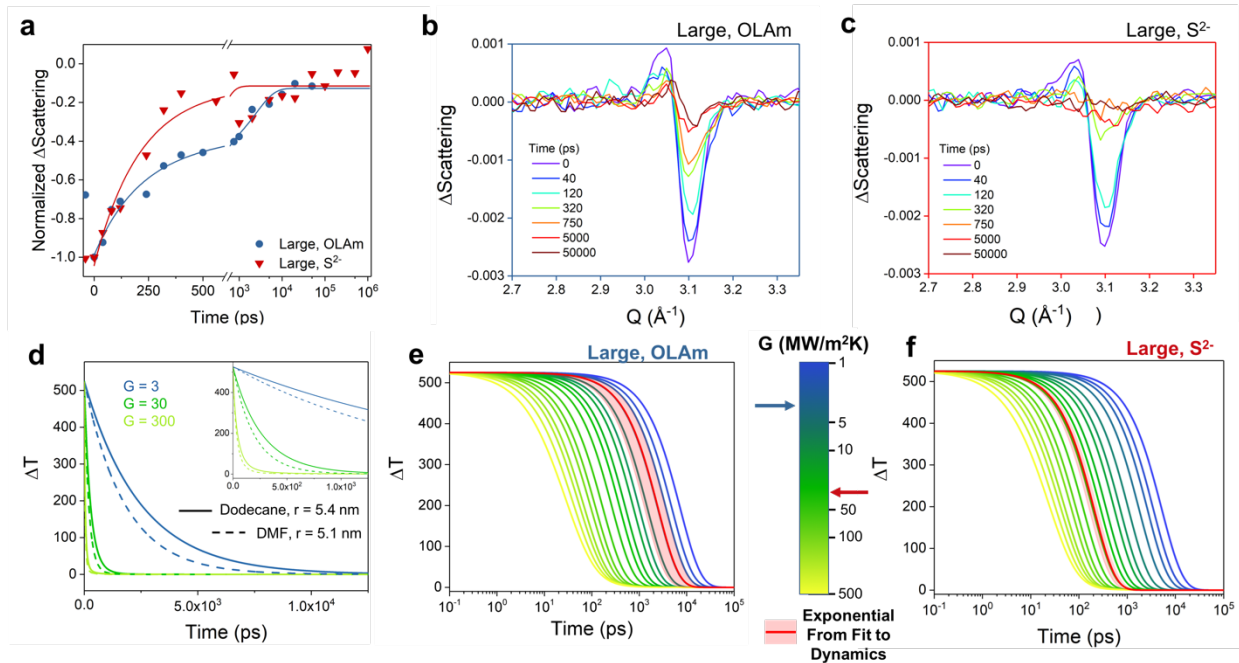


Figure 4.10: Effect of S^{2-} ligand on dynamics. (a) The S^{2-} sample recovers with only one exponential in the dynamics that is similar to the τ_1 lifetime of the OLAm sample. Transient diffraction signals as a function of time delay of the (220)/(204) feature in the (b) OLAm and (c) S^{2-} samples showing different recrystallization and cooling behavior. (d) Effects of solvent and radius on G . The S^{2-} sample has a reduced diameter and different solvent, both of which cause faster cooling, but cannot explain the order of magnitude difference in lifetime. (e) and (f) show calculated functions of G with the experimentally derived exponential functions overlaid for OLAm and S^{2-} respectively. Ligand exchange from OLAm to S^{2-} results in a drastic increase in G from ~ 3 MW/m²K to ~ 28 MW/m²K.

Recovery dynamics, however, are markedly different between the two ligand types for the large NCs as shown in Figure 4.10a. The inorganically-terminated sample presents only a single exponential recovery component that is nearly identical to the τ_1 component of the OLAm sample. Figure 4.10b-c shows that the (204)/(220) and (116)/(312) features of the S^{2-} sample recover rapidly as compared to the OLAm sample. The lack of a second, slower component suggests that the inorganically-capped NCs not only recrystallize within this time, but also cool almost completely. Together, the fluence dependence and dynamics suggest negligible impact of S^{2-} ligands on melting but accelerated cooling and recrystallization. Whereas several factors may influence the observed behavior, we suspect that thermal transport from the NC to solvent occurs

more rapidly through the compact anionic ligands rather than the many-atom OLAm ligand, and that direct interactions between the NC surface and solvent more readily occur and facilitate cooling.

To explore whether these differences could be attributed to the ligand and not the different solvent or slight reduction in NC diameter, we modeled the cooling of the particles using established thermal dissipation equations.²¹³ Plech and coworkers previously derived Eq. (4.1) to model the temperature of Au NCs as a function of time assuming a finite thermal interfacial conductance (G) and a negligible temperature gradient within the particle. We assumed that the initial temperature for both large samples was 525 °C based on the melting threshold determined from the TR-XRD dynamics (Figure 4.8d).

$$\text{Eq. 4.1} \quad T_p(t) = \frac{2kR^2g^2T_0}{\pi} \int_0^\infty \frac{\exp\left(\frac{-\kappa u^2 t}{R^2}\right)}{(u^2(1+Rg)-kRg)^2 + (u^3 - kRgu)^2} u^2 du$$

Here, we have substituted in k , κ , and g for simplicity. They are defined below and described in Table 4.2.

$$\kappa = \frac{K}{\rho c} \quad k = \frac{4\pi R^3 \rho c}{Mc_p} \quad g = \frac{G}{K}$$

Table 4.2: Variables used in calculation of interfacial thermal conductivity. References are denoted in red.

Variable	Definition	Large, OLAm	Large, Na ₂ S	Dodecane	DMF
T_p	Temperature of Nanocrystal as a function of time	-	-	-	-
T₀	Initial Temperature	525°C	525°C	-	-
R	Radius	5.4 nm	5.1 nm	-	-
M	Mass	3.81 x 10 ⁻²¹ kg	3.21 x 10 ⁻²¹ kg	-	-
C_p	Specific heat of nanocrystal	98 J/molK ²¹⁴	98 J/molK ²¹⁴	-	-
K	Thermal conductivity of solvent	-	-	0.140 W/mK ²¹⁵	0.1842 W/mK ²¹⁶
ρ	Density	-	-	750 kg/m ³ ²¹⁷	944 kg/m ³ ²¹⁸
c	Specific heat of solvent	-	-	376 J/molK ²¹⁹	148 J/molK ²²⁰
G	Interfacial thermal conductivity	-	-	-	-

Figure 4.10d shows effects that both solvent and radius have on the cooling rates for three different values of interfacial thermal conductivity (G). While DMF (rather than dodecane) and the slightly smaller particle radius of the S²⁻ sample do cause a reduction in the cooling lifetime, such effects are less significant than the order-of-magnitude difference that we observe. We then used this model to approximate G values for both large samples. Figures 4.10e and 4.10f display a variety of G values for the large samples with the lifetime of cooling derived from the fits of the TR-XRD overlaid in red. From this comparison, we find G values of 3 and 28 MW/m²K for the OLAm sample and the S²⁻ samples, respectively. Such values are comparable to those determined theoretically for other semiconductor NC compositions.^{143, 152}

Ligand selection is critical to implementation of a given nanocrystal composition in applications owing to significant effects on, *e.g.*, solution processing and electrical conductivity.²²¹⁻²²⁴ Ligand identity impacts the rate of thermalization as observed in this pulsed excitation mode with isolated NCs dispersed in solvent. The temperature-time profile of a film of nanocrystals, whether in a light-emitting application or additive manufacturing process, is

influenced not only by the rate of thermalization, but also on thermal properties (heat capacity, thermal transport) of surrounding or proximal media. For continuous- or high frequency excitation, interfacial thermal conductivity impacts the rate at which the NC together with the surroundings will exchange heat and establish a quasi-equilibrium, which would occur more rapidly here for the inorganic ligand. Several effects play a role in photonic curing or sintering such as the available thermal energy, the time available for inter-particle bond formation, NC packing density, ligand identity, fractional ligand coverage, surface binding energy, and any ligand chemical processes. Here, for instance, the compact S^{2-} inorganic ligand offers close NC proximity although the NC core can cool more rapidly than the studied organic ligand. From this analysis, we suggest that ligand identity yields significant consequences for thermal dissipation at interfaces of these materials and due to facile routes to manipulate composition, a perhaps highly effective tool for controlling such processes.

4.4 Conclusion

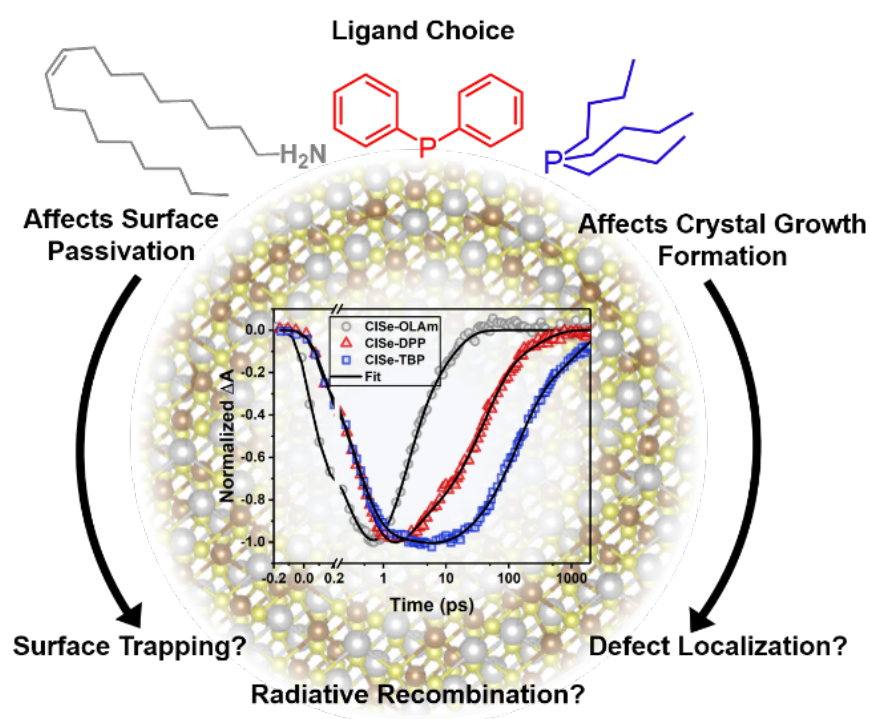
In conclusion, we have performed TR-XRD and temperature-dependent static XRD to probe photo-induced heating and melting in $CuInSe_2$ NCs as functions of both particle size and ligand identity. We found NC size dependence in both melting threshold and recrystallization/cooling dynamics. In addition, we found that the NC size affects lattice expansion with static temperature elevation and melting temperature in TR-XRD. Using this approach, we were able to study the effects of ligand identity on lattice response and thermal dissipation. Exchange of long, bulky OLAm ligands to short sulfide anions did not alter the photo-induced disordering threshold, but appreciably impacted cooling and recrystallization lifetimes. We were also able to obtain interfacial thermal conductivity values for the two different ligand terminations.

Taken together, these findings suggest several means exist to manipulate nanoparticle phase and thermal profile, and the amount of energy deposited (which here is pulsed, but could also be continuously input), particle size, surface termination, and surroundings physically alter the nanocrystalline material in appreciable manner.

4.5 Outlook

TR-XRD continues to be a powerful tool to monitor thermal properties in semiconductor NCs with studies on anisotropic⁶² and plasmonic TiN²²⁵ NCs expanding the research. There are numerous compositions, sizes, and morphologies that could improve understanding of how different materials and their facets behave under intense photoexcitation. Studies of solid samples, whether single crystals or films of NCs are promising directions. This is particularly relevant in the case of CISE; studies of sintering using TR-XRD could be instrumental in understanding and improving photonic curing technologies. Expansion of current systems by varying ligands and solvents as ways to modulate thermal dissipation would continue the work discussed here and match well with future directions in FSRS.

Chapter 5: Ligand Effects on Carrier Dynamics in CuInSe₂



This chapter is adapted from:

Harvey, S. M.; Houck, D. W.; Liu, W.; Liu, Y.; Gostzola, D. J.; Korgel, B. A.; Wasielewski, M. R.; Schaller, R. D., Synthetic Ligand Selection Affects Stoichiometry, Carrier Dynamics, and Trapping in CuInSe₂ Nanocrystals, *ACS Nano*, **2021**

5.1 Introduction

Colloidal semiconductor nanocrystals (NCs) garner significant interest owing to their unique optoelectronic properties that derive from size-dependent quantum confinement. The tunability of these materials places them at the forefront of many technologies including displays,²²⁶⁻²²⁷ light-emitting diodes,^{12, 228} and photovoltaics (PVs).^{79, 229-230} Over the last few decades, nanomaterial synthesis has advanced substantially, allowing fine control over composition, shape, size homogeneity, and surface passivation with the aim of controlling the properties of the inorganic core.²³¹⁻²³³ Of particular note, many reports have shown that ligands can serve important roles beyond passivation of undercoordinated surface sites and stabilization of colloidal suspension.^{24, 68} Surface ligands can directly affect trap state distribution, impact both intra- and interband relaxation, as well as alter electronic and thermal transport.^{21, 24-25, 64, 73, 75, 234-235} Oftentimes desirable ligands, such as compact inorganic ions, short organic alkanes, or more tightly bound phosphines and thiols, are introduced via exchange with the ligand utilized during synthesis in order to achieve such properties.^{23-25, 68, 71}

The I-III-VI semiconductors, such as CuInS₂ (CIS) and CuInSe₂ (CISE), have been hailed as candidates to replace more developed, but toxic Cd- and Pb-based chalcogenide nanocrystals, yet encounter additional complexity with regard to ligand selection.¹⁹¹ Significant research into these compositions has centered around synthesis and size control, which face particular challenges related to the inclusion of hard (In³⁺) and soft (Cu⁺) Lewis acids.²³⁶ To address this, a variety of ligand precursors have been employed to balance the reactivity of the two metal ions.²³⁶⁻²³⁷ At present, CISE NC synthesis is less developed than CIS, but recently, combinations of Se-precursors with different reactivity have allowed tunability of size, shape, and crystal structure (e.g. chalcopyrite vs. zincblende vs. wurtzite).^{236, 238} Whether intentional or not, CISE NCs can

easily be produced in off-stoichiometric ratios and resultant defects are common (i.e. vacancy, interstitial, or antisite defects).²³⁶ The bulk compositions of these materials are marked by a large tolerance for such defects, that when combined with the high NC surface areas offer the potential for a variety of electronic trap states that may significantly reduce carrier transport and light emission.²³⁹⁻²⁴² Furthermore, the optoelectronic properties such as broad absorption linewidths and large Stokes shifts are often attributed to such defects, the precise identity of which are still under debate.^{236-237, 243-244 245}

Despite these challenges, CISE NCs have garnered considerable interest owing to near-IR bandgaps of $\sim 1.2 - 1.75$ eV for NCs,^{236, 238} and 1.01 eV for bulk CISE,¹⁸⁸ which are comparable to bulk silicon (1.12 eV).²⁴⁶ In addition, large scale solution processability enables synthesis of large quantities of monodisperse particles, which is important for engineering commercial devices.²⁴⁷⁻²⁴⁸ Incorporation into PV devices has led to efficiencies of up to 19% for bulk CISE and beyond 22% with the incorporation of small amounts of Ga to form $\text{Cu}(\text{In,Ga})\text{Se}_2$.²⁴⁹⁻²⁵³ NCs enable the opportunity to print these materials to achieve flexible devices.¹⁹³⁻¹⁹⁴ High temperature sintering or photonic curing can yield bulk-like thin films while sometimes maintaining nanoscale features.^{64, 66}

Towards the goal of solution processed CISE PVs, a variety of different Se-precursors and ligand compositions have been investigated that yield different nascent PV efficiencies.^{203, 236, 238, 254-258} The underlying photophysical processes responsible that impact efficiency remain elusive and while CISE NCs are generally believed to behave similarly to CIS, far less research is available for this composition. In this work, we examine CISE NCs passivated with three different ligands commonly used for synthesis of this material, namely oleylamine (OLAm), diphenylphosphine (DPP), and tributylphosphine (TBP). Using transient absorption, distinct spectral features and

lifetimes are determined that depend strongly on ligand identity. Photoluminescence (PL) quantum yield (QY) and PV device efficiency mirror these results suggesting that the charge carriers of the inorganic crystalline core are heavily influenced by the ligands, which impart trap states. To determine the nature of these defects, X-ray diffraction (XRD), Raman, and inductively coupled plasma optical emission spectroscopy (ICP-OES) are utilized to study the NC lattices, while FTIR and NMR provide insight into ligand coverage and identity. Taken together, these results suggest a mixture of defects, both within the interior of the NC and at the surface where the ligand composition dictates the predominance of one type of trapping over another. Finally, thermal annealing of the NCs followed with in-situ PL characterization shows heat-induced brightening of the DPP passivated sample with PL at room temperature increasing more than 600% after heating to 600K. Understanding of the role ligands play in both formation and passivation of these materials along with post-synthetic material processing can offer appreciable benefits for device performance.

5.2 Experimental Methods

CISE-OLAm Synthesis

In a N₂-filled glovebox, 40 mL OLAm, 5 mmol (0.49 g) CuCl, 5 mmol (1.11 g) InCl₃, and 10 mmol (0.79 g) Se were added to a 100 mL three-neck flask. The flask was sealed with septa and wires, transferred out of the glovebox to connect to a Schlenk line. The reaction mixture was heated to 110 °C under vacuum (<200 mTorr) for 1 h, followed by blanketing with N₂ for 12 h to allow the precursor complexes to form completely. Then the reaction was carried out at 240 °C for 10 min. The heating mantle was then removed to allow the reaction mixture to cool down to room temperature. CuInSe₂ nanocrystals were purified through antisolvent precipitation, by addition of

20 mL ethanol and centrifugation at 2600 rcf for 5 min. After discarding the supernatant, the nanocrystals were redispersed in 10 mL of toluene and centrifuged again at 2600 rcf to remove poorly capped nanocrystals. The supernatant was transferred to another centrifuge tube, and one more antisolvent precipitation steps was carried out. Ethanol (4mL) was added, followed by centrifugation at 2600 rcf for 5 min, and the supernatant was discarded. The collected nanocrystals were dried and redispersed in anhydrous toluene, stored in the glovebox.

CISe-DPP Synthesis

In a N₂-filled glovebox, 40 mL OLAm, 5 mmol (0.49 g) CuCl and 5 mmol (1.11 g) InCl₃ were added to a 100 mL three-neck flask. The flask was sealed with septa, removed from the glovebox, and transferred to a Schlenk line. The reaction mixture was degassed under vacuum (<200 mTorr) at 110 °C for 30 min, followed by blanketing with N₂ at 110°C for another 10 min. The flask was then heated to 240 °C; at 180 °C, Se-DPP solution, prepared from dissolving 10 mmol (0.79 g) Se by 10 mL of diphenylphosphine in the glovebox, was injected into the flask. The flask was maintained at 240°C for 10 min. Then the heating mantle was removed to allow the reaction mixture to cool down to room temperature, and CuInSe₂ nanocrystals were purified by the same procedures in the CISe-OLAm synthesis above.

CISe-TBP Synthesis

CISe-TBP synthesis was performed following the same steps as CISe-DPP synthesis, expect that 10 mmol (0.79 g) Se was dissolved in 10 mL of tributylphosphine.

Device Fabrication and Characterization

Polished soda-lime glass substrates (25 x 25 x 1.1 mm) purchased from Delta Technologies were cleaned before thermal evaporation of the chromium (Cr) and gold (Au) layers, by placing in an ultrasonic bath of 1:1 vol% acetone: isopropanol for 5 min, followed by 5 min of sonication in DI-H₂O (resistivity as 18.2 MΩ-cm at 25 °C), and drying with compressed air. Cr (10 nm) and Au (80 nm) layers were deposited in a Denton thermal evaporator through a patterned mask.²⁵⁹ A Sonotek ExactaCoat ultrasonic automated spray system was used to deposit CuInSe₂ nanocrystals (dispersed in toluene at a concentration of 5 mg/mL), equipped with a 120 kHz ultrasonic nozzle, rastering across the substrates with a 3 mm raster spacing, at a speed of 10 mm/sec, an ink injection rate of 0.1 mL/min, an air pressure of 1.6 psi and a nozzle-to-substrate height of 11.5 cm. The substrates were heated to 100°C prior to spray coating.²⁶⁰ The CdS device layer was deposited onto the nanocrystal films through a chemical bath deposition (CBD) process.²⁶¹ Aqueous solutions of 160 μL of 15 mM CdSO₄, 275 μL of 1.5 M thiourea, and 350 μL of 18 M NH₄OH were mixed and dropped onto each substrate maintained at 90°C. The substrates were covered with a glass dish for 2 min, then rinsed with DI-H₂O and dried with compressed N₂. Layers of intrinsic ZnO (50 nm) and ITO (300 nm) were deposited in a AMOD Sputtering system through Radio Frequency (RF) sputtering in Ar atmosphere, using ZnO (99.9%) and ITO (In₂O₃:SnO₂ 9:1, 99.99%) targets supplied by Kurt J. Lesker. The sputter deposition area was shadow-masked into 8 rectangular regions corresponding to 8 individual devices on each substrate. The active device area varies slightly from 0.08 cm² to 0.11 cm², and was measured in each case to determine all reported power conversion efficiencies (PCE).

Current-voltage characteristics of the PVs were measured with a Keithley 2400 general purpose source meter and a Xe lamp equipped with an A.M. 1.5 filter. Conductive silver paint (SPI Supplies) was applied to make contact between the ITO layer and the electrical probes.

5.3 Results and Discussion

Multiple syntheses of CISE NCs with approximately identical size were synthesized using previously described methods, with details provided in the Experimental Methods (Section 5.2).^{189, 193, 205, 260, 262} Notably, the main difference between these syntheses is the means of incorporating Se into the reaction mixture. To prepare the first sample, Se was dissolved in OLAm along with other precursors and heated to produce the NCs. For the second and third samples, Se was dissolved in a phosphine-based ligand, i.e. DPP or TBP, and injected into the reaction flask at high temperatures. In these later cases, OLAm is still present in the reaction as a solvent. The chemical structures of OLAm, DPP, and TBP are given in Figure 5.1a. Transmission electron microscopy (TEM) images and size histograms of the associated NCs (hereafter labeled **CISE-X** where **X** is the respective ligand) are given in Figure 5.2.

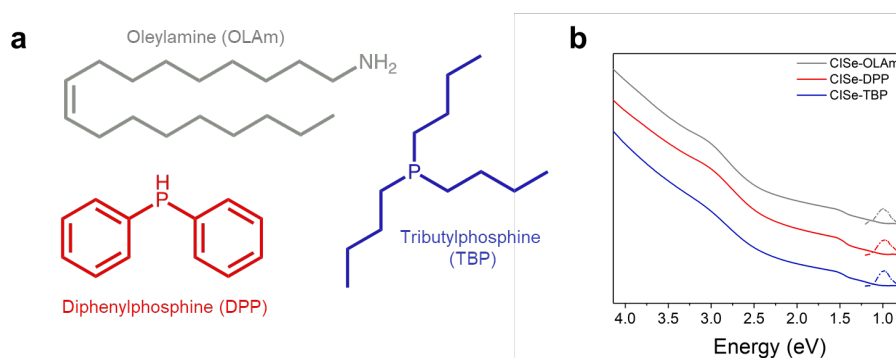


Figure 5.1: (a) Molecular structure of the three Se-precursor molecules used in this study, oleylamine (present in all three samples), diphenylphosphine, and tributylphosphine. (b) Static absorption spectra (solid lines) and photoluminescence (dashed lines) of the CISE NCs. (c-e) Transmission electron microscopy images of the samples synthesized from left to right with OLAm, DPP, and TBP. Scale bar is the same for all three.

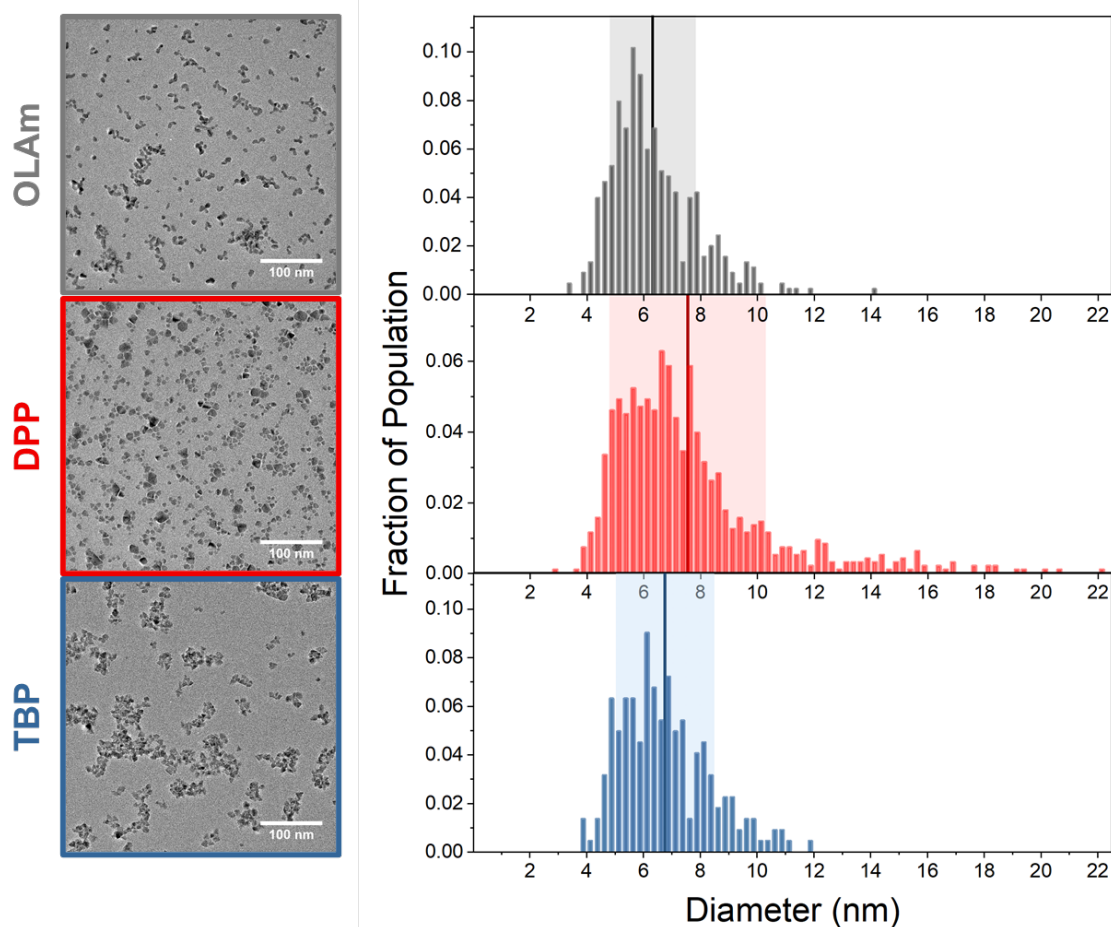


Figure 5.2: Transmission electron microscopy images of the three samples along with corresponding size histograms. (Top) CISE-OLAm, diameter 6.3 ± 1.5 nm, 229 particle measurements. (Middle) CISE-DPP, diameter 7.5 ± 2.8 nm, 480 particle measurements. (Bottom) CISE-TBP, diameter 6.8 ± 1.7 nm, 112 particle measurements. Darker vertical lines signify the average and shaded areas are the standard deviation in diameter.

Normalized static absorption and emission spectra of the samples in hexanes are given in Figure 5.1b (solid and dashed lines respectively). As is common with this class of materials, the absorption spectra exhibit features that extend into the NIR with broad linewidths that preclude facile identification of the lowest energy excitonic transition. To distinguish the bandgap energy,

we examined the square of the absorption²⁶³ and found it to be approximately ~ 1.3 eV for each sample; the absorption that extends to lower energy can be attributed to mid-gap states. PL produced upon excitation of these samples is also broad and appears around 1.0 eV. This large Stokes shift is similarly characteristic of I-III-VI NCs. Similarity in absorption and emission spectra confirm that these samples are nearly identical in size. Given that the emission of all three occurs at the same energy, we can assume that radiative recombination arises from the same electronic state, but that it cannot be due to the conduction to valence band transition owing to the 300 meV difference in energy between absorption and emission.

Table 5.1: Photophysical Properties and Device Efficiencies

	τ_1 (ps)	τ_2 (ps)	τ_3 (ps)	τ_4 (ps)	PLQY (%)	PV Device Efficiency
CISE-OLAm	0.25 ± 0.05	0.42 ± 0.07	1.9 ± 0.2	9.3 ± 0.7	0.003	0.5 ± 0.3
CISE-DPP	0.411 ± 0.009	2.3 ± 0.1	39 ± 1	250 ± 14	0.14	0.84 ± 0.09
CISE-TBP	0.336 ± 0.008	3.4 ± 0.2	127 ± 2	1110 ± 30	1.2	1.5 ± 0.3

PLQYs (Table 5.1) for the three samples are low (less than 2%), suggesting an abundance of non-radiative trapping that tends to outcompete emission. Despite all samples exhibiting low QYs, an order of magnitude difference from **CISE-TBP** (1.2%) to **CISE-DPP** (0.14%) to **CISE-OLAm** (0.003%) indicates that the prevalence of this trapping is dictated in part by the ligand, either through controlling defect formation in the synthesis or afterwards by passivation of surface sites (or lack thereof). Similar trends are observed when the samples are drop cast as thin film PV devices with **CISE-TBP** exhibiting the highest efficiency and **CISE-OLAm** the lowest (Table 5.1) The impact of ligand identity here suggests that the NCs capped with TBP offer the longest carrier lifetimes and/or transport carriers much more effectively than the those passivated with DPP or

OLAm. From these measurements alone we cannot determine the nature of the electronic states involved in radiative or non-radiative recombination (electron and/or hole traps).

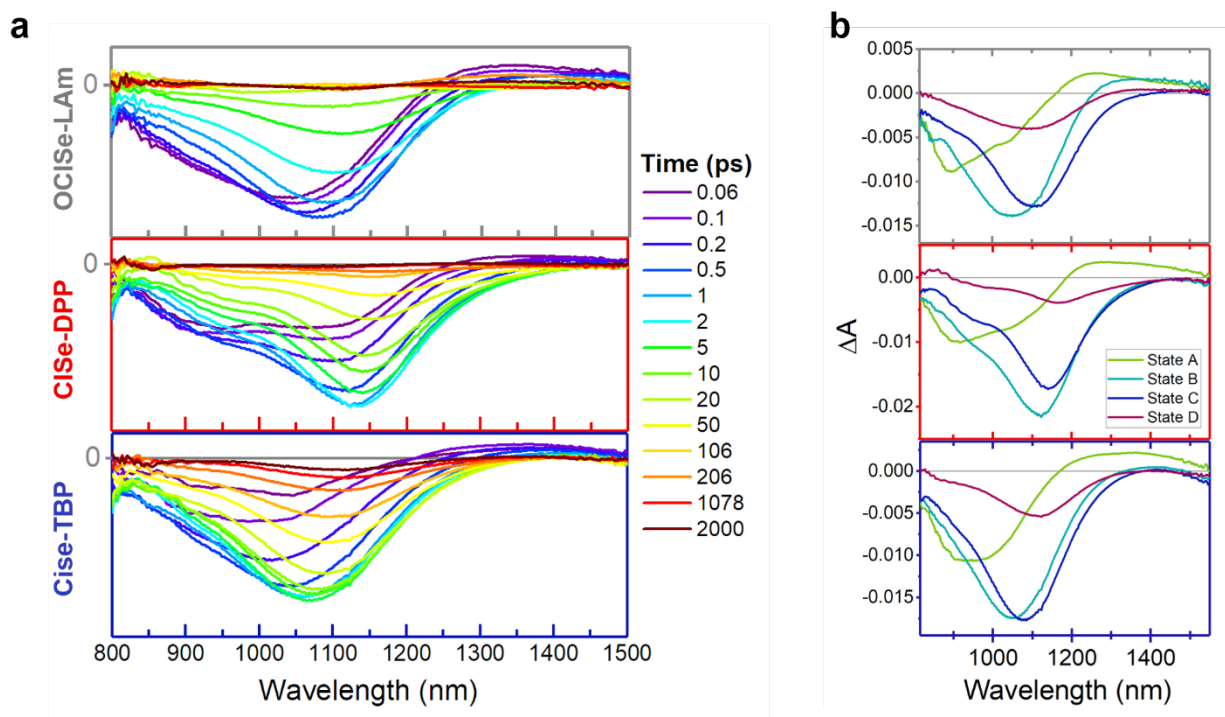


Figure 5.3: Transient absorption data. (Left) Transient spectra for each sample up to 2 ns. (Right) Evolution associated spectra determined from fitting the data using a three species model.

To further characterize the photophysics we used near-infrared transient absorption (TA) spectroscopy. The samples were pumped with an 800 nm laser pulse at a low fluence of $j = 76 \mu\text{J}/\text{cm}^2$, which produces a comparable average number of excitons ($\langle N \rangle \approx 1$) in each sample. TA at other fluences showed similar behavior and does not affect the results discussed here. Transient spectra at time points up to two nanoseconds are given in Figure 5.3a. Early time traces are dominated by a higher energy ground state bleach and lower energy excited state absorption. As time progresses the bleach shifts to lower energy followed by a reduction in intensity while the positive signal decays rapidly within the measured spectral window. While the overall shape of the spectra are similar across samples, they evolve over drastically different timescales wherein

the **CISE-OLAm** NCs fully recover within 20 ps, the **CISE-DPP** NCs within 500 ps, and the lifetime of the **CISE-TBP** NCs extends beyond the two nanosecond time range measured. To determine lifetimes for the various processes and elucidate their origin, we used a sequential $A \rightarrow B \rightarrow C \rightarrow D \rightarrow \text{Ground}$ model and globally fit the data using nine to ten wavelengths (Figure 5.4). Fitted time constants appear in Table 5.1. While τ_1 (corresponding to the lifetime of $A \rightarrow B$) is similar across the three samples, τ_2 (State $B \rightarrow$ State C), τ_3 (State $C \rightarrow$ State D), and τ_4 (State $D \rightarrow$ Ground), show a strong ligand dependence where **CISE-OLAm** is the shortest lived, followed by **CISE-DPP**, and finally **CISE-TBP**. Figure 5.5 shows a kinetic trace for the three samples corresponding to the wavelength at the lowest energy bleach (minimum ΔA of State C) along with the corresponding fit to demonstrate the stark difference in formation and decay rates across samples.

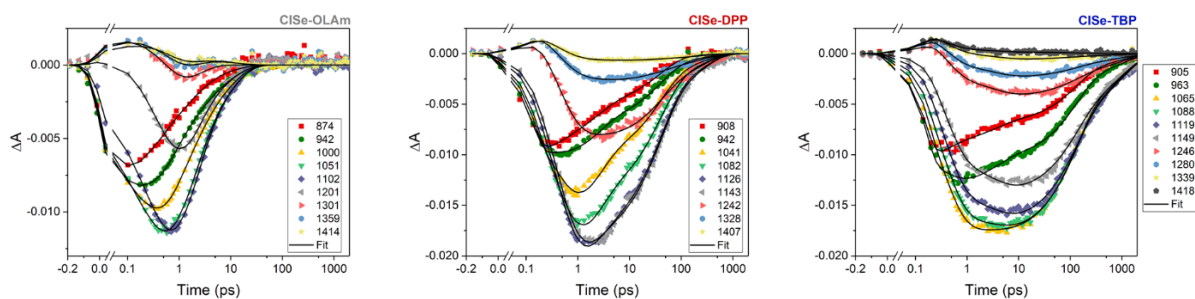


Figure 5.4: Kinetic traces (symbols) and their corresponding fits used in the species associated fitting for (a) **CISE-OLAm**, (b) **CISE-DPP**, and (c) **CISE-TBP**. Wavelengths were chosen across the spectral range and to include all features.

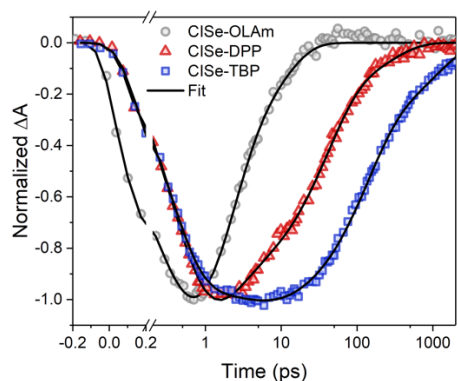


Figure 5.5: Kinetic traces at the bleach minimum along with corresponding fits showing the difference in early and late time dynamics.

Despite the difference in ligand identity and resultant rate constants by TA, each sample produced similar evolution associated spectra (EAS) as seen in Figure 5.3b: **(A)** a higher energy bleach feature ($\sim 1.24 - 1.37$ eV) with an excited state absorption below 1.03 eV, **(B)**, a lower energy bleach ($\sim 1.1 - 1.18$ eV) with minimal positive features that decays into **(C)** a similar bleach that is redshifted by 10 – 60 meV, **(D)** a further redshifted bleach (10 – 60 meV) with significantly reduced intensity before recombining to the ground state. The similarity in linewidth across the bleach features in states B-D suggests that we are chiefly monitoring one population as it moves to different electronic transitions (Figure 5.6).

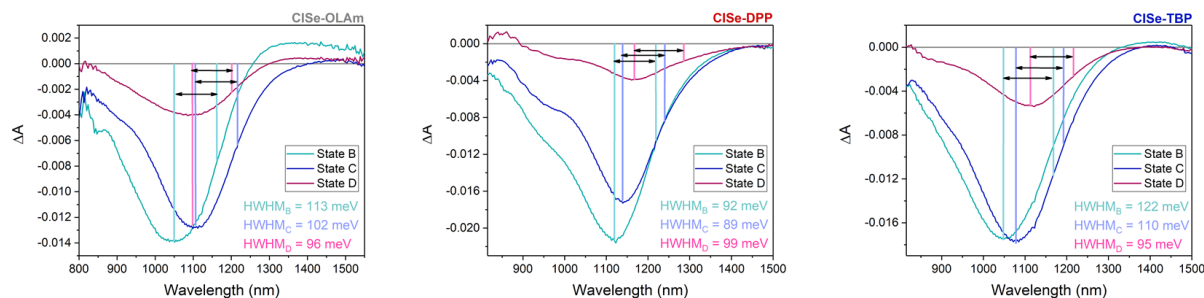


Figure 5.6: Half-width half maximum (HWHM) of States B, C and D for all the three samples. State A was not included as the lineshape made HWHM analysis difficult.

From these EAS we can begin to assign the identity of the four states (A, B, C, and D). A previous report on **CISe-DPP** NCs saw spectral shifting of bleach features and attributed this to intraband relaxation as carriers moved from the 1P state to the 1S state before recombination.²⁶² However, that study only monitored single wavelength kinetics and the lowest energy bleach that they attributed to 1S was far below that of the bandgap. With global analysis we can separate out the lifetimes and spectra of these four identifiable components. Given the bandgap of ~ 1.3 eV, our pump is generating hot carriers and therefore we ascribe τ_1 to intraband relaxation. Reports of ultrafast processes of similar timescales in CIS have been attributed to carrier cooling and more generally, semiconductor NCs are expected to undergo intraband relaxation on the order of hundreds of femtoseconds, which is consistent with our data.^{19, 264-267} The lineshapes of States A and B provide evidence of this assignment as well. It is well documented that hot carriers produce derivative-like spectra due to interactions of the pump and probe photons; these biexciton shifts are characterized by a higher energy bleach and an induced absorption that drops in intensity for longer probe wavelengths.⁵³ State A exhibits this lineshape, while the structure of State B is almost completely negative with evidence of slight absorption at the edge of our detection. We would not expect the ligands to affect intraband relaxation and given the instrument response function for the utilized apparatus (~ 0.15 ps) these lifetimes are all within error of each other. To further confirm our assignment for τ_1 , we measured **CISe-OLAm** samples of varying sizes with 400 nm excitation. Similar to the study on **CISe-DPP**, we found size affecting the energy of these spectra (e.g. smaller NCs had higher energy bleaches and absorptions). For the smallest NCs we were able to resolve the absorption features changing shape with time, from that of a derivative-like biexciton shift towards an induced absorption that increased in intensity towards redder wavelengths as one would expect of a bandedge exciton experiencing intraband transitions (Figure 5.7).²⁶⁸ Furthermore, we

find that the dynamics for carrier cooling are slightly elongated (0.2 – 0.6 ps) when samples are excited with higher energy photons, consistent with carriers dissipating more energy upon relaxation through more electronic states.

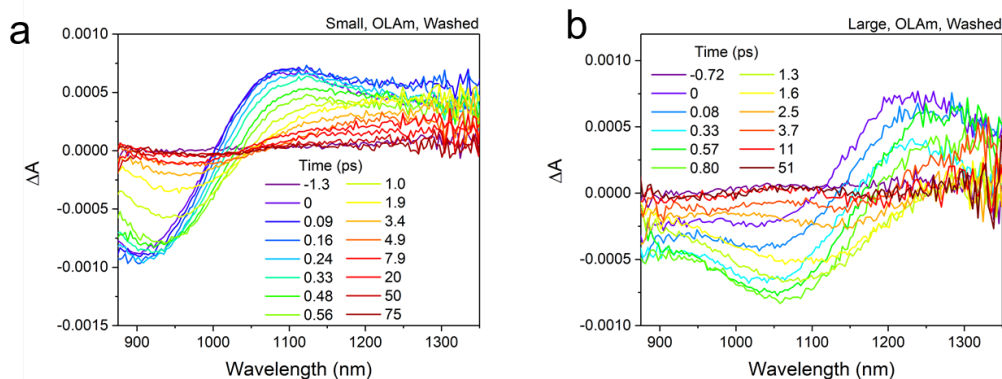


Figure 5.7: TA measurements of small (a) and large (b) CISE-OLAm samples excited at 400 nm.

From the TA alone, the nature of States C or D are not immediately apparent. We can rationalize that none of the states measured are emissive as they are all too high in energy. In addition, the low PLQY suggests that only small fractions of carriers are meaningfully populating the emissive state, suggesting that any TA signals that correspond to radiative recombination are overwhelmed by non-radiative ones. We note that a shift in bleach signals has been noted in other compositions of semiconductor NCs, namely quantum-confined InSb. In that case it was due to a multiple conduction band valleys,²⁶⁹ which is not likely the source of our signals due to the band structure of CISE. There have been several reports that the electrons may trap at surface states on these timescales,^{244, 265} and there is also literature precedence for intrinsic electron and hole traps.^{236, 238, 243}

XRD and Raman (Figure 5.8) were employed to probe the crystallinity of our samples and offer insight into defect states that could serve as carrier traps. XRD confirms that all three samples

exhibit the chalcopyrite crystal structure. At first glance there are no discernable differences between the diffraction data. Slight broadening in the **CISE-DPP** sample can be attributed to size distribution (i.e. Scherrer broadening), but the position and amplitude of all peaks are consistent. Upon closer inspection there is a weak feature around 35.6° , most evident in the **CISE-TBP** sample, that corresponds to the (211) reflection. The lack of this feature has been attributed to cation disorder and point defects within the crystalline lattice, namely ordered vacancy defect pairs of indium copper antisites ($\text{In}_{\text{Cu}}^{2+}$) and copper vacancies ($\text{V}_{\text{Cu}}^{1-}$).²⁷⁰ It is also seen in In-rich thin films of CISE, which is consistent with the aforementioned defects.²⁷¹ The **CISE-OLAm** sample is lacking this feature whereas it is weakly present in the **CISE-DPP** NC diffraction.

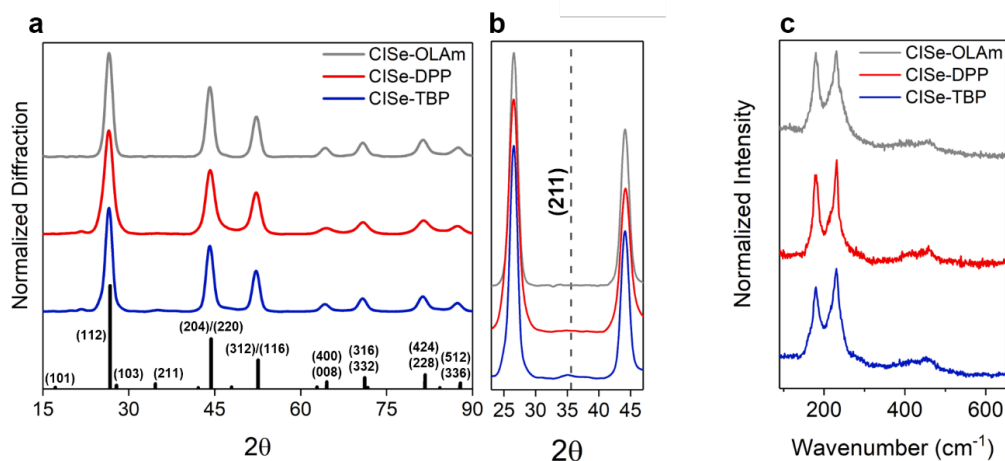


Figure 5.8: Investigation of the CISE crystalline lattice. (a) X-ray diffraction of all three samples showing the chalcopyrite crystal structure. (b) Slice of the XRD focusing on the (211) feature at 36° (c) Raman spectra display features around 180 and 230 cm^{-1} . The low intensity peaks between 300 and 500 cm^{-1} are second order features.

Raman spectra of the samples also show nearly identical features for the three different NC-ligand compositions. The strong signal at $\sim 180\text{ cm}^{-1}$ corresponds to the A_1 vibrational mode of the CISE lattice.²⁷² The higher energy feature at 230 cm^{-1} has previously been used as a benchmark for point defects such as $\text{V}_{\text{Cu}}^{1-}$ and $\text{In}_{\text{Cu}}^{2+}$ in CISE NCs synthesized with OLAm.²⁷⁰ We

observe that this feature is prevalent in all three samples with similar amplitudes. Fitting of the peaks provides a more quantitative ratio between the two modes (Figure S30). **CISE-DPP** displays the weakest proportion of the defect state with **CISE-OLAm** and **CISE-TBP** showing nearly identical proportions (Table 5.2). We note that this analysis is potentially complicated by a lower-energy feature around $\sim 115\text{ cm}^{-1}$ which also arises from defects.²⁷⁰ Due to limited range on our Raman spectrometer we cannot resolve this feature or completely deconvolute contributions from Rayleigh scatter. Despite this, the intensity of the lower wavenumber mode shows similar behavior to the 230 cm^{-1} defect feature with more intensity for **CISE-OLAm** and **CISE-TBP**. The features at higher wavenumbers correspond to phonon overtones and were too noisy to fit individually.

CISE NCs can easily be synthesized in off-stoichiometric ratios, Cu- or In-rich are particularly prevalent and can lead to distinct photophysical properties due to inclusion of different midgap electronic states.²³⁹ ICP-OES analysis was used to determine the ratio of Cu:In present in our samples. We find that the CISE NCs are In rich and while **CISE-OLAm** and **CISE-DPP** exhibit very similar ratios ($\text{Cu/In} \approx 0.94$), **CISE-TBP** has an increased amount of In present ($\text{Cu/In} \approx 0.81$).

With this information we can determine the identity of States C and D from TA. A wide range of defects are known to produce energy levels within the bandgap of CISE, however In-rich CISE is predominately characterized by pairs of $\text{In}_{\text{Cu}}^{2+}$ and $\text{V}_{\text{Cu}}^{1-}$ defects to produce the off-stoichiometric ratio. State C is approximately 15 – 60 meV below that of Species B. Given the lighter nature of the electron we can assume that the TA is mostly monitoring its movement to a new state.²⁷³ In this case the energy gap corresponds well with the difference in conduction energy levels and $\text{In}_{\text{Cu}}^{2+}$ antisite defects, which are known electron traps. Species C and D have nearly the same half-width half max (HWHM) suggesting the same population moving together to a slightly lower energy state. The energy difference (10 – 40 meV) matches well with the energy gap

between the valence band and V_{Cu}^{1-} , commonly thought to be hole traps in CISE.^{236, 239-240, 243} Reduction in bleach signal intensity is consistent with depletion of band-edge states (both conduction and valence band) so despite the hole not being as evident in TA, the opening of the bandgap transition and loss of bleach is noticeable.

Despite being able to characterize the identity of these defects, recombination of a localized electron and hole from these trap sites must be non-radiative. From the TA, we know that neither of these states are low enough in energy to correspond with PL, nor is this type of recombination (donor-acceptor model) consistent with reports of size dependent PL for CISE.²⁷⁴⁻²⁷⁵ Given the low proportion of population that radiatively recombines we are likely not seeing the emissive state by TA. Instead, we propose that it is occurring from Cu^+/Cu^{2+} defect couples that are theorized to be the radiative pathway in CIS NCs. These defects have been shown to produce broad emission and a Cu^{2+} can be paired with a V_{Cu}^{1-} to still produce In-rich CISE. It is hotly debated the origin of these defects and their role in the radiative process, for example whether the Cu^{2+} is an intrinsic defect or formed from a photogenerated hole recombining with a Cu^+ ion and whether the Cu^{2+}/Cu^+ defects occupies a lattice position or are interstitial defects.²⁷⁶⁻²⁷⁹

To understand non-emissive trap states further, we performed temperature dependent PL at both cryogenic and elevated temperatures (Figure 5.9). Both **CISE-OLAm** and **CISE-TBP** samples exhibited similar behavior, with increased PL intensity as the temperature was lowered to 80K and decreased PL at elevated temperatures. Similar results have been found in a variety of semiconductor nanocrystals such as CdSe, Si, InP, and $CuInS_2$.^{87-90, 278} The **CISE-DPP** sample similarly showed higher PL at low temperatures. Upon heating, it began to brighten, a trend that continued with rising temperature. After returning to 290K the sample remained brighter. To ensure that this increase was not due to photobrightening from the laser, the sample was moved to

fresh spots. While PL intensities differ due to film thickness, all showed at least twice the PL intensity found before heating (Figure 5.10).

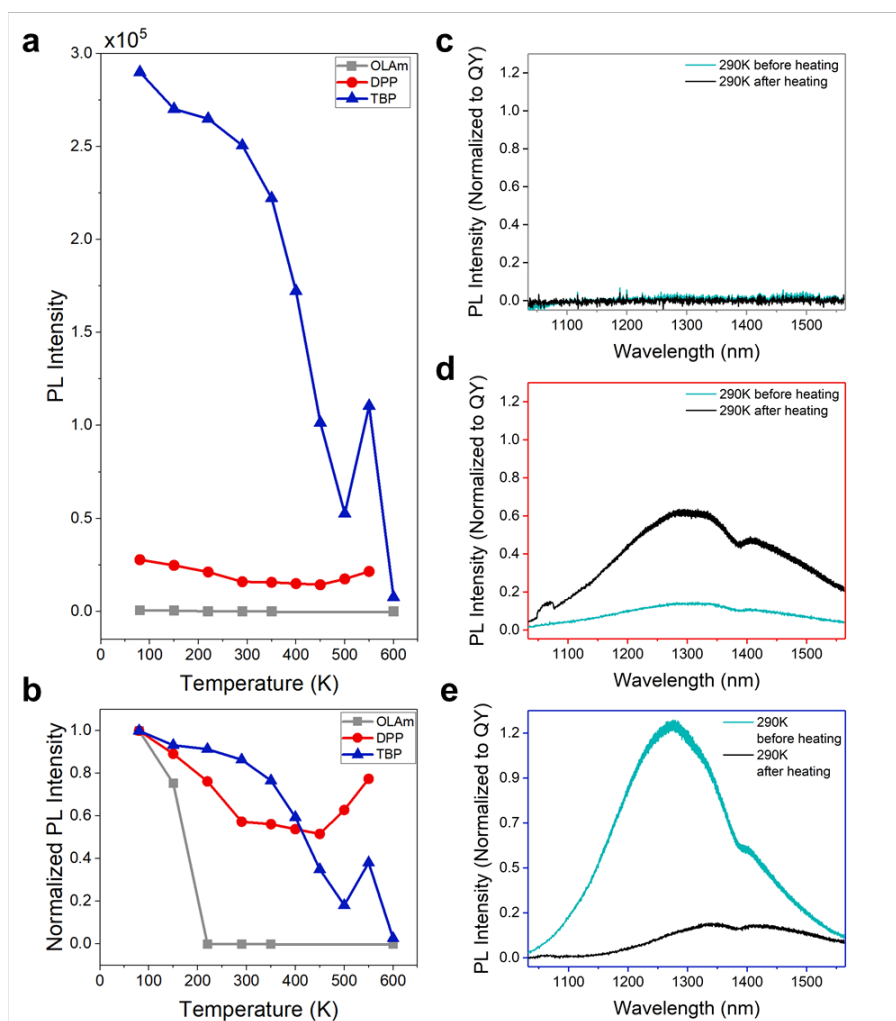


Figure 5.9: Temperature dependent PL of the three CISE samples. Integrated (a) and normalized (b) PL intensity for the three samples as a function of temperature. (c-e) The PL spectra of the three samples before and after heating to 600K.

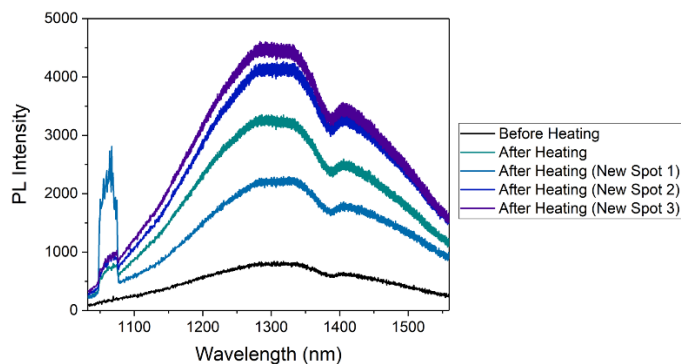


Figure 5.10: PL measured at different spots on the **CISE-DPP** film after heating to 600K to ensure that continued laser excitation did not induce brightening. Differences in PL intensity are due to film thickness inhomogeneity, but importantly all spots show at least two-fold enhancement of PL.

To further study the origin of this brightening in the **CISE-DPP** sample, we performed a pendulum (cyclic) heating experiment where the temperature was raised incrementally with consistent returns to room temperature to examine PL intensity and lineshape (Figure 5.11a,b). Initial heating from 290K to 400K and back increased the PL intensity by 115%. Heating to 500K and 600K further increased PL by 188% and 623% respectively. A return to 600K caused the PL intensity of the film to drop. Throughout the pendulum experiment, we observed no shift in the spectral maximum of the PL at room temperature suggesting that no sintering was occurring. Since the lineshape and peak did not change during these experiments, we are monitoring the same emissive state as before, but are either increasing its prevalence or reducing competing non-radiative pathways.

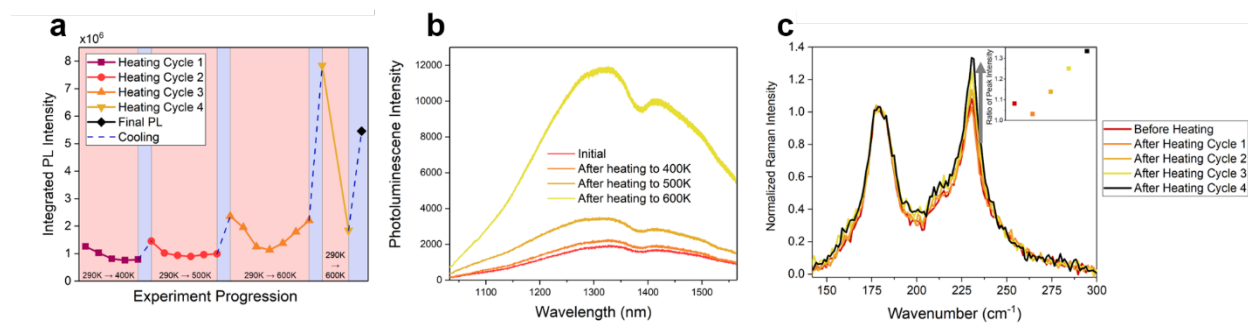


Figure 5.11: Pendulum heating of the CISE-DPP sample. The sample underwent a total of four heating cycles, from room temperature to 400, 500, 600K with intermittent steps and a final ramp from room temperature to 600K. (a) Integrated PL intensity during the heating cycles. (b) PL spectra of the sample initially and after the first three heating cycles. (c) Portions of the sample were removed after each heating cycle and examined using Raman spectroscopy. An increase in the 230 cm⁻¹ feature occurred after heating to higher temperatures.

Raman and TA (measured at room temperature) were used to examine film duplicates removed from thermal treatment at 400, 500, and 600K as well as the final increase to 600K. These results from the Raman are summarized in Figure 5.11c. Interestingly, an increase of the higher wavenumber Raman feature (230 cm⁻¹) is observed as the temperature is increased with the highest increase occurring in the single 600K ramp experiment. This suggests that not only does this feature provide information about In_{Cu}²⁺ and V_{Cu}¹⁻ defects, but also the Cu⁺/Cu²⁺ couple. TA lifetimes upon heating show differences in lifetimes and lineshapes and although a clear trend in time constant is not evident, a reduction in the amplitude of State C occurs consistently with each ramp cycle. A report on annealing in **CISE-OLAm** NCs saw that at much higher temperatures there was a decrease in the defect Raman feature and increase in the (211) diffraction peak which they attributed to reduction of defects.²⁷⁰ Since we saw a reduction in PL of the **CISE-DPP** sample upon multiple ramps to 600K as well as sintering in the **CISE-TBP** after heating the balance between ligands, surface, and intrinsic defects is delicate and highly dictated by the temperature.

Lastly, we turn to techniques that are sensitive to the organic ligands, namely FTIR and NMR to better understand surface passivation in these materials. Figure 5.12a shows the FTIR spectra of the NCs along with the corresponding spectra of the ligands alone. All samples show strong OLAm features around 2850 and 2925 cm^{-1} , which is not surprising since all NCs were synthesized in the presence of OLAm. The **CiSe-DPP** and **CiSe-TBP** samples do show IR bands associated with their respective phosphine ligand, suggesting that it is present to some degree. Importantly, FTIR is sensitive to all molecular species present regardless of whether they are bound to NC surfaces. Since these samples were cleaned and purified via multiple centrifugation steps, it is unlikely that the signal would be dominated by excess ligands.

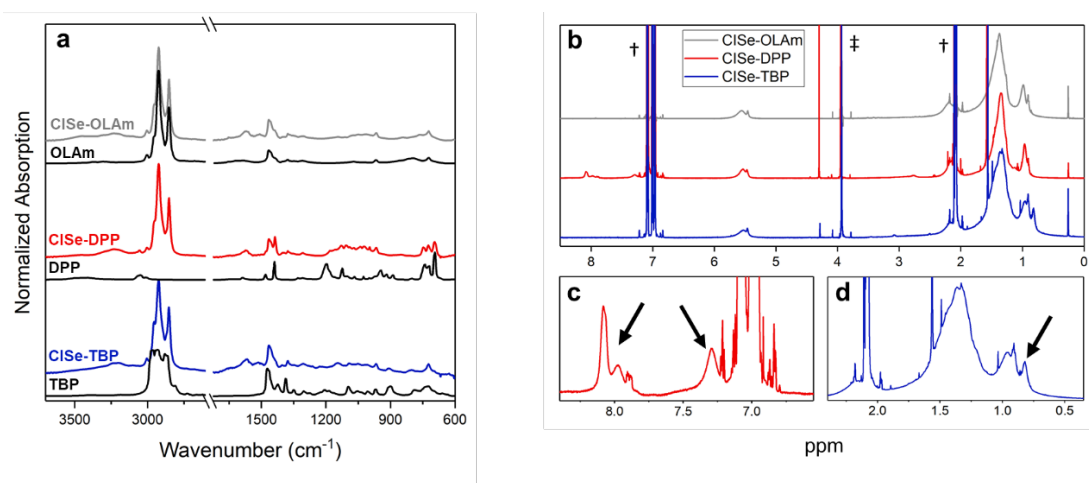


Figure 5.12: (a) FTIR of the three samples of CiSe NCs compared to that of the pure ligand (black lines). (b) NMR of the three samples. The broadened feature around 5.6 ppm corresponds to the alkenyl hydrogens of oleylamine. † denotes toluene features while ‡ is from CH_2Br_2 used as a standard to calculate ligand concentration. (c) and (d) are insets showing features corresponding to bound DPP and TBP respectively.

We utilized NMR spectroscopy to differentiate bound vs. free species and quantify the ligand density, these results are summarized in Figure 5.12b-d. Signals broaden and shift downfield when a molecule is bound to a particle compared to one freely moving in solution.¹²²

While OLAm has a large variety of peaks between 0 and 3 ppm that are spectrally dense and complex to interpret, the region between 5 – 6 ppm (corresponding to the alkenyl hydrogens) is less populated and has commonly been used for analysis. A broad feature around 5.6 ppm is evident in all three samples suggesting that OLAm is in fact bound to the surface in all cases. A sharper feature at 5.4 ppm corresponds to free OLAm in solution and confirms our hesitation from FTIR in assuming all signals are due to bound species.

In the case of **CISE-DPP** (red trace), features above 7 ppm (panel b) match the expected proton shift of the phenyl protons. Here the signals are complicated due to multiplicity and various confirmations possible for this ligand as well as strong features from trace toluene solvent protons. In addition, other work has shown that a disubstituted phosphine such as DPP can react with a primary amine during the synthesis of NCs, which will likely present different NMR signatures.²⁸⁰ Regardless the region around 8 ppm was fit to determine the ratio of DPP:OLAm ligands bound on the surface. From this analysis we determine that DPP constitutes approximately ~18% of bound ligand.

Similar analysis was performed for **CISE-TBP**. The prevalence of alkanyl hydrogens on this ligand means that its signals are almost completely obscured by those of OLAm. However, a discernable feature at 0.9 ppm corresponds to the terminal protons of TBP, which is not present in the other samples (panel c). Fitting of this feature again provides a rough estimate of the ratio of TBP to OLAm, which we find to be ~11%. These results are summarized in Table 5.2. We furthermore calculated the ligand density on the surface of the NCs using CH₂Br₂ as an internal standard. An average of 1.5 – 1.8 ligands/nm³ was determined for these samples, which is lower than most measurements of ligand density on NCs.^{122, 281} While OLAm is bound to the surfaces of all three samples, increase in both the ligand density and the appearance of bound phosphines in

the **CISE-DPP** and **CISE-TBP** points to passivation of additional surface states. One of the unique features of this class of ternary materials is the combination of hard/soft Lewis acids/bases. In the case of CISE, Cu^+ is a soft Lewis acid while In^{3+} is a hard Lewis acid. As mentioned above we also argue the incorporation of Cu^{2+} defects, which serves as an intermediate Lewis acid. Furthermore, OLAm is known to be a hard Lewis base and TBP, a soft base. DPP likely falls in between based on its pK_a values.²⁸² Given the differences in basicity between these ligands we can assume they are binding to different surface sites (In vs. Cu). We cannot overlook the trend in basicity that matches much of our results above and potentially points to stability of certain reaction intermediates or surface states.

Table 5.2: Structural and Surface Characterizations

	Ratio of Raman Peaks	Cu:In Ratio	Surface Coverage Ligands/ nm^2	% Phosphine Ligand
CISE-OLAm	2.19	0.936 ± 0.006	1.58	-
CISE-DPP	1.78	0.937 ± 0.002	1.76	18
CISE-TBP	2.12	0.806 ± 0.008	1.89	11

From these results it is clear that surface trapping serves as an additional source of non-radiative pathways in all these samples, but particularly **CISE-OLAm** since it lacks a phosphine-based ligand and is unable to passivate both types of metals. This is supported by studies on both CIS and CISE NCs with different ligand compositions where amines were found to produce poor surface passivation while phosphines were better.^{245, 283} This comparison is complicated by the studies primarily focusing on post-ligand exchange which can cause deterioration of the surface.^{69,}

With all of these results we can now build a picture of the complicated photophysics of this system, which we have summarized in Figure 5.13. OLAm, DPP, and TBP act during the synthesis to change the ratio of In/Cu within the NCs, afterwards they passivate specific surface states. In the end, the NCs have a variety of different traps and the number of each kind determines the probability of a carrier localizing on the surface or in an internal defect. Localization at $\text{In}_{\text{Cu}}^{2+}$ and $\text{V}_{\text{Cu}}^{1-}$ defects is non-radiative and competes with the slower radiative process wherein a delocalized electron recombines with a localized hole.

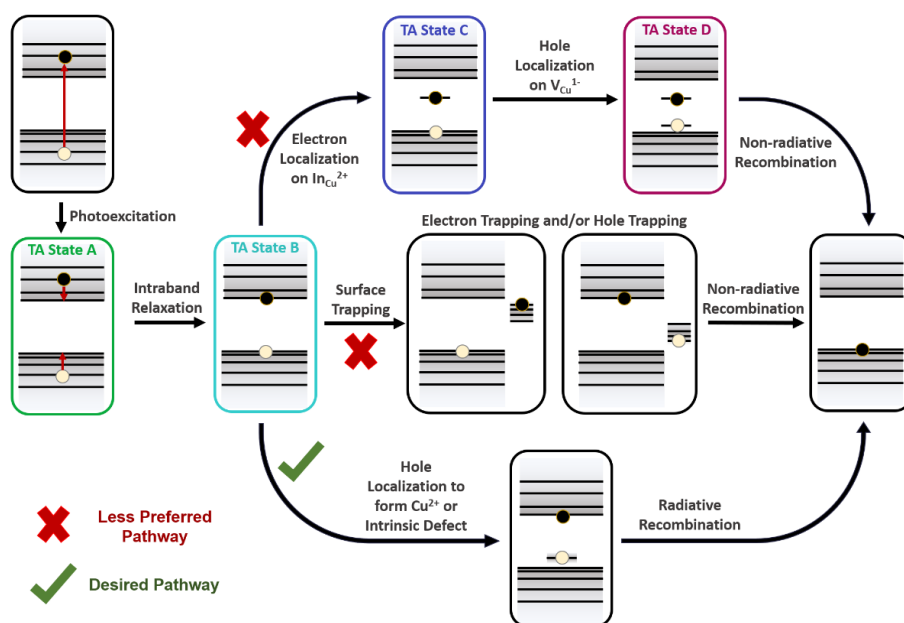


Figure 5.13: Diagram showing the different electronic states involved in carrier processes in CISE NCs. After excitation, electrons and holes undergo intraband relaxation followed by intrinsic trapping or surface trapping. Localization at intrinsic defects can be radiative ($\text{Cu}^+/\text{Cu}^{2+}$) or nonradiative ($\text{In}_{\text{Cu}}^{2+}$, $\text{V}_{\text{Cu}}^{1-}$). Ligands dictate the preference of one path over another.

5.4 Conclusion

There are two main mechanisms from which ligands can cause drastic changes in photophysical behavior, namely incorporation of defects within the crystalline lattice upon synthesis of the materials or poor passivation of trap states at the surfaces. Here, ligands play a direct role in both the synthesis of the NCs *and* passivation of the surfaces afterwards. In this study we examined the effects that the synthetic ligand/Se-precursor has on the photophysical, structural, and temperature dependent properties of CISE NCs. The inorganic crystal and the organic ligands must be considered as an entire system given the drastic changes they can have on optoelectronic properties. We found that differences in Cu:In ratios, defects within the lattice as well as complex surface-ligand bonding are contributing to the unique properties seen here. Depending on the ligand present localization at V_{Cu}^{1-}/In_{Cu}^{2+} defects or undercoordinated surface metal ions can prevent radiative recombination that occurs at Cu^{2+}/Cu^{+} couples. Using an amine based ligand (OLAm) produces the highest quantity of trap states and resulted in very short lifetimes and PLQY. Phosphine based ligands (DPP, TBP) reduced the prevalence of surface trapping, but produced stark differences in the Cu:In ratio depending on the identity of the phosphine. Thermal annealing at 600K of **CISE-DPP** produced a 600% increase in PLQY suggesting a post-synthetic mechanism for increasing emission intensity.

Future studies of new Se-precursors may produce NCs with longer charge separation lifetimes that prove to be better in photovoltaic applications. Thiols, another soft Lewis base, is oftentimes used in the synthesis of CIS NCs and has been found to produce higher PLQYs than phosphines suggesting that the surface of these materials are very sensitive to the ligand and also highlights the importance of HSAB theory for proper alignment of ligand and surface reactivity.^{238,}

²⁸⁴ Thiols are less commonly used in the synthesis of CISE NCs due to formation of CISSe hybrid

structures, precluding direct comparison.²⁸⁴ The reduction of trapping with shells in both CIS and CISE NCs has been reported by a variety of groups and may reduce some non-radiative surface sites.²⁴³ However, the ligands present in those studies are not the same as the ones here and a direct comparison should not be made. Shelling of nanocrystals can also lead to incorporation of the shell composition's cation due to diffusion or alloying at the surface, potentially changing the electronic structure of the material.²⁴³ Further studies that add shells to NCs with these three ligand compositions would need to be undertaken to determine the extent of surface trapping. To enable better understanding of emission, spectroelectrochemistry and magneto-optical experiments, similar to what has been done for CIS, are needed to unravel the nature of the $\text{Cu}^+/\text{Cu}^{2+}$ couple.^{276-279, 285}

5.5 Outlook

CuInSe_2 NCs are a promising candidate for solar cells, but in order for them to be used to their fullest extent their fundamental photophysics must be understood. While CuInS_2 NCs are a good starting point, CuInSe_2 must be treated as a separate composition with its own properties. Full investigations into this composition should cover a wide range of ligand compositions, shell growths, and annealing procedures. Even amongst the ligands studied here, there are many unanswered questions. Do the different sizes of CISE-DPP and CISE-TBP behave similarly to the lack of strong size effect in CISE-OLAm? Could TBP and DPP be added post-synthesis to improve PLQY? What is happening to the samples upon heating? While a basic understanding is broached with this work, more pendulum heating should be coupled with NMR, FTIR, Raman, XRD, and TEM to unravel the nature of the NCs afterwards.

Full investigations into this composition should cover a wide range of ligand compositions, shell growths, and annealing procedures. Can PLQY be improved by utilizing different ligand

precursors? What about combinations of precursors? Do these ligand compositions behave similarly upon shell growth? Should annealing be done at lower temperatures similar to what was used here or are the higher temperatures commonly used necessary? Synthesis, spectroscopy, and theory must be used in conjunction to understand and optimize preps.

Chapter 6: Photoinduced Ligand Loss and Fragmentation

6.1 Introduction

Since their first colloidal synthesis, semiconductor nanocrystals (NCs) have been the focus of intense research due to their unique photophysical properties that derive from quantum-confinement, i.e. absorption and narrow photoluminescence (PL) energies that are readily tunable through size and shape. With large absorption cross-sections, low size dispersity, ability to absorb multiple photons, and high quantum yield these materials are rapidly being incorporated into a variety of devices from lasers to LEDs to photovoltaics.¹² These properties along with rapid electron or hole transport have also paved the way for the study of photoetching, light-induced synthesis, and photocatalysis.²⁸⁶⁻²⁸⁹

Over the last decade, a lot of study has been invested into understanding the role of ligands in semiconductor NCs and their interface with the surface. This has proven critical as the large surface-to-volume ratio in NCs ensures that a large quantity of atoms are on the surface and coordinated to these organic molecules. Using techniques such as NMR, FTIR, TGA, and CV the binding strengths, covalent attachment, and density of ligands has been investigated.¹⁰⁵ The role of native ligands as well as post-synthetic ligand exchange has opened another dimension to these nanoscale materials beyond composition, size, and shape.²⁴ Amongst these techniques, NMR stands apart due to its non-destructive nature, ability to measure NCs in solution, and differentiation of bound vs. free species.¹²² Most studies utilize standard ^1H NMR, but many groups have expanded to 2D NMR, different pulse sequences (e.g. dynamic nuclear polarization), and non-proton experiments (i.e. ^{113}Cd , ^{31}P). See Section 2.6 for more details.

CdSe is, in many ways, the quintessential semiconductor NC. It is often cited as a model for a variety of compositions due to deep understanding of its synthesis and photophysics. Despite the vast research that has been done on these materials, nearly all studies on ligand – NC relationship focus on static behavior or monitor exchange using additional ligands being added to the solution. In many applications these materials will undergo photoexcitation, at times under quite intense illumination as their optical properties are the desired characteristics. Even in lab settings, these materials are excited to study electronic behavior with little regard to the effects of laser pumping. It is unclear the effects that photoexcitation of the inorganic core may produce in the organic ligands. Will the ligands be removed from the surface? If so, will the less dense covering of the NCs cause aggregation or precipitation? Can the nanocrystals potentially fracture, change shape or structure? Can the high energy surfaces react with the ligands to cause them to undergo chemical change? Oftentimes NCs that could have exhibited much of this behavior are discarded without care to *what* is occurring and *why* because they are considered “dead” optically, their photoluminescence drops substantially and after precipitation they are likely unusable. Here, we aim to understand some of the changes that occur in these NCs after intense illumination. Using NMR as our main tool, we monitor ligands as they become unbound from the surface of the NC and the chemical changes they undergo. In conjunction with transmission electron microscopy (TEM), X-ray diffraction (XRD) and photoluminescence, an unusual range of properties are studied, from sintering of NCs to photobrightening. This study serves as a first look into photoinduced changes in CdSe NCs passivated by oleic acid and aims to address some of the questions raised above while providing future directions for further study.

6.2 Experimental Methods

Synthesis of CdSe Nanocrystals

We followed previously established synthetic protocols with slight modifications.²⁹⁰ To make the Se:ODE precursor, 5mL of ODE and 1 mmol of Se were placed in a roundbottom flask, purged with nitrogen, and left stirring. Meanwhile a roundbottom flask, condenser, and thermocouple jacket were assembled and placed in oven. While still hot, the assembly was attached to a Schlenk line and placed under nitrogen. CdO (0.8 mmol) and a stir bar were added, and the flask capped with a septa. Using a syringe, ODE (10 mL) and oleic acid (0.8 mL) were added. Solution was rapidly stirred and heated to 270°C causing it to change from cloudy to clear to yellow. At 270°C and upon complete dissolution of solids, 2 mL of the Se:ODE mixture were injected. After approximately 45 seconds the heating was stopped, and the reaction vessel moved away from the heating mantle to allow it to cool. Once at room temperature, 10 mL of toluene was added and used to clean the resulting nanocrystal solution into a centrifuge tube. For cleaning, 10mL of isopropanol and 10mL of methanol were added to crash out the nanocrystals. The sample was centrifuged at 8000 r.p.m. for 5 minutes. Afterwards, the supernatant was discarded and the solid dissolved in toluene. After another round of centrifugation any solids that crashed out were discarded and another 10mL of isopropanol and methanol were added followed by another round of centrifugation to crash out particles. The resulting solid was kept and pumped into the glovebox where it was dissolved in toluene and kept until experiments.

6.3 Results and Discussion

To ensure continuity between experiments one batch of NCs was used. Oleic acid capped CdSe NCs were synthesized using protocols that are described in the Methods section.²⁹⁰ To ensure that excess oleic acid and unreacted reagents were not present in solution three rounds of centrifugation were performed and the resulting sample was stored in toluene in a glovebox until experiments. For experiments, the sample was dried down under nitrogen and suspended in

deuterated toluene. Six aliquots of equal concentration and volume (600 μ L) were separated into standard NMR tubes. Samples were excited at 400 nm using a 1kHz pulsed femtosecond laser and the tubes were mechanically rastered such that the entirety of the sample volume was illuminated. Incident power on the NC dispersions was adjusted using a neutral density wheel and laser spot size was controlled using an iris and changing the focal distance. One tube was maintained as a control and had a standard added afterwards (CH_2Br_2) to determine ligand density. Four samples were exposed to laser radiation in set time increments (0 – 150 minutes). Three of the samples experienced a constant laser power (140 mW) but three different spot sizes to study the effects of fluence (spot sizes for Tubes 1, 2 and 3, respectively were 9.8 mm², 0.85 mm², and 0.071 mm²). Two samples, Tubes 3 and 4, maintained the same small spot size but different powers (140 vs. 75 mW). The average number of excitons ($\langle N \rangle$) varied between 4.2 – 584 for the photoexcited samples. Exposures were halted after various elapsed times and NMR measurements were conducted to follow sample evolution. A summary of the experimental parameters is given in Table 6.1. Tube 5 was not illuminated but was examined using variable temperature NMR to monitor the effects that static heating may induce on the sample.

To start, we confirmed the attachment of oleic acid to the surface as well as the lack of any free ligand remaining in solution using ^1H NMR (Figure 6.1a). As has been observed for bound ligands, all proton features are broadened substantially and shifted downfield relative to free ligand due to reduced diffusion while attached to the NC surface. Throughout this study we will focus on the vinylic proton features of oleic acid that occur around 5.6 ppm since this region is less congested and easier to analyze than the alkyl protons between one and three ppm. No sharp peaks are evident around 5.4 ppm confirming that the NCs were successfully purified of unbound oleic acid. Initial TEM measurements prior to any illumination show monodisperse NCs with an average

diameter of ~ 4.2 nm (Figure 6.1b). The absorption spectrum (Figure 6.1c) shows the typical lineshape of CdSe NCs with a clearly defined lowest-energy absorption at 585 nm.

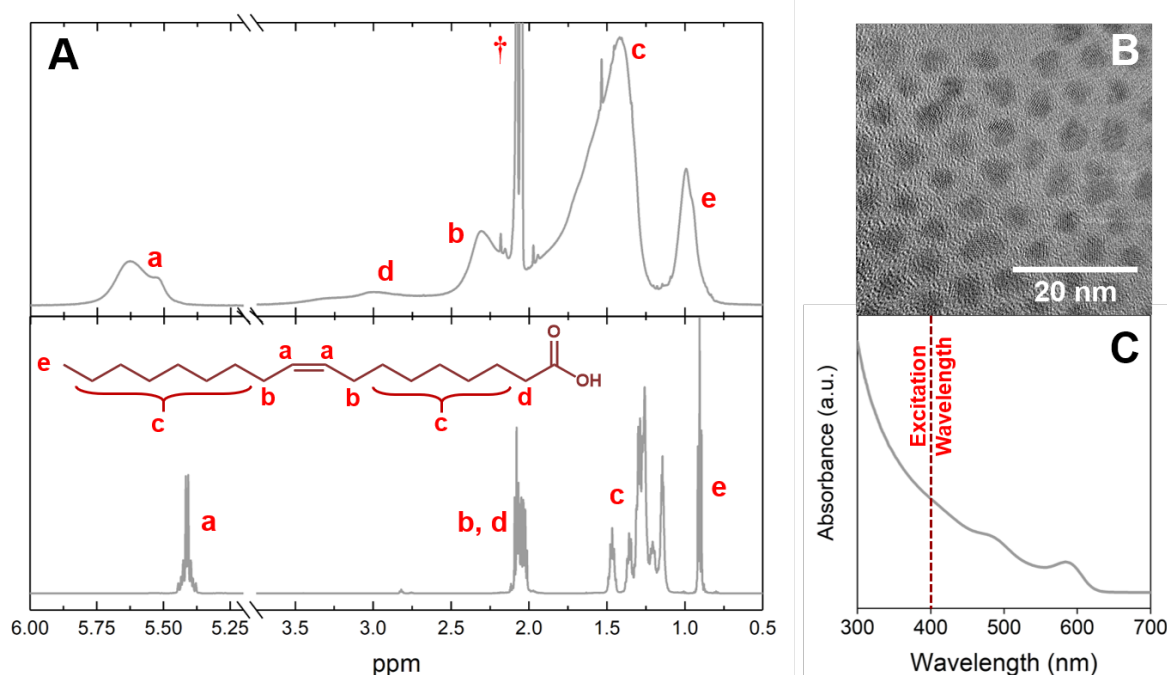


Figure 6.1: CdSe NCs before photoexcitation. (A) NMR spectra of the NCs (top) and oleic acid (bottom). Protons are marked for both along with residual toluene features (†). (B) Transmission electron microscopy image of the NCs. Diameter was measured to be 4.2 ± 0.8 nm. (C) Absorption spectrum with excitation wavelength (400 nm) marked.

Table 6.1: Photophysical properties and diameter of CdSe NCs before and after photoexcitation

Sample	Laser Power and Spot Size	<N>	Photoexposure times (min)	Abs. Max (nm)	PL Max (nm)	Diameter (nm)	< τ > _{PL, 5ns} (ns)	< τ > _{PL, 50ns} (ns)
Control	-	-	-	585	598	4.19 ± 0.81	4.9 ± 0.3	7.4 ± 0.4
Tube 1	140 mW, 9.8 mm ²	4.2	30, 90, 150	583	599	4.19 ± 0.71	6.1 ± 0.5	8.3 ± 0.3
Tube 2	140 mW, 0.85 mm ²	49	15, 30, 60, 85	583	599	4.19 ± 0.75	4.6 ± 0.5	7.4 ± 0.4
Tube 3	140 mW, 0.071 mm ²	584	15, 30, 60, 85	580	603	4.36 ± 0.83	1.6 ± 0.1	3.1 ± 0.3
Tube 4	75 mW, 0.071 mm ²	313	15, 30	583	599	4.28 ± 0.79	4.4 ± 0.5	6.8 ± 0.3

The NMR spectra collected for Tubes 1 and 3 are given in Figures 6.2a-d. Over the course of the experiments more ligands dissociate from the surfaces of the NCs as indicated by the appearance of the sharp features around 5.4 ppm and reduction in the broad 5.6 ppm peak. The alkyl features also shift upfield and sharpen due to desorption. Due to the smaller spot size, Tube 3 experienced a higher fluence and $\langle N \rangle$, which in turn induces a greater extent of ligand loss as observed by NMR. A comparison of Tubes 1 – 3 at 85 or 90 minutes of total exposure is given in Figure 6.6a showing the difference in ligand loss depending on fluence. To determine the ratio of bound vs. free ligand the region between 5.3 – 6.0 ppm was fit using the MNova software. Peak areas were separated into “bound” or “free” depending on ppm and width. The results of this analysis are given in Figure 2e. As the fluence is increased (by decreasing spot size) more ligands are dissociated from the surface with a maximum of ~50% desorbed from Tube 3 after 85 minutes. The NCs remained stable in solution with no aggregation evident over the course of the experiments. Given months in solution, Tube 3 did experience some aggregation of particles as noted by precipitation of solid, but the other tubes did not. Tube 4 showed similar ligand loss to Tube 3 despite approximately half the power (and therefore half the absorbed photon dose) suggesting a $\langle N \rangle$ threshold above which no further photon absorption promotes ligand loss.

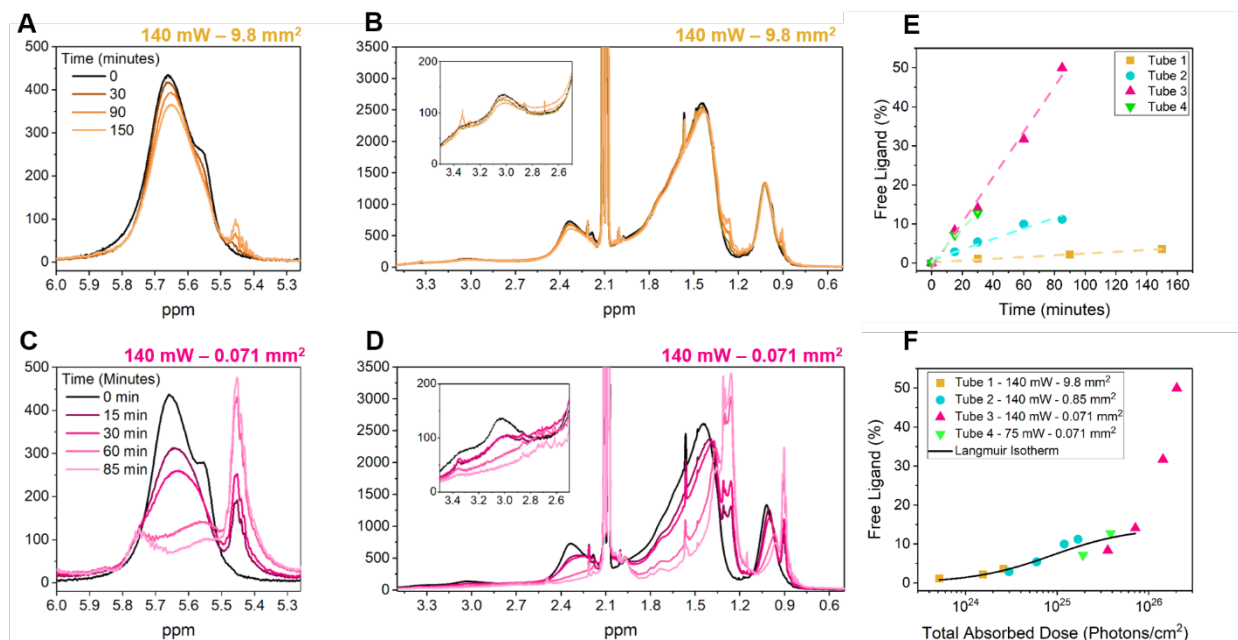


Figure 6.2: Photoinduced ligand desorption. NMR spectra of Tube 1 (A, B) and Tube 3 (C, D) as a function of laser exposure time. (E) Ratio of integrated free ligand signal vs total ligand for the four samples. (F) Total absorbed dose in photons/cm² fit to a Langmuir isotherm.

Linear fitting of the desorbed ligand ratio versus time provides a rate of ligand loss per minute (Figure 6.3). As we described above this rate does not increase linearly with $\langle N \rangle$, instead it seems to approach a maximum rate of ligand loss upon which higher fluences yield similar results. This also allows us to approximate the length of time required for an arbitrary percentage of ligand dissociation at low $\langle N \rangle$. For example, if $\langle N \rangle$ is 0.05 then to achieve 1% ligand loss would require ~13 hours and 50% ligand loss would require over 27 days of constant laser exposure.

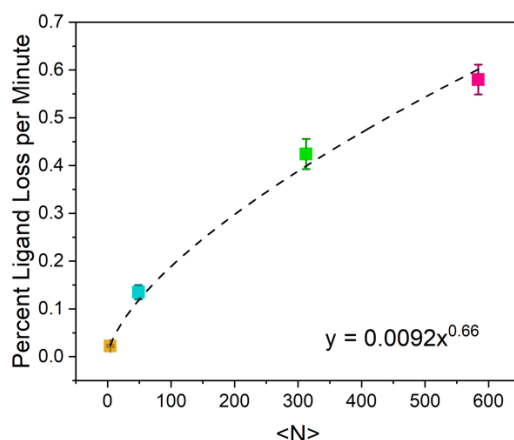


Figure 6.3: Rate of ligand loss (determined from the linear fits in Figure 6.2e) vs. $\langle N \rangle$. The data was fit to a power law with the fitted equation shown.

To determine whether static heating from laser illumination could cause ligand desorption, we used variable temperature NMR to monitor changes in the population of bound and free ligand upon heating to 100°C. Even after maintaining the sample at 100°C for one hour, no solvated oleic acid features were observed (Figure 6.4). We do note the shoulder present on the lower side of the feature disappears concurrently with increased intensity of the main peak, potentially due to rearrangement of ligands on the surface into more energetically favorable configurations., suggestive of some form of sample annealing.

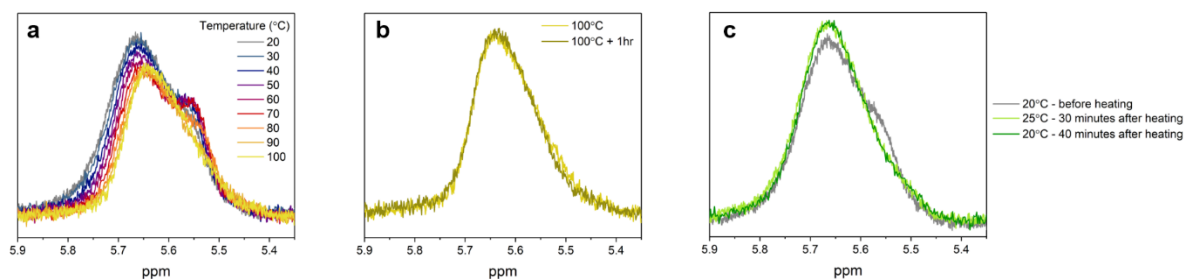


Figure 6.4: NMR spectra of the alkenyl region of oleic acid for variable temperature experiment. (a) Temperature ramping from 20°C to 100°C. (b) Sample at 100°C initially and after one hour. (c) Before and after heating.

By converting to photons/cm² we can monitor total absorbed dose across the four samples. We find that ligand loss is tied inherently to the number of photons absorbed with increasing desorption occurring as the number of photons absorbed increases. We were able to fit most of the data to a Langmuir binding isotherm (Eq. 6.1) where θ is the fraction of free ligand, K_d is the dissociation constant, $[hv]$ is the total absorbed dose, and constant a relates saturation.

Eq. 6.1
$$\theta = \frac{aK_d[hv]}{1+K_d[hv]}$$

Ligand desorption above ~14% ceases to follow a simple Langmuir model and were excluded from the fit. Despite this, the fit for ligand desorption at this lower ranges provides valuable insight. We find that the dissociation constant (K_d) is 1.12×10^{-27} for this binding isotherm. While we were unable to fit to a two isotherm model, the data fit well to a biphasic equation (Eq. 6.2) that is commonly used to describe two binding sites (often observed in drug release²⁹¹ The need for two phases suggests a difference in binding motif/strength, potentially due to unique covalent bonding (e.g. bidentate vs. monodentate, edge vs. facet).¹²⁸ This model provides an upper limit for ligand dissociation of $61 \pm 12\%$ suggesting that above this point NCs lose colloidal stability and will precipitate.

Eq. 6.2
$$y = A \left[\frac{p}{1+10^{(n_1(c_1-x))}} + \frac{1-p}{1+10^{(n_2(c_2-x))}} \right]$$

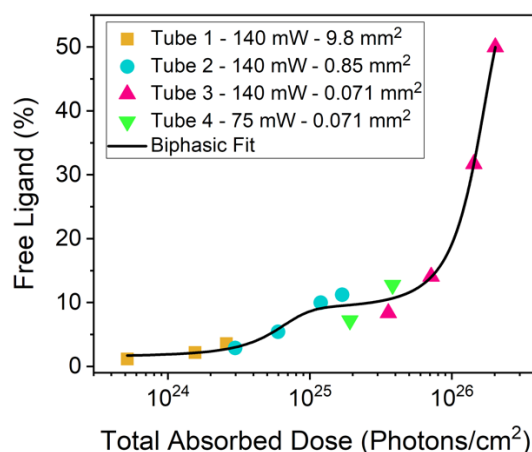


Figure 6.5: Figure 6.2f from the main text with a biphasic fit (Eq. 6.2): $A = 0.6 \pm 0.1$, $p = 0.13 \pm 0.07$, $n_1 = 2.2 \times 10^{-27}$, $n_2 = 1.1 \times 10^{-28}$, $c_1 = 5.3 \times 10^{26}$, $c_2 = 1.5 \times 10^{28}$. We do not attribute much physical meaning to these values except A and p which represents the maximum value of free ligand (saturation point) and the weight between the two binding modes.

Unexpectedly, Figure 6.6 shows that following photoexcitation NMR resonances develop that are neither consistent with bound nor unbound oleic acid, but instead clearly indicate other chemical species. At 4.9 – 5.05 ppm and 5.65 – 5.8 ppm clear signatures of the vinylic hydrogens of undecane or undecanoic acid are evident.²⁹² We are not able to distinguish between these chemical species given the similarity in their proton shifts, but integration confirms their identity. In addition, a strong feature at 5.25 ppm grows in that corresponds to water. Given the nonpolar nature of toluene any water formed would produce clusters that yield a distinctive chemical shift.²⁹³⁻²⁹⁴ Around 4.3 ppm sharp peaks demarking molecular hydrogen are present.²⁹⁵ Indeed, in some experiments bubbles clearly form in the tube consistent with this assignment. Furthermore, the integrated peak area for these features is relatively constant suggesting formation of dissolved gases that eventually leave solution. Features around 9 ppm demarcate aldehyde protons although again we cannot be quite clear in their identity. They could arise upon loss of the hydroxide group from oleic acid or oxygen addition to the double bond. Two distinct features in this region show

different behavior with photoexcitation. The peak at ~ 9.3 ppm forms on similar timescales regardless of fluence. The peak at 9.13 ppm, however shows a similar behavior to the other chemical species.

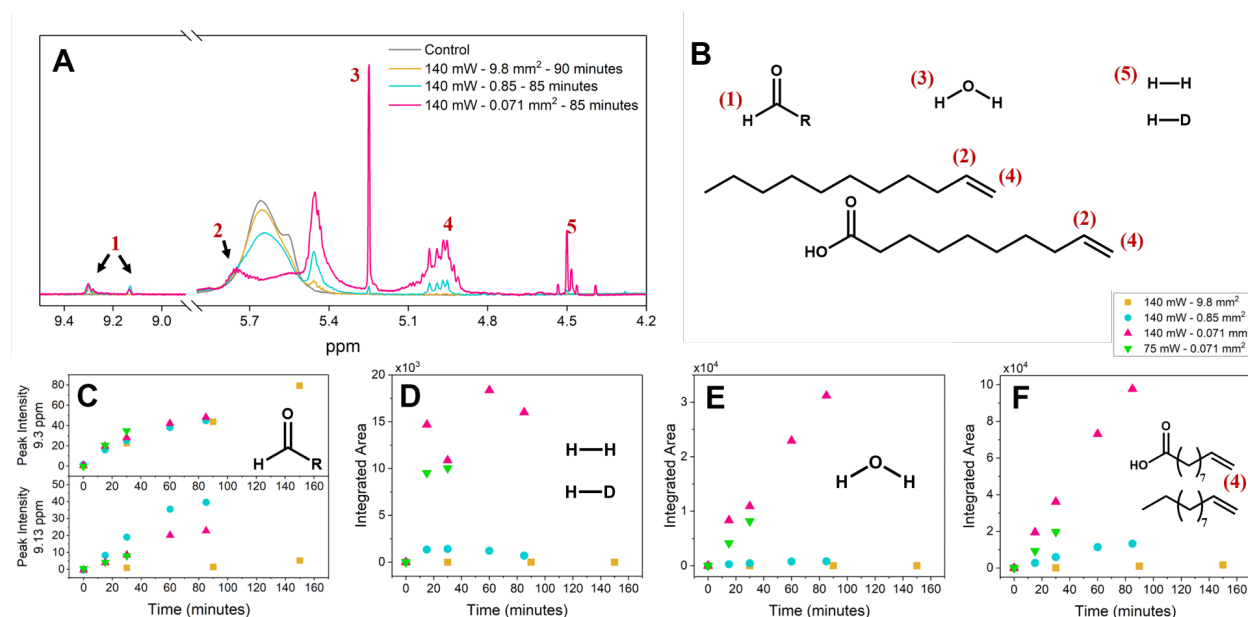


Figure 6.6: Ligand Fragmentation. (A) Tubes 1-3 at similar photoexcitation dose times. Chemical shifts of new molecular species are marked by red numbers. (B) The corresponding chemical species that arise from fragmentation of the oleic acid ligand or reaction with toluene. (C-F) Production of the molecules as a function of laser exposure time. (C) Aldehyde features at 9.13 and 9.3 ppm, (D) water clusters peak at 5.25 ppm, (E) hydrogen features between 4.4 – 4.55 ppm and (F) terminal protons of undecane or undecanoic acid between 4.9 and 5.1 ppm.

We note that no chemicals were added to these samples to cause fragmentation. The NMR spectrum of our oleic acid showed no evidence of these chemical species nor were they present in the NC spectrum before photoexcitation. As a control experiment to determine if the CdSe NCs were necessary for this oleic acid degradation process we illuminated a tube of concentrated oleic acid in deuterated toluene using a higher fluence than the other tubes for a longer length of time (Figure 6.7). Incredibly small amounts of undecane/undecanoic acid and aldehydes were seen but no evidence of hydrogen or water. Along with the temperature dependent NMR this suggests that

a combination of laser irradiation, CdSe, and oleic acid is necessary to generate the observed photoproducts.

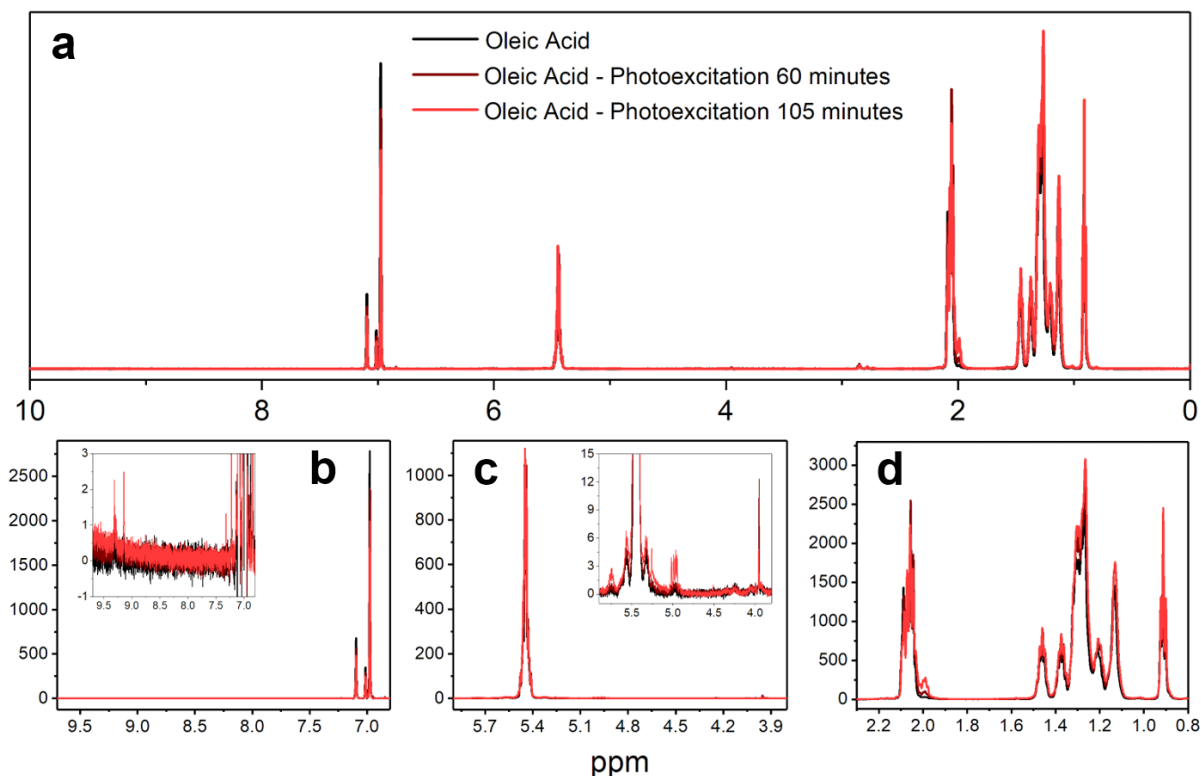


Figure 6.7: Oleic acid photoexcitation experiment (no NCs). (a) Full NMR spectrum of oleic acid before excitation and after intense laser exposure for 60 and 105 minutes. (b) 6.8 – 9.7 ppm region, inset is the same area zoomed in. (c) 3.8 – 5.9 ppm region, inset is again a zoomed in version of the same data range. (d) 0.8 – 2.3 ppm region. Note the difference in y-axis for the insets in b and c.

TEM images of the NCs after photoexcitation reveal particle shape and size remain largely unchanged. NCs exposed to the highest intensity (Tube 3) experienced trace amounts of sintering between some NCs to form larger, agglomerated structures (~8-10 nm). Given that distinct crystallographic domains can be seen within these larger NCs we suggest that ligand loss likely produces colloidal instability and close contact of NC surfaces. Tubes 1 and 2 showed no discernable difference in NC diameter with potentially a slight narrowing in distribution, consistent with annealing. X-ray diffraction shows that the NCs maintain the zincblende crystalline phase.

Broadening of diffraction peaks in Tube 3 suggests smaller crystalline domains have formed consistent with loss of surface layers and ligands that lead to agglomeration.

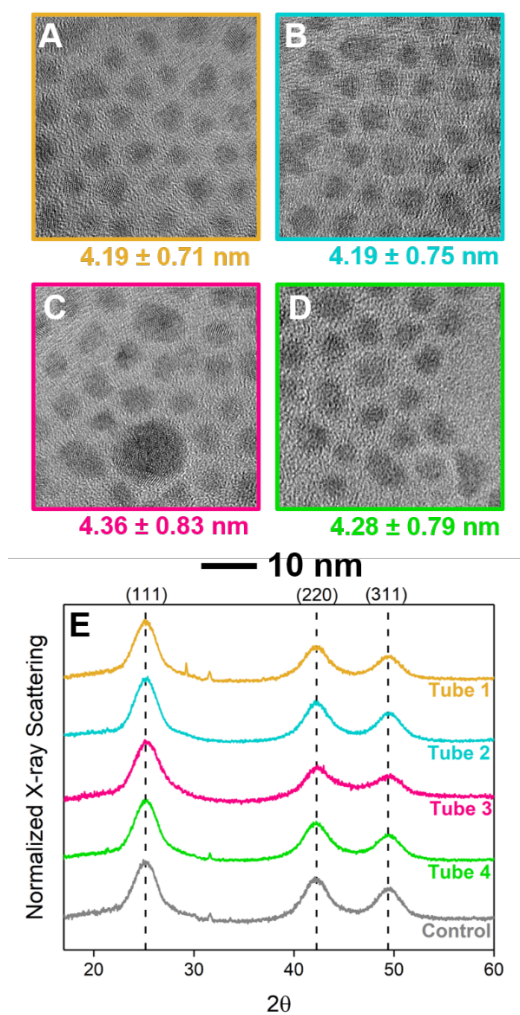


Figure 6.8: Characterization of the samples after photoexposure. (A-D) TEM images of Tubes 1-4 and the corresponding diameters measured. (E) X-ray diffraction patterns of Tubes 1-4 and the control.

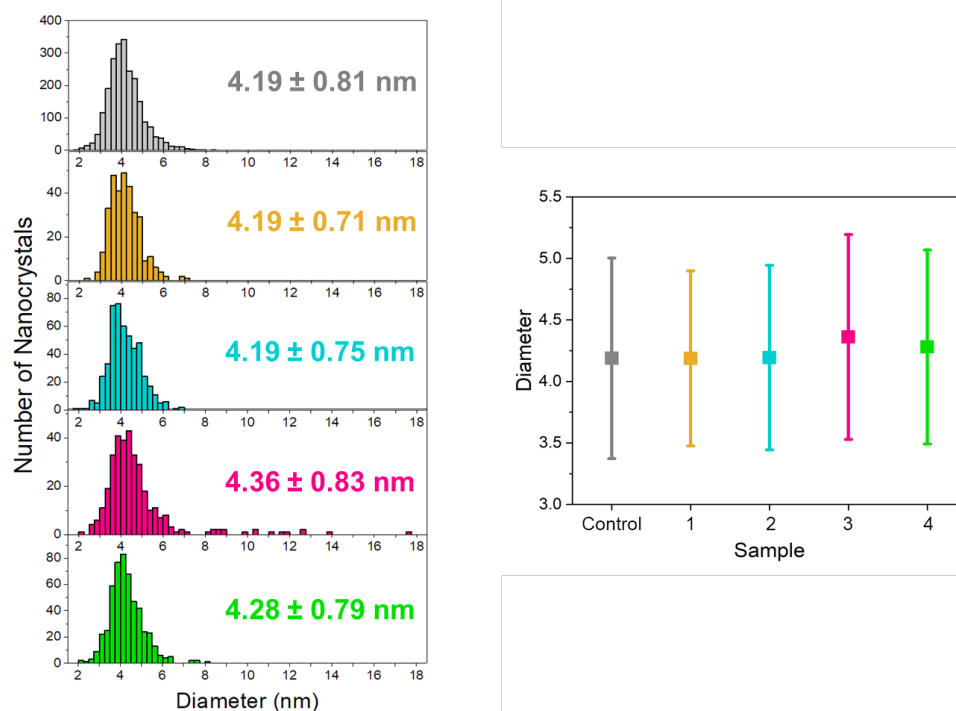


Figure 6.9: Size histograms for the control and Tubes 1-4. NC size was not impacted strongly by prolonged, intense photoexcitation. Tube 3 (and to a much lesser extent, Tube 4) experienced some agglomeration and sintering of NCs resulting in a higher average and larger standard deviation.

Optical properties offer additional information regarding impact of exposure and ligand loss, which is imperative for performance in devices. UV-Vis shows that the absorption has not shifted much (2-5 nm, see Table 6.1) although Tube 3, and to a lesser extent Tube 4, show broadening of features and a tail towards the red. This absorption is lower in energy than bulk CdSe (marked by the dashed line at 713 nm) and we attribute this to trap state formation within the bandgap. Low concentrations and solvent correction were used to ensure that this was not an artifact of scattering. As noted above, despite ligand loss, all samples showed no precipitation initially.

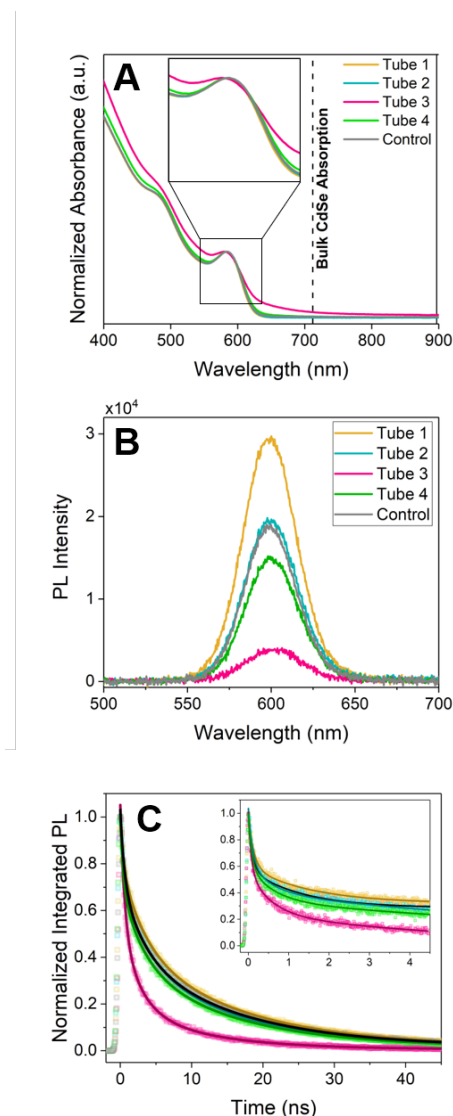


Figure 6.10: Optical characterization. (A) Absorption spectra for photoexcited samples and the control. Inset shows the lowest energy absorption in finer detail. Bulk CdSe absorption at 713 nm is given as a dashed line. (B) Static PL spectra. (C) Time-resolved PL spectra over 50 ns and 5 ns (inset) along with triexponential fits.

Static and time-resolved photoluminescence (Figure 6.10b-c) provide further insight into impacts of surface passivation. Despite broadening and the appearance of midgap trap states by absorption, no emission red of the main band-edge feature is observed. Tube 3 did exhibit some broadening and slight red shift of PL as well. All samples maintained a similar emission wavelength, consistent with the bandgap and size remaining close to the control. After correcting

for intensity, we find that Tubes 1 and 2 showed brightening after ligand loss suggesting a reduction of trap states either through annealing of intrinsic defects or reorganization of ligands into a position or binding motif that is more favorable for radiative recombination. Tube 3 showed a drastic reduction in intensity, likely due to formation of many trap sites. We observed similar trends using a streak camera to monitor time- and wavelength-resolve PL. Tube 1 exhibited longer lifetimes, while Tube 3 showed a more substantial reduction in lifetime. Although not evident with static PL, all samples exhibited a higher energy emission (< 525 nm) at short times. This feature, which could easily be missed in the control, intensifies strongly in Tube 3. We attribute this to formation of small CdSe clusters that are formed from surface layer removal of larger structures.

6.4 Conclusion

Intense photoexcitation of semiconductor NCs induced ligand loss that depended strongly on the number of photons absorbed per NC. Beyond ligand loss some samples showed an increased in PL suggesting that some form of annealing occurs and if it could be controlled may produce NCs with higher QYs. Other samples showed a sharp reduction in PL that is detrimental for their incorporation into applications that require high currents or illumination such as LEDs or photovoltaics. For all samples, fragmentation of the ligand and/or reaction between organic species in solution caused the formation of a variety of products including aldehydes, water, hydrogen, and undecane/undecanoic acid. After intense photoexcitation, the NCs remained almost identical in size suggesting their ability to be used as reusable photocatalysts.

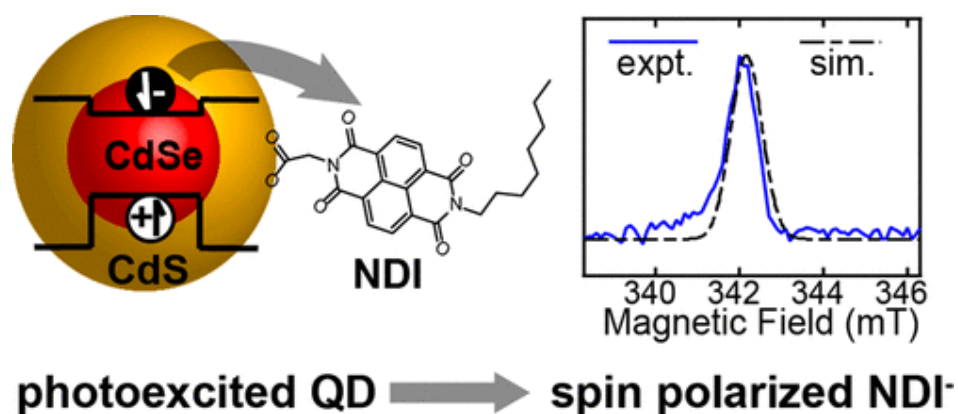
6.5 Outlook

Use of NMR techniques to understand NCs has expanded rapidly over the last few years. For example, non-proton NMR (i.e. ^{113}Cd , ^{77}Se , ^{31}P) and more complicated pulse sequences have

enabled observation of particle growth, surface composition, and metal distribution (surface vs. core). Combining such experiments with the photodoping done here may help unravel more of the complex surface and ligand transformations. In many ways this study was limited by its novelty and exploratory nature. Future experiments could benefit greatly from in-situ photoexcitation wherein a NMR spectrometer is coupled to a light source.²⁹⁶ This would allow a more continuous series of time points as well as potentially show spin-polarized ligand fragments through chemically induced dynamic nuclear polarization (CIDNP) if the photochemical reactions are radical in nature.²⁹⁷ Even with regards to the mechanism of photodegradation of ligands and solvent, this study could only speculate. What part of the ligand is fracturing? Is it reacting with the deuterated toluene? If benzene d₆ was used instead would some fragments not form?

There are many other parameters that can be altered as well in order to study the dependence of these results on them. The use of 400 nm laser light was chosen purely for convenience, but 800 nm light would only produce changes with two photon absorption and therefore allow more penetration depth. What about excitation at the band edge? Only one size of CdSe NCs was studied, would different sizes show the same results? Does the number of ligands desorbed scale with $\langle N \rangle$? In PbS NCs different sizes of particles causes different facets to be exposed, will any discernable difference occur in ligand loss from these? What effects will varying morphology (0D vs. 1D vs. 2D) and composition induce? CdSe NCs can be synthesized with phosphonic acid ligands as well as oleic acid, how does the difference in identity and binding strength affect photoinduced ligand loss? Hopefully this study will lay the foundation for a new area of NC research that will bridge our understanding of ligands, surfaces, photophysics, and degradation.

Chapter 7: Hybrid Inorganic-Organic Donor-Acceptor SCRPs



This chapter is adapted from:

Olshansky, J. H.; Harvey, S. M.; Pennel, M. L.; Krzyaniak, M. D.; Schaller, R. D.; Wasielewski, M. R., Using Photoexcited Core/Shell Quantum Dots To Spin Polarize Appended Radical Qubits. *Journal of the American Chemical Society* **2020**, 142 (31), 13590-13597.

7.1 Introduction

The promise that quantum information science (QIS) holds to revolutionize computation, communication, and sensing is accelerating research in this field.²⁹⁸⁻²⁹⁹ However, the exact materials that will comprise these emergent technologies remain an open question.²⁹⁹⁻³⁰⁰ A particularly prominent class of materials, semiconductor quantum dots (QDs), have been proposed for quantum computation and communication applications.³⁰¹⁻³⁰⁶ QDs grown by molecular beam epitaxy in all-solid-state devices are the most widely studied form for these applications,³⁰⁵ but colloidal QDs are also attractive candidates owing to the tunability of their size,³⁰⁷ shape,³⁰⁸ and composition.³⁰⁹ Optical excitation in colloidal QDs is particularly intriguing because it offers a way to selectively address specific QDs (i.e. by size or composition)³⁰⁴ and can generate well-defined spin states,^{38, 310} thus satisfying two key criteria of functioning qubits.³¹¹

The spin dynamics of photoexcited charges in the archetypal cadmium chalcogenide (CdE) colloidal QDs have been probed by a variety of optical and magneto-optical techniques, including: time-resolved Faraday rotation,^{303-304, 310, 312} degree of emissive circular polarization,³¹³ polarized pump-probe spectroscopy,³¹⁴ and cross-polarized transient grating spectroscopy.^{38, 315} From this, a generalized picture of spin dynamics in these colloidal QDs has been developed. Due to extensive spin-orbit coupling, the spin states in CdE QDs are best described by their total angular momentum. The two lowest energy states have total angular momenta of $F = 1$ and $F = 2$ and are termed “bright” and “dark” excitonic states, respectively. The $F = 2$ dark state lies approximately $\Delta E_{BD} = 2\text{-}20$ meV below the bright state.^{39, 316} Spin relaxation between these two states is suggested to occur on the sub-picosecond to tens of picoseconds time scale as a result of hole spin-flips, resulting in rapidly equilibrated Boltzmann populations.^{38, 313-314} A slow component to spin relaxation is also observed (hundreds of picoseconds to a few nanoseconds), and is ascribed to

both intra-level relaxation (e.g. $+2 \rightarrow -2$ within the dark state) and electron spin-flips.^{38, 303, 313-314}

In either case, photogenerated spin coherence in these systems does not live long enough to support the microwave-based spin manipulations required for quantum computation (> 100 ns).³¹⁷ A strategy to harness these spin states prior to relaxation is therefore necessary.

Organic molecules offer a promising platform for supporting long-lived spin coherences owing to their weak spin-orbit coupling.³¹⁸ Therefore, transferring spin coherence, or at least spin polarization, from a photoexcited QD to an organic molecule is of keen interest. With this aim in mind, it is worth briefly reviewing efforts to understand and control spin in QD-molecular conjugate systems. Coherent spin transfer has been demonstrated from photoexcited QDs of one size to molecularly-linked QDs of another size.³⁰⁴ Spin selective charge extraction from QDs has also been demonstrated when functionalized with chiral molecules *via* the chiral-induced spin selectivity (CISS) effect.³¹⁹⁻³²³ Photoexcited QDs have been used to efficiently sensitize molecular triplet states *via* triplet energy transfer.³²⁴⁻³²⁶ Furthermore, spin state control in photoexcited QD-organic molecule conjugates has been shown in the context of the spin-correlated radical pair (SCRp) model.^{133, 327-328}

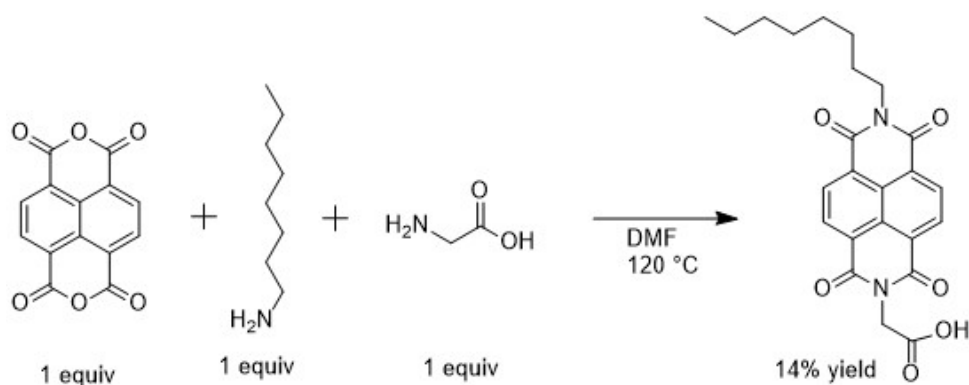
In both of the triplet energy transfer studies and the SCRp work, longer-lived QD excited states display primarily triplet character. The SCRp studies are of particular interest in the context of the research presented here. In two of these studies, photoexcitation of an organic chromophore and subsequent electron transfer to a QD results in a radical pair state ($\text{QD}^{\cdot-}\text{-molecule}^{\cdot+}$) that undergoes radical-pair intersystem crossing to recombine as a molecular triplet state.^{133, 327} This process is further verified by transient EPR measurements.¹³³ In a third study, spin control is demonstrated by selectively exciting either the organic molecule or the QD.³²⁸ When the molecule is excited, rapid charge separation and recombination outcompetes spin interconversion, allowing

for return to the singlet ground state. When the QD is excited, however, the QD^- -molecule⁺ state recombines to a molecular triplet state.³²⁸ The studies described above demonstrate the possibilities for spin control in photogenerated QD-molecular systems. However, they have been limited to QD^- -molecule⁺ radical pairs, and furthermore do not directly probe the charge-separated state.

In the work presented here, we directly probe *via* transient EPR spectroscopy a QD^+ - molecule⁻ state that is generated by QD photoexcitation. These measurements are enabled by using core/shell CdSe/CdS QDs that can support long-lived charge-separated states. We first investigate the dynamics of photoexcited electron transfer from CdSe/CdS core/shell QDs to a naphthalenediimide (NDI) electron acceptor as a function of both CdS shell thickness and NDI surface coverage. This serves both as a means to more confidently determine the charge transfer rates relevant for the EPR measurements, but also to benchmark shell thickness-dependent electron transfer in the less explored CdSe/CdS core/shell system (compared to CdSe/ZnS). A polarized spin state assigned to the NDI radical anion is observed in the transient EPR data. The signal is nearly entirely absorptive, suggestive of a polarization mechanism analogous to the triplet mechanism (TM), in which polarized spins are generated by charge separation from a photogenerated triplet state.³²⁹⁻³³³ In this case, the photoexcited QD serves as the “triplet.” Temperature-dependent EPR measurements suggest that this polarization may arise from the population difference in the dark and bright states of the QD. Spin polarization transfer from a photoexcited QD to a surface bound molecule is an important step towards harnessing the rich spin physics and synthetic tunability of colloidal QDs for QIS applications.

7.2 Experimental Methods

NDI ligand synthesis



Scheme 7.1 Synthetic route to NDI ligand

The NDI ligand was synthesized in accordance with a previously published procedure (compound 25 in the referenced work).³³⁴ NDA (2.68 g, 10 mmol), glycine (0.75 g, 10 mmol), octylamine (1.30 g, 10 mmol) and anhydrous DMF (40 mL) were combined in a 100 mL round-bottomed flask, purged with nitrogen gas, and heated to 120 °C for four hours while stirring. The tan cloudy solution was allowed to cool to room temperature and then poured into 200 mL of water, rinsing the flask with minimal DCM. The aqueous suspension was vacuum filtered to yield the crude product. An NMR of the crude product in DMSO- d_6 indicated a 74: 22: 4 ratio of desired product : diglycine product : dioctyl product. The crude product was purified *via* column chromatography with a 10 cm column and a 95:5 DCM:MeOH eluent mixture, that was adjusted to 90:10 DCM:MeOH to more efficiently elute the desired product. The dioctyl product eluted first, followed by the desired asymmetric product. Fractions containing the asymmetric product were combined, solvent removed *in vacuo*, and the product was recrystallized from a MeOH/DCM mix. Pink solid, 604 mg, 14% yield. ^1H NMR (500 MHz, DMSO- d_6): δ 8.70 (m, 4 H), 4.74 (s, 2 H), 4.06 (t, 2 H), 1.67 (quin, 2 H), 1.39-1.24 (m, 10 H), 0.86 (t, 3 H) ppm.

CdSe Synthesis

Synthesis of CdSe NCs has been described elsewhere.³³⁵⁻³³⁷ To begin, glassware (round-bottomed flask, condenser, thermocouple jacket) was assembled and placed in an oven for 15 minutes before being transferred (while hot) onto a Schlenk line and immediately placed under vacuum. CdO (60 mg), ODPa (280 mg), TOPO (3 g), and stir bar were added to the flask, which was then sealed and heated to 150°C while still under vacuum for 30 minutes. Afterwards the flask was degassed with three nitrogen/vacuum cycles and the temperature brought up to 320°C. At approximately 240°C, 1 mL of TOP was injected into the flask. Solution was kept at this temperature until all solids had dissolved. Prepared Se/TOP solution (60 mg Se dissolved in 0.5 mL of TOPO in the glove box and stirred for one hour to dissolve) was quickly injected into the flask. After ~30 seconds the flask was removed from the heating mantle and rapidly cooled using nitrogen. At 50°C, ~15 mL of IPA were added. The suspended QDs were then transferred to centrifuge tubes and centrifugation produced a pellet composed of both QDs and excess Cd-phosphonate. The pellet was resuspended in 10 mL of hexanes, centrifuged again to remove impurities, then the supernatant was combined with 15 mL of IPA and centrifugation was repeated. This process was repeated three times until the QD solution in hexanes was clear. The final pellet was transferred to a glovebox and resuspended in 4 mL of toluene.

Oleic Acid Ligand Exchange

When our NDI ligand was added to a solution of the phosphonate capped CdSe core NCs we did not see evidence of charge transfer by transient absorption suggesting that the free NDI ligands were not able to displace the tightly bound phosphonic acid moieties and confirming that covalent attachment is necessary for electron transfer. We therefore substituted for oleic acid to allow attachment of the NDI ligand using a modified procedure from Zeger Hens and coworkers.³³⁸

CdSe NCs (300 μ L, 273 μ M) and oleic acid ($\sim$ 0.5 mL) were added to a 25 mL round bottom flask. The solution was degassed under vacuum and then heated to 80°C for 15 minutes. The vacuum was substituted for nitrogen and the solution stirred at 100°C for 20 hours. After cooling, a small amount of toluene ($<$ 4 mL) was added to the flask to extract as many NCs as possible. The resulting solution was added to a centrifuge tube and $\sim$ 30 mL of methanol added and centrifuged. Supernatant was decanted. NCs were once again dissolved in toluene ($<$ 3 mL) and $\sim$ 7 mL of methanol. The solution was centrifuged again and the supernatant decanted. The dry NCs were pumped into a glove box and suspended in a small amount of toluene for future experiments.

CdS Shell Addition

We followed previously published procedures for CdS shell addition.³³⁶⁻³³⁷

Cd-Oleate Solution: CdO (0.6426 g), oleic acid (15.9 mL), and ODE (9.1 mL) were added to a 50 mL round bottom flask along with a stir bar. The mixture was stirred for 15 minutes and then degassed under vacuum for 15 minutes. The solution was heated to 120°C and left stirring under vacuum for 45 minutes before switching to nitrogen flow and raising the temperature to 220°C. The solution was stirred for one hour until it turned clear. The nitrogen was then evacuated and cooled to 110 °C for one hour. Finally, it was sealed, and cooled under vacuum before being pumped into the glove box until shell synthesis.

Shell Synthesis (1 nm): Glass apparatus (four necked 30 mL round bottom flask, condenser, thermocouple glass jacket) were assembled, greased, secured, and placed in oven for 15 minutes. After removal from oven, the apparatus was added to the Schlenk line and placed under vacuum for 15 minutes. The flask was then filled with nitrogen before ODE (3 mL) and

oleylamine (3 mL) were added and allowed to degas under vacuum for 30 minutes. While under nitrogen CdSe NCs (360 μ L, 100 nmol) were added to the flask. The flask was switched to vacuum again and temperature raised to 40°C. The solution stirred for one hour before being raised to 110°C. Meanwhile, two syringe solutions were prepared in the glove box. The first was a mix of octane thiol (28.5 μ L) and ODE (4 mL). The second included the already prepared Cd-oleate solution (680 μ L) with ODE (3.32 mL). The two syringe solutions were simultaneously injected using a syringe pump at a rate of 2 mL/hr. The samples were then annealed for 10 minutes at 310°C before being rapidly cooled by nitrogen.

Shell Synthesis (2 nm): The 2 nm shell synthesis followed the same procedure as the 1 nm except the syringes were filled with approximately 3x the concentration of Cd and Se. Thus the first syringe was prepared with 0.086 mL of octane thiol and 3.9 mL of ODE, while the second had 2.1 mL of Cd-oleate solution and 1.9 mL of ODE.

NC Cleaning: Acetone was added to the solution (~ 40 mL) to crash out the NCs. Then two washes of hexanes and IPA (3 mL, 10 mL) were used to crash out impurities and NCs respectively. The resulting dry NCs were pumped into the glovebox and resuspended in toluene.

7.3 Results and Discussion

The system explored in this paper is shown in Figure 7.1. CdSe/CdS core/shell QDs serve as both the light absorber and electron donor. A modified NDI ligand with a carboxylate functional group linker serves as the electron acceptor (NDI absorbs blue of 400 nm, avoiding co-excitation). Approximate energetics for the system are shown in Figure 7.1b. Prior electrochemical measurements have shown that the approximate valence band energy of similar CdSe/CdS core/shell QDs is 1.2 V vs. SCE.³³⁹ However, it should be noted that electrochemical

measurements on QD band energies are subject to large errors (hundreds of meVs) and therefore we represent these states as a distribution.³⁴⁰ The reduction potential of NDI has been previously measured at -0.48 V vs. SCE.¹⁰³ With a 2.1 eV QD excited state, the approximate driving force for charge separation is -0.4 eV (i.e. favorable). The optical absorption and emission of the QDs are shown in Figure 7.1c. Both core/shell samples are grown from the same batch of 3.3 nm CdSe core QDs following previously published synthetic procedures.^{337, 339} The 2 nm shell sample exhibits red-shifted emission and absorption due to carrier delocalization and also shows enhanced absorption in the 400-450 nm range as a result of increased CdS volume. The photoluminescence quantum yields were 13% and 68% for the 1-nm and 2-nm shell samples, respectively. Transmission electron microscopy (Figure 7.2) was used to calculate average diameters of X nm, 5.6 nm, and 7.7 nm for the core, 1 nm, and 2 nm shell samples respectively.

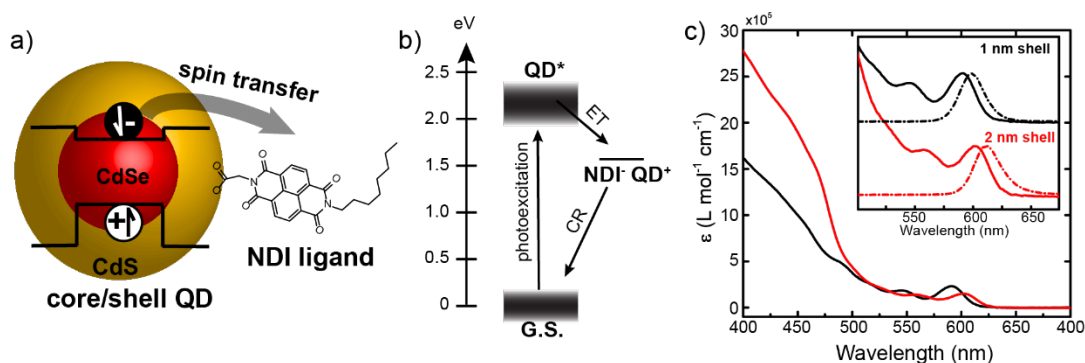


Figure 7.1. Schematic of the donor-acceptor system. a) Diagram of CdSe/CdS core/shell QD and the NDI ligand that acts as the electron acceptor. b) Energy diagram of electron transfer (ET) to create the NDI^{•-} - QD⁺ species and charge recombination (CR) to the ground state. c) UV-Vis absorption (solid lines) and photoluminescence (dashed lines) of 1 nm shell (black) and 2 nm shell (red) QDs. d) TEM images of QDs.

The QD-NDI conjugates were prepared with a range of NDI equivalents per QD by adding progressively more NDI ligand to a dilute QD solution in toluene. The carboxylate group serves as the binding head to the QD surface. The as-synthesized CdSe/CdS core/shell QDs are primarily

coated with oleic acid, which can be ligand-exchanged for other carboxylic acid ligands (such as our NDI ligand). We believe all NDI added binds because: 1) the NDI ligand is only sparingly soluble in toluene, but produces a scatter-free solution when combined with QDs, and 2) the free NDI does not show up in NMR when mixed with the QDs. We additionally found that the NDI ligand did not bind to the native CdSe QDs, which were functionalized with phosphonic acid ligands. This is consistent with previous work,³³⁸ and was remedied by heating the CdSe QD samples in oleic acid for a day prior to treatment with NDI.

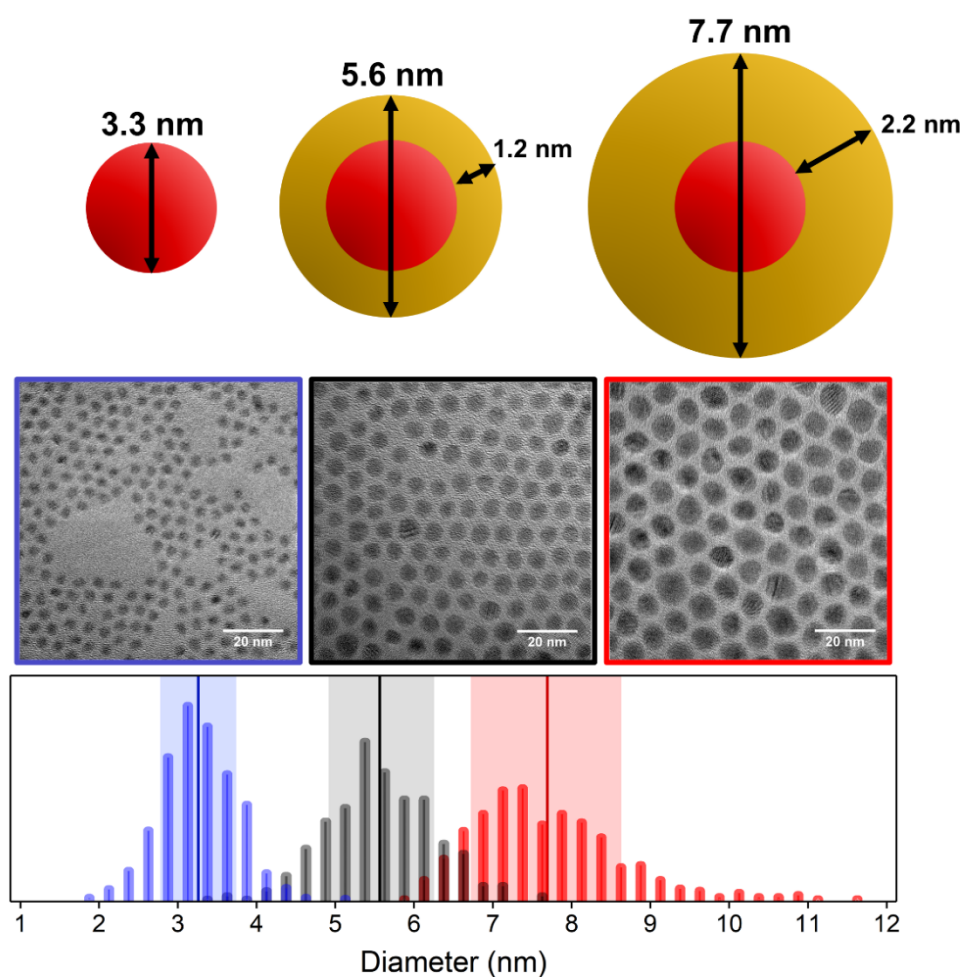


Figure 7.2. Size schematic of core CdSe and core/shell CdSe/CdS QDs (top), TEM micrographs (center), and sizing distributions based on 371, 266, and 213 individual particle measurements for cores (blue), ~1 nm shell CdSe/CdS (black), and ~2 nm shell CdSe/CdS QDs (red) respectively.

Prior to analyzing the spin characteristics in this QD-molecular dyad, we first aimed to obtain a full picture of the charge transfer dynamics. Such information aids in our interpretation of the spin dynamics as well as provides benchmark rates for shell-dependent electron transfer from CdSe/CdS core/shell QDs. To probe these charge transfer dynamics, we turned to transient absorption spectroscopy. Transient absorption data were collected for the CdSe core, 1 nm shell, and 2 nm shell CdSe/CdS QDs with a range of NDI equivalents per QD. Example transient spectra are shown in Figure 7.3, highlighting the core/shell QDs with either no NDI or many NDI ligands. The slower dynamics of the 2-nm shell sample precluded the collection of meaningful data on the fs to ps timescale. In the absence of NDI, all samples exhibit a multi-exponential QD bleach recovery corresponding to all radiative and non-radiative recombination pathways native to the QDs (Figure 7.3a,d). Upon addition of NDI, we observe new spectral features associated with both $\text{NDI}^{\bullet-}$ and QD^+ , confirming the presence of photoinitiated charge separation. $\text{NDI}^{\bullet-}$ most notably has a prominent absorption feature at $\sim 480 \text{ nm}$,¹⁰³ which is observed in all transient spectra that include NDI. The derivative-like feature near the QD band edge is assigned to a Stark-shifted QD absorption resulting from the electric field between the separated charges, and has been described previously in similar systems.³⁴¹⁻³⁴² Importantly, both $\text{NDI}^{\bullet-}$ and QD^+ features appear in the same ratio regardless of the number of NDI equivalents, and decay in concert. This suggests that we are generating a one-to-one $\text{NDI}^{\bullet-}$ and QD^+ pair that annihilates *via* charge recombination.

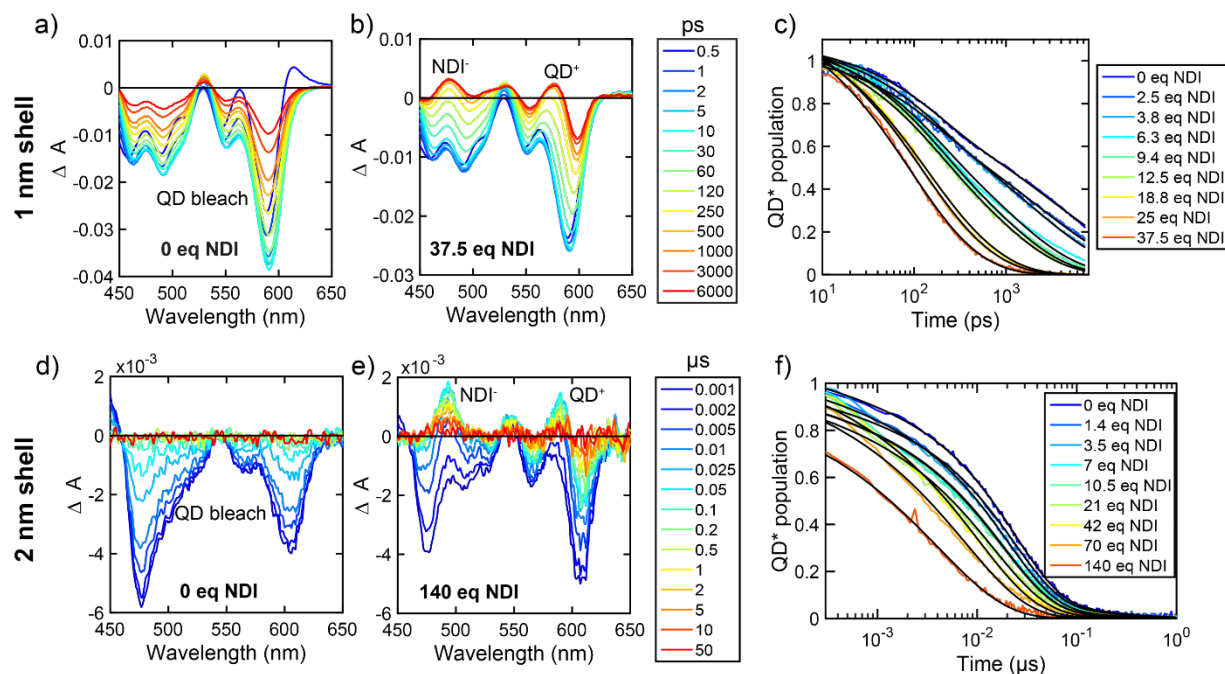


Figure 7.3: Ultrafast transient spectra and population dynamics in the 1 nm shell (a-c) and 2 nm shell (d-f) QD-NDI systems. a,d) Transient spectra of the QDs with no NDI added, illustrating the QD bleach recovery. b,e) Transient spectra of the QD-NDI conjugates illustrating evolution from the QD bleach at early times to an $\text{NDI}^{\bullet-}$ - $\text{QD}^{\bullet+}$ state at longer times. c,f) Relative population of the QD^* state (based on basis spectra deconvolution into a QD bleach and $\text{NDI}^{\bullet-}$ - $\text{QD}^{\bullet+}$ components). Increasing equivalents of NDI per QD result in a faster decay of the QD^* population.

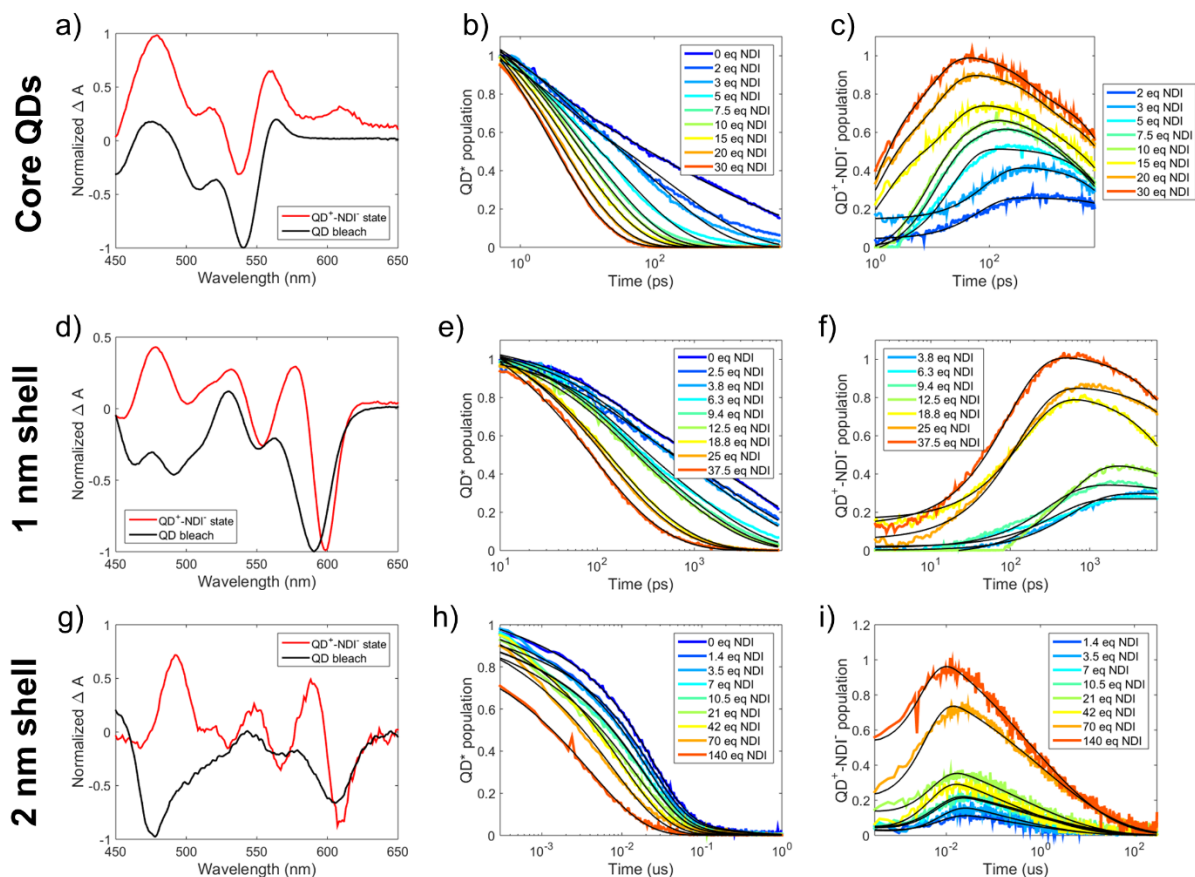


Figure 7.4. Basis spectra for the QD* state (black) and the NDI^{•-} - QD⁺ basis spectra state (red) (a,d,g). Extracted time dependent QD* (or QD bleach) populations (b,e,h) and time dependent NDI^{•-} - QD⁺ populations (c,f,i) for varying NDI concentrations per QD. Black lines represent fits, as described above.

In order to quantify charge separation rates, we deconvolved all transient spectra into a QD bleach (i.e. a QD excited state, QD*) basis spectrum and an NDI^{•-} - QD⁺ basis spectrum. From these basis spectra, we could construct time-resolved population traces for the QD* and NDI^{•-} - QD⁺ states. The QD* populations for the core/shell samples are shown in Figure 7.3c,f. All other basis spectra and population traces are shown in the 7.4. Population transients were fit to multiexponential functions, to yield two independent estimates for the charge separation rate constant. These two independent estimates come from either fitting the decay of the QD* state or

fitting the rise of the $\text{NDI}^{\bullet-} - \text{QD}^+$ state. By plotting these rate constants as a function of NDI equivalents per QD (Figure 7.5a,b), one can extract a bimolecular electron transfer rate constant (k_{cs}) in accordance with the relation: $k_{cs,tot} = Nk_{cs}$, where N is the number of acceptors per QD. The linearity of these plots further validates our method and assumption that each NDI ligand added does indeed bind to the surface in the range studied. The bimolecular rate constants (utilizing either QD^* or $\text{NDI}^{\bullet-} - \text{QD}^+$ populations) are plotted as a function of shell thickness in Figure 7.5c. Although both populations yield similar charge transfer rate constants, the rate constant from the QD^* population is consistently smaller than that derived from the $\text{NDI}^{\bullet-} - \text{QD}^+$ populations. This is likely a result of using a stretched exponential for the QD^* fits, and an intensity weighted average of two exponentials in the $\text{NDI}^{\bullet-} - \text{QD}^+$ fits. It should be noted that stretched exponentials have been demonstrated as an adequate and physically meaningful way to fit QD PL quenching by molecular charge acceptors.³⁴³

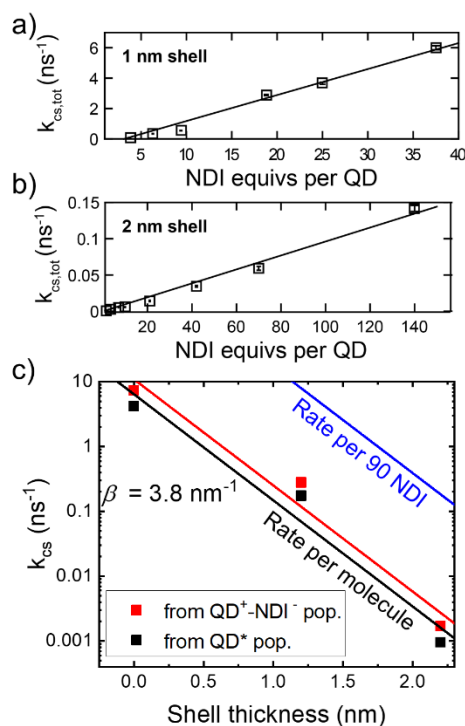


Figure 7.5: Extracting bimolecular charge separation rates for QD-NDI conjugates. a-b) Charge separation rates constants as a function of NDI equivalents per QD, extracted from the QD^* population. The slope of the linear fits gives a bimolecular rate constant per NDI ligand. c) Bimolecular rate constants as a function of shell thickness using either the QD^* population (black) and $NDI^- - QD^+$ population (red) to extract rates. Also show are the expected rate constants with 90 NDI per QD, the approximate concentration used for EPR experiments.

With the bimolecular rate constants determined, we can now analyze the shell thickness dependence of these values. The rate constants can be fit to an exponential decay ($k_{cs} \propto e^{-\beta d}$) with a tunneling coefficient of $\beta = 3.8 \text{ nm}^{-1}$. This value is comparable to $\beta = 3.5 \text{ nm}^{-1}$ determined for electron transfer from CdSe/ZnS core/shell QDs³⁴⁴ as well as $\beta = 3.3 \text{ nm}^{-1}$ from CdSe/CdS core/shell QDs.³⁴⁵ However, there exist conflicting reports on this value, with a third study using CdSe/CdS core/shell QDs reporting $\beta = 1.3 \text{ nm}^{-1}$.³⁴⁶ Effective mass-based approximations have also predicted tunneling coefficients for CdSe/CdS electron transfer of $\beta = 1.8 \text{ nm}^{-1}$ and $\beta = 2.2 \text{ nm}^{-1}$.³⁴⁶⁻³⁴⁷ The variety of reported values likely arises from conflicting methods for determining the rates, preparing the QDs, and assessing the number of molecular acceptors.

For the purposes of the current study, determining the shell-thickness-dependent bimolecular charge transfer rate constant serves as a first step towards predicting the relevant rates in the EPR experiments presented below. We can use it to estimate the rate constant with ~ 90 NDI ligands bound per QD (blue line), which is the approximate concentration used in the EPR experiments. From this analysis, we expect electron transfer to occur in about ~ 100 ps for the 1-nm shell and ~ 5 ns for the 2-nm shell, values close to or slower than spin relaxation in the QD. Additionally, it should be noted that the transient absorption experiments were all done at room temperature, while the EPR experiments are performed between 5 and 80 K. In the absence of trap-mediated charge transfer, which would enhance observed charge transfer rates, photoexcited charge transfer from CdSe/CdS core/shell QDs has been shown to be relatively temperature independent.³³⁶ Therefore, the rate constants indicated by the blue line in Figure 7.5c serve as an upper bound, and likely a reasonable estimate, of the rate constants that will be present in the EPR experiments. To ensure that the charge separated states live long enough for EPR measurements, recombination rate constants were analyzed by fitting $\text{NDI}^\bullet - \text{QD}^+$ populations to stretched exponentials. The core/shell samples had recombination time constants on the order of a few microseconds, while the core sample was closer to ~ 20 ns. The more rapid recombination seen in the core-only samples, precludes their utility for conducting EPR-based spin manipulations.

With the charge dynamics established for the NDI-QD conjugates, we turn to time-resolved EPR to better understand their spin dynamics. At the outset, there is scant evidence that a measurement technique as slow as EPR (~ 10 ns) can detect spin states in cadmium chalcogenide QDs because the numerous heavy cadmium atoms lead to rapid spin relaxation, as mentioned in the introduction. In fact, our own attempts to measure conduction-band electrons photogenerated in CdSe QDs (following work from the Gamelin group³⁴⁸) by continuous-wave (CW) EPR yielded

no signal, even at 5 K. This is in contrast with first row transition metal oxide nanoparticles such as ZnO and TiO₂. The Gamelin group has shown size-dependent CW EPR signals from electrons in ZnO QDs,³⁴⁹ and the radical pair model has been used to describe transient EPR spectra of photogenerated species on TiO₂ nanoparticles.³⁵⁰⁻³⁵¹ In the present study, despite the lack of a direct EPR signal from any charges within the CdSe QD, we demonstrate photogenerated spin polarization transfer from the QD to the NDI electron acceptor.

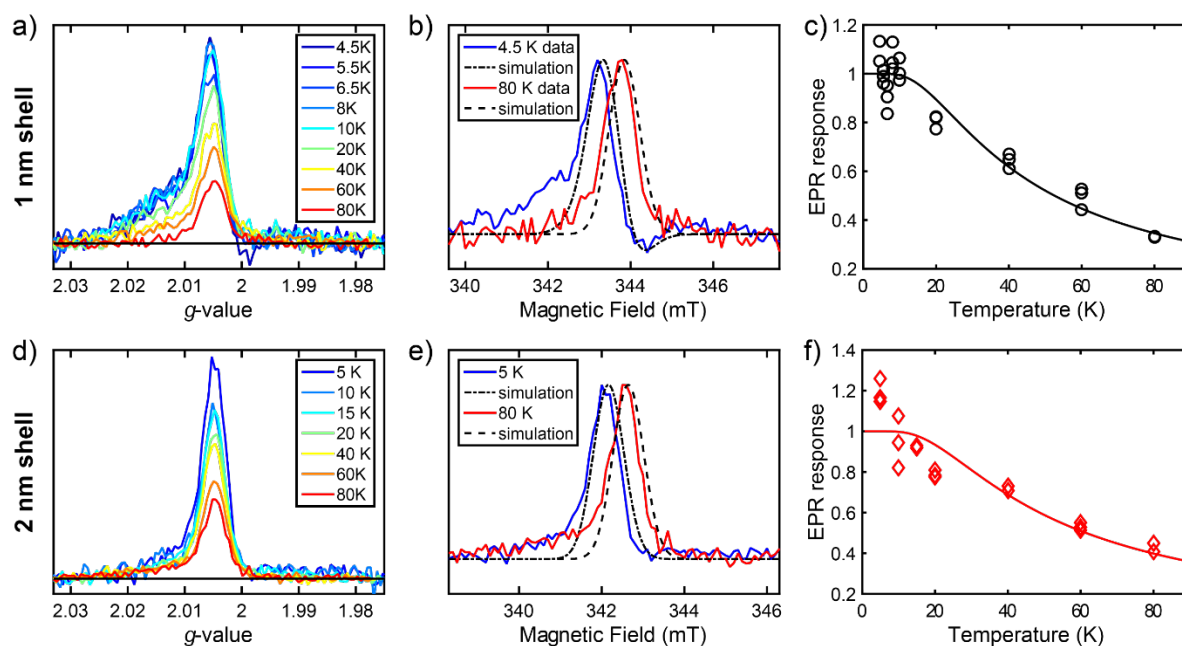


Figure 7.6: Temperature dependent transient EPR spectra of QD-NDI conjugates. a,d) Temperature dependent transient EPR spectra recorded 100 ns after a 550 nm (7 ns, 2 mJ) laser pulse. Data are shown vs. g -value since the resonant frequency was temperature dependent. b,e) Data for the lowest and highest temperature data overlain with simulations derived from the NDI anion. Again, data are shifted due to temperature dependent frequency shifts. c,f) Maximum EPR response 100 ns after laser flash in each of three scans collected at each temperature. Data are fit to Equation 7.1.

In the transient EPR experiments, we observe a polarized and mostly absorptive signal associated with the NDI^{•-} (Figure 7.6). The signal intensity is temperature dependent and can be fit to an absorptive peak centered at the NDI^{•-} g -value of 2.003. We propose that this absorptive signal is a result of the triplet mechanism (TM) for spin polarization.³²⁹⁻³³⁰ In this case, the

photoexcited QD serves as the triplet, consistent with numerous studies that observe significant triplet character of this state.^{133, 326, 328} At the lowest temperatures, there is evidence of an emissive EPR feature in the signal (Figure 7.6b). This spectrum was simulated by including a small contribution from an absorptive/emissive (A/E) response, which is common to triplet-generated, spin-correlated radical pairs (SCRPs).^{333, 352} Employing a combination of the SCRPs mechanism and the TM to model transient EPR spectra of charge-separated states has precedent in studies on hole transfer from photoexcited C₆₀ to either tetramethylbenzidine³⁵³ or a zinc porphyrin.³³³ In both of these studies, transient spectra were fit to a superposition of absorptive signals ascribed to the TM and E/A or A/E signals resulting from a SCRPs. This precedent bolsters our interpretation, but the precise spin states in the QD that are responsible for the spin polarization transfer remain an open question.

To better understand the origins of spin polarization from the QD, it is worth revisiting the relevant spin relaxation times. Equilibration between the dark and bright states occurs in a few picoseconds, well before electron transfer occurs in our case. The slower spin relaxation component, associated with intra-level relaxation, occurs on the order of a few nanoseconds. This is slower than electron transfer from the 1-nm shell (~100 ps) but outcompetes electron transfer from the 2-nm shell (~5 ns). The similarity of EPR signals in the 1-nm and 2-nm shell samples, however, suggests that this relaxation process is not important for spin polarization transfer; if it was important, the 1-nm and 2-nm samples should be quite distinct. This begs the question: can spin polarization transfer occur on a slower timescale than spin relaxation in the QD? We believe that this would be possible if the thermally equilibrated bright and dark exciton states (total angular momenta of $F = 1$ and $F = 2$, respectively) populate spin sub-levels in the charge-separated state

with different efficiencies. In this scenario, the observed polarization would be proportional to the population difference between the bright and dark state, expressed by the following equation:

$$\text{Eq. 7.1} \quad \text{EPR signal} \propto P_{F=2} - P_{F=1} = \frac{1 - \exp\left(\frac{-\Delta E_{BD}}{kT}\right)}{1 + \exp\left(\frac{-\Delta E_{BD}}{kT}\right)}$$

where $P_{F=1}$ and $P_{F=2}$ are the bright and dark state Boltzmann populations respectively, which have an energy difference of ΔE_{BD} . The temperature dependent EPR signal is fit to this functional form (Figure 7.6c,f) and yields values of $\Delta E_{BD} = 5.1$ and 5.7 meV for the 1-nm and 2-nm shells respectively. These values are well within the range of reported ΔE_{BD} ,³¹⁶ and their similarity is not unsurprising for their geometries, which are predicted to produce similar electron-hole overlap integrals.³⁵⁴ This analysis offers one possible explanation for the origin of spin polarization in our QD-molecular system, and a first step towards understanding this interesting phenomenon.

7.4 Conclusion

In conclusion, we have designed a QD-molecular system that can generate long-lived spin polarization on the molecular acceptor following photoexcitation of the QD. We first establish an understanding of the photoexcited electron transfer dynamics by varying the shell thickness of CdSe/CdS core/shell QDs and the number of NDI electron acceptors per QD. We then use transient EPR to show that this electron transfer process also conveys spin polarization from the QD to the NDI. The spin polarization on the NDI survives for >100 ns, which is significantly longer than the rapid (few nanoseconds) spin relaxation inherent to colloidal QDs. These experiments represent a promising route towards generating long-lived and well-defined spin qubit states. Specifically, the highly absorbing and tunable QD entity can be used to photogenerate a polarized state, and the

rapid spin relaxation inherent to QDs can be avoided by extracting this polarization onto an organic molecule.

7.5 Outlook

See Section 8.3 as Chapter 8 is a continuation of this work.

Chapter 8: Charge Separation and Recombination Effects on Spin Polarized Electron Transfer

8.1 Experimental Methods

Samples were prepared as follows. A ligand solution with concentration of 1 mg/mL was prepared in DCM. 90 equivalents of the resulting turbid solution were added to 1 equivalent of QDs in toluene. Insolubility in the nonpolar solvent drove the ligands onto the surface of the dots where it displaced oleic acid. Upon addition, the fluorescence was immediately quenched. Samples were dried down under nitrogen and resuspended in d14-methylcyclohexane. In a 4 mm EPR tube the sample was subjected to three freeze-pump-thaw samples before being flame-sealed. All EPR experiments were done at 5K in a 5 mm ENDOR resonator with optical excitation at 570 nm. After completion of EPR experiments the tubes were cracked open for TA experiments. For room temperature experiments the samples were loaded into air-free cuvettes and subjected to another two cycles of freeze-pump-thaw. For low temperature TA experiments the samples were loaded into a sample holder in a nitrogen purge box and a liquid nitrogen cryostat was used. For all TA measurements 570 nm excitation was used.

8.2 Results and Discussion

To expand upon the results presented in Ch. 7, four new molecular electron acceptors were synthesized (Figure 8.1). Pyromellitimide (PI) exhibits a similar distance dependence as NDI, but different reduction potential. PI-NDI serves as a two-step electron transfer ligand to extend the distance between carriers. Phenyl spacers replaced the glycine linkages for Ph-NDI and Ph-Ph-NDI to maintain rigidity and increase distance without changing the acceptor. For all experiments, the same 2 nm shell CdSe/CdS QDs were used as in Ch. 7.

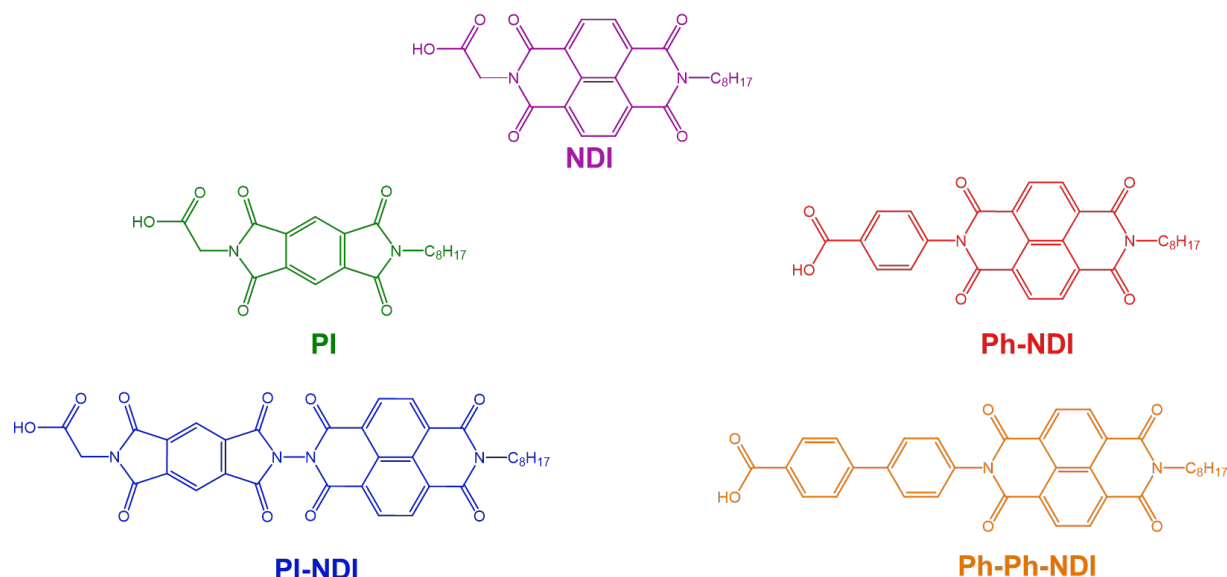


Figure 8.1: Ligands used as molecular acceptors alongside the QD donors. PI = pyromellitimide, NDI = naphthalene diimide.

To certify that electron transfer occurs in all system, and to calculate charge separation and recombination lifetimes, we used TA spectroscopy. Time slices from femtosecond (7 ns time window) and nanosecond (343 μ s time window) are provided for the bare QDs and QD-NDI complex in Figures 8.2 (room temperature) and 8.3 (85K). Due to the large extinction coefficient of the QDs all NDI radical anion features are obscured. However clear absorptive structures appear at later times in the QD-NDI TA measurements around 494 nm, 555 nm, and 585 nm that we attribute to the QD^{•-}. At lower temperatures we see less of these characteristics features suggesting reduced charge separation and yield which is reasonable given the difference in ΔG .

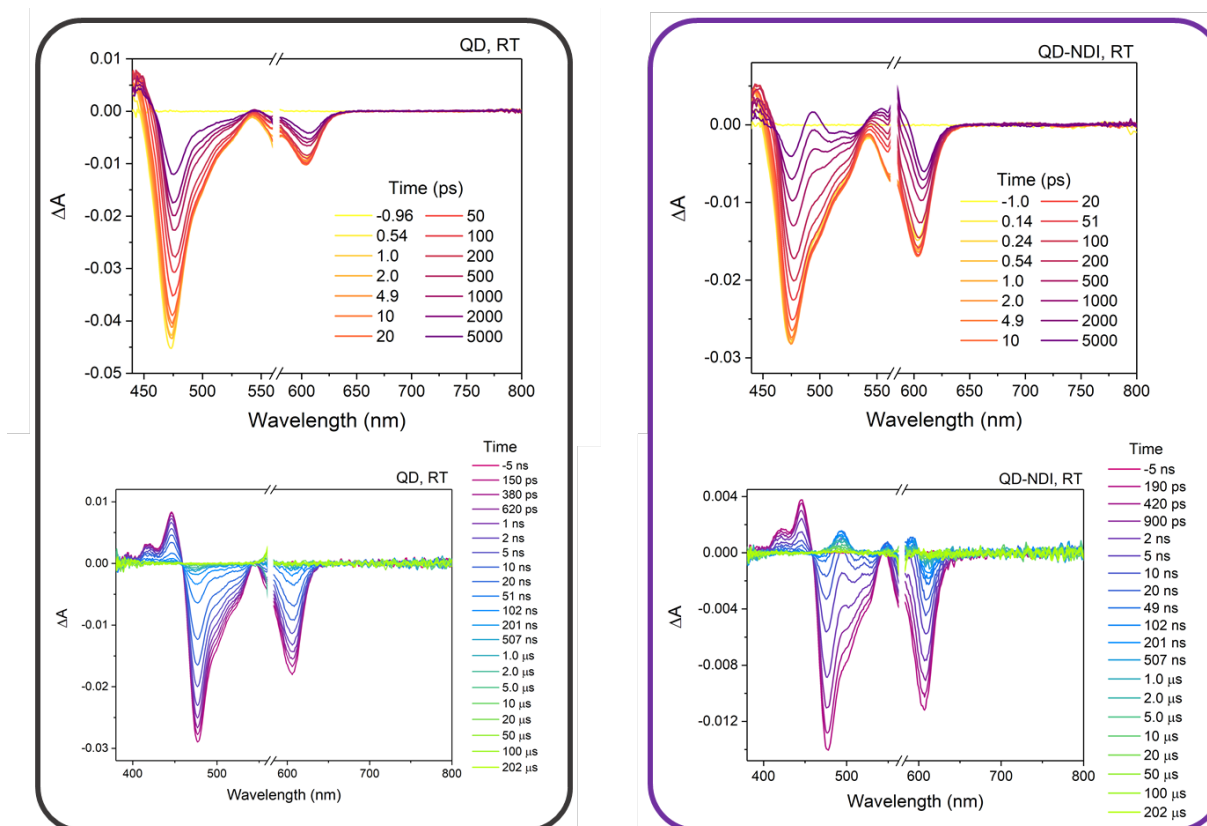


Figure 8.2: Femtosecond (top) and nanosecond (bottom) TA measurements of QD (Left) and QD-NDI (right) at room temperature. Most NDI radical anion features are obscured, but the 494 nm band is characteristic of a QD hole state.

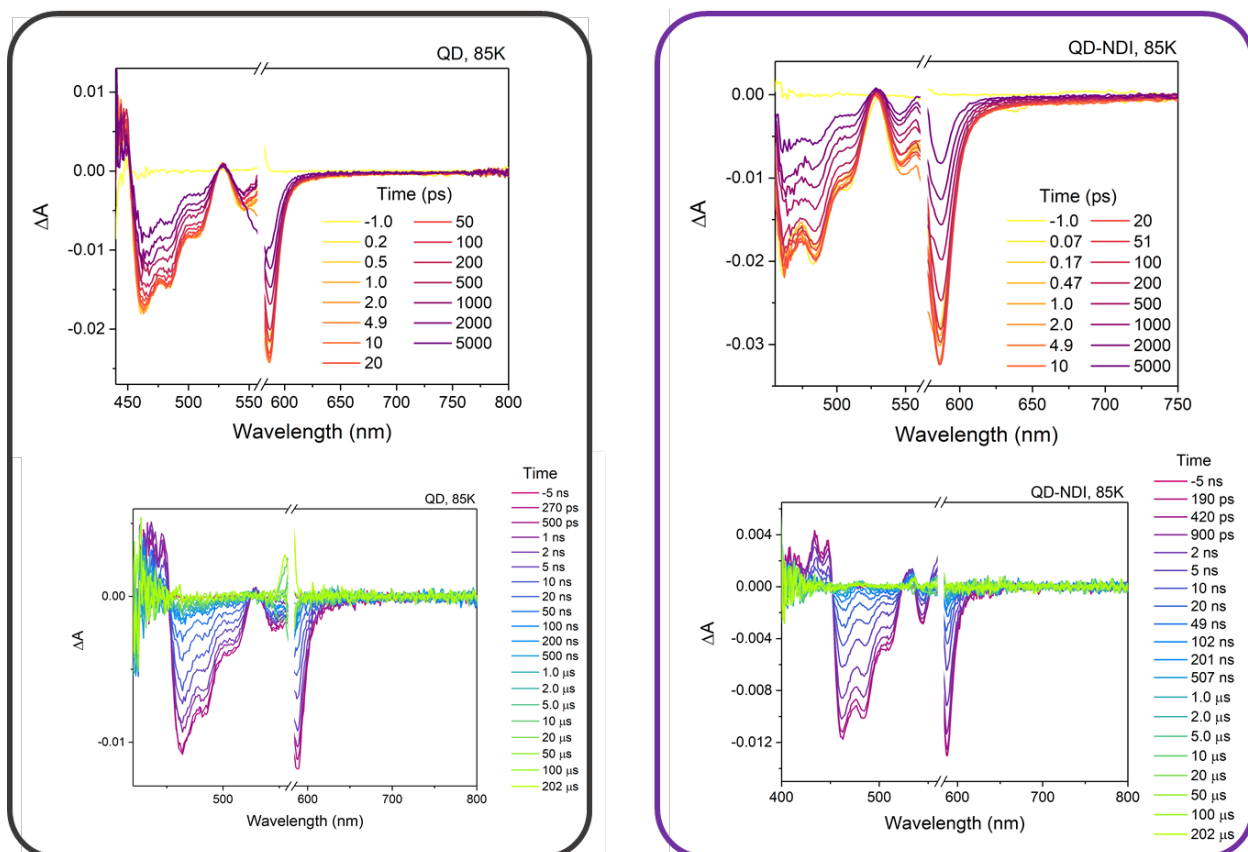


Figure 8.3: Femtosecond (top) and nanosecond (bottom) TA measurements of QD (Left) and QD-NDI (right) at 85K in methylcyclohexane. Charge separation and yield is much lower than at RT but the 494 nm confirms that it is still occurring.

In Figure 8.4 the kinetic traces at 494 nm from the room temperature TA are provided for all QD-ligand complexes and the bare QDs. With the addition of ligands the signal amplitude recovers more rapidly and appears absorptive for all ligands. While lifetimes differ, charge separation occurs on hundreds of picoseconds and recombination is on the magnitude of microseconds for all samples.

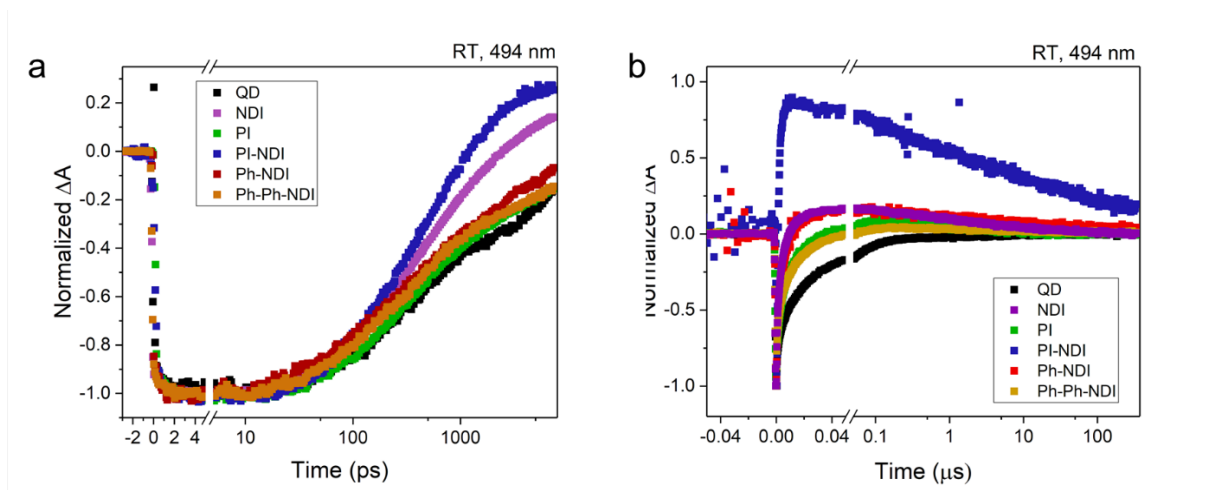


Figure 8.4: Femtosecond (a) and nanosecond (b) TA kinetics at 494 nm for the bare QDs and the QD-Ligand complexes.

TCW EPR experiments (Figure 8.5) confirm that spin polarization is maintained upon electron transfer from the QDs to the ligands. Like the results presented in Ch. 8 the signal is centered around the g -value of the organic acceptor. For QD-NDI, QD-PI, QD-Ph-NDI, and QD-Ph-Ph-NDI the signal is mostly absorptive indicative of a triplet state precursor to the SCRP. The asymmetry in the spectra are due to some mixing of the QD excited spin state between “triplet-like” and “singlet-like” which incorporates a singlet state initiated SCRP lineshape (E/A). Over time the QD-NDI and QD-PI signals progress towards more of a typical derivative lineshape associated with a singlet SCRP which could be due to a few processes: (i) spin relaxation within the QDs from an electronic level that is more triplet-like to one that has more singlet character such that charge separation is evolving over this timescale, (ii) continuous microwave irradiation causing the opposite, moving population upwards from a triplet-like state to a singlet-like state, or (iii) charge recombination of $[\text{QD-Ligand}]^{3*}$ occurs faster than that of $[\text{QD-Ligand}]^{1*}$. We can likely eliminate (i) as a possibility given that in QDs the lower energy state is forbidden and therefore the opposite trend should be occurring, however as will be shown below this mechanism

is the most consistent with our results. QD-Ph-NDI and QD-Ph-Ph-NDI do not show this evolution in signal, instead over time the absorptive feature just decays. This could suggest that the orientation of the ligand is important for spin-recombination processes wherein the more rigid structure of these two ligands limits any formation of a $[\text{QD-Ligand}]^{1*}$ state.

QD-PI-NDI presents an interesting case where the signal completely inverts with time and is consistently a mix of absorptive and emissive. From TA measurements this ligand showed the fastest charge separation lifetime potentially pointing to once again charge separation being the main culprit, however again this doesn't make much sense given the ordering of electronic states in the QDs.

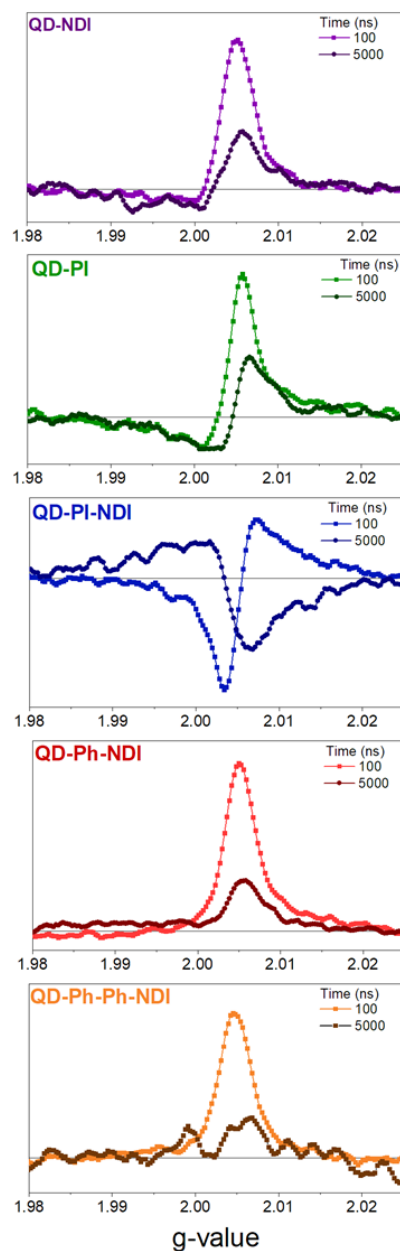


Figure 8.5: TCW EPR time slices at early and late time showing the progress of the spin-polarized signal for each QD-Ligand complex. Peaks are centered at g-values consistent with NDI or PI radical anion.

Using pulsed-EPR we performed a Hahn echo sequence to measure ESEEM and T_2 lifetimes which are presented in Figure 8.6. Most of the systems present a lifetime that is around 1.5 microseconds. QD-PI-NDI is noticeably shorter than the other ligands, potentially due to the initial rapid charge separation. Regardless all lifetimes are remarkably long given the close

proximity of the heavy atoms of the QDs. This timescale should be long enough for further microwave manipulation and presents a promising situation for QIS applications.

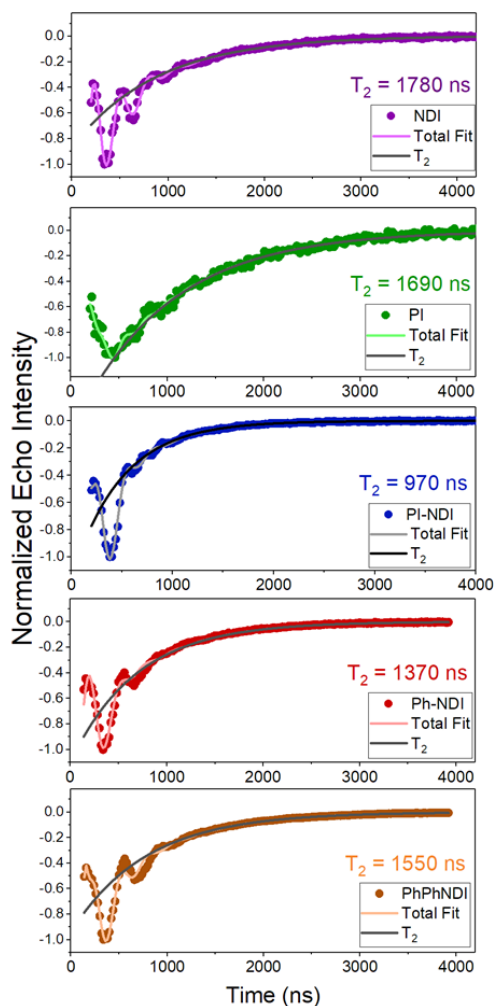


Figure 8.6: Pulsed-EPR ESSEM measurements along with the corresponding fits. T_2 lifetimes are calculated from exponential decay of the signal.

In addition to ESEEM, we were able to collect out-of-phase (OOP) ESEEM measurements for the samples. While fitting this data has proven difficult, it confirms that we are maintaining spin-polarization. (Figure 8.7).

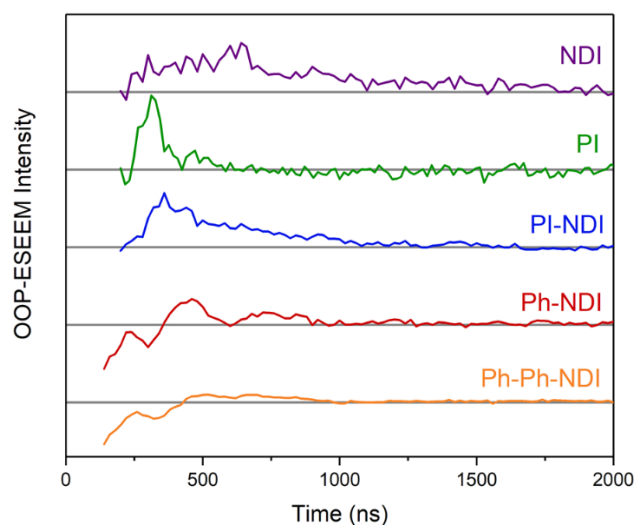


Figure 8.7: OOP-ESEEM measurements for the QD-Ligand complexes

Lastly, we studied three different concentrations of PI-NDI conjugated to the QDs. (< 90 eq., 90 eq. > 90 eq., currently we are working on determining actual quantities). TA measurements (Figure 8.8) show that charge separation varies as expected, with the sample containing the most equivalents having the fastest lifetimes. Charge recombination appears consistent between samples consistent with electron transfer from one ligand back to the QD.

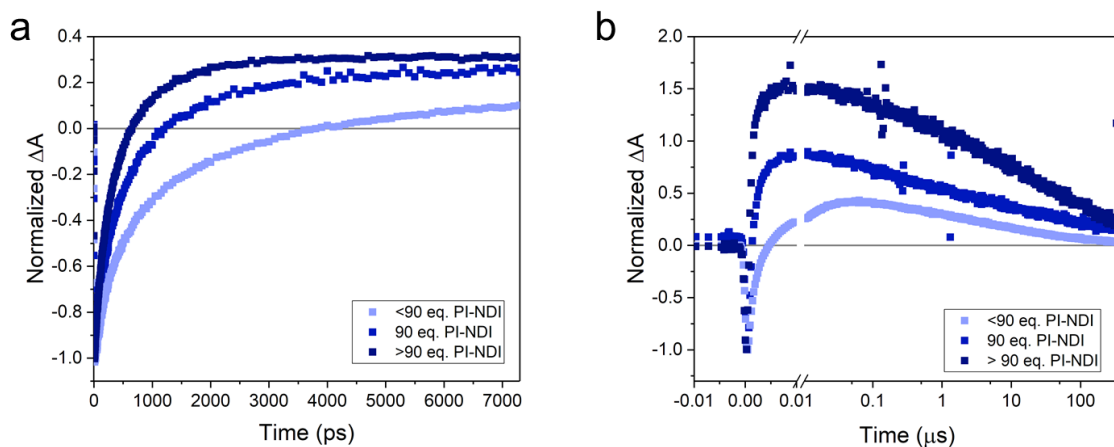


Figure 8.8: Femtosecond (a) and nanosecond (b) TA kinetic traces for QD-PI-NDI with varying ligand concentrations to change charge separation lifetimes.

TCW spectra as a function of time are presented in Figure 8.9. From the sample with the lowest number of equivalents we can see the absorptive signal that was present in the other samples shift from a g-value consistent with PI to one consistent with NDI consistent with two step electron transfer. In the other two samples we see more drastic evolution of signal. Importantly all three should have the same radical pair distance and therefore the same value of J and D. Furthermore, charge recombination is the same so changes to the signal should solely be due to differences in charge separation.

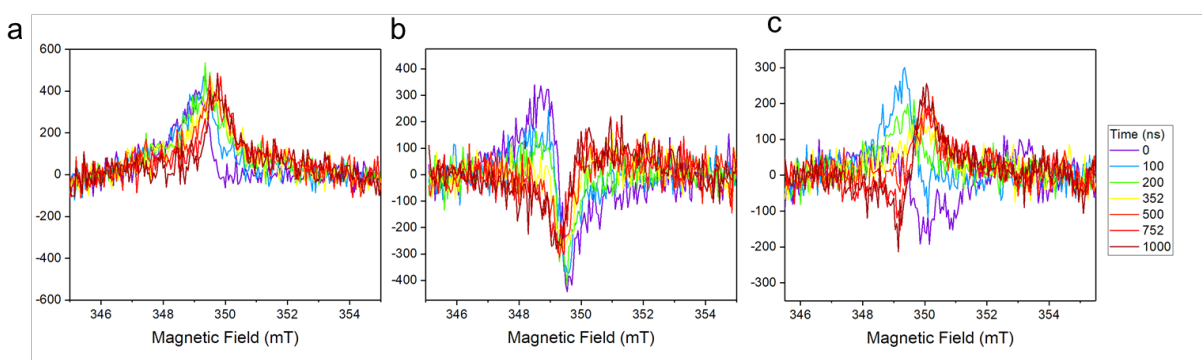


Figure 8.9: TCW time slices for QD-PI-NDI with different ligand concentrations, (a) < 90 eq, (b) 90 eq, (c) > 90 eq.

ESEEM and T_2 fits are shown in Figure 8.10. The spin coherence lifetime is similarly affected by the quantity of ligand present suggesting once more than charge separation dictates decoherence. This could be due to more rapid charge separation maintaining a pure spin state.

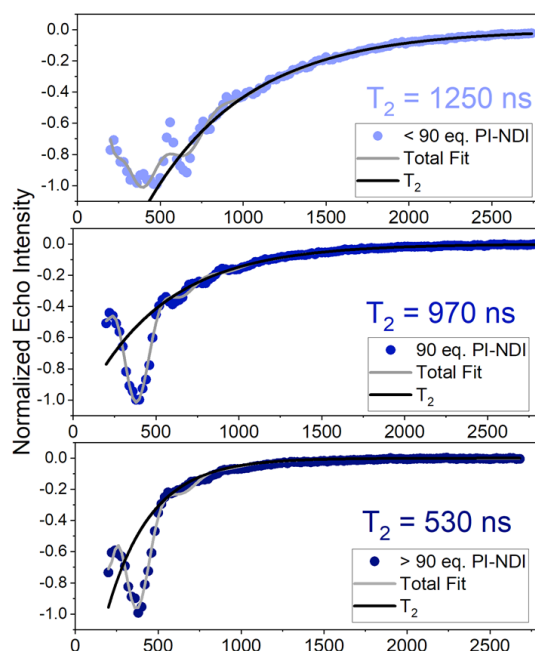


Figure 8.10: ESEEM measurements for QD-PI-NDI at different concentrations along with the fitted T_2 lifetimes.

8.3 Conclusion

In this chapter we expanded previous work on spin-polarized electron transfer in hybrid QD-molecular systems by studying four new molecular acceptors: PI, Ph-NDI, Ph-Ph-NDI, and PI-NDI. Using optical spectroscopy, we confirmed that charge separation occurs for all systems both at room temperature and 85K. EPR measurements show spin-polarized signals centered around the g -value of the organic acceptor. Over time these signals evolve in structure and a few different mechanisms for this are examined. T_2 lifetimes are presented that seem to correlate with charge separation, but are on the order of microseconds for all samples. Lastly, the effects of ligand concentration are studied and we find that both TCW and pulsed-EPR data are impacted correlating that charge separation dictates spin state and coherence lifetime.

8.4 Outlook

The use of hybrid quantum dot-molecule donor-acceptor systems is a promising avenue for QIS applications due to the rich spin physics of semiconductors coupled with the precision of molecules. Given the novelty of these projects there are many interesting avenues one could pursue. For example, the composition of the molecular acceptor was changed throughout these studies, but the donor (CdSe) remained the same, even the addition of shells, as shown in chapter seven, was merely a means of extending distance. Other core compositions such as ZnS, InP, or one of the many perovskite structures may show entirely unique spin properties. Moving towards lighter atoms could in principle reduce spin-orbit coupling and increase T_2 lifetimes, an important step towards incorporation into functional devices.³⁵⁵⁻³⁵⁶ Even while maintaining CdSe as the primary composition there are many parameters that can be altered. As mentioned, shell growth extended the charge separation and recombination, but the core was always the same. The exciton fine structure of CdSe QDs is sensitive to size and therefore the contrast between singlet/triplet TCW signals may become more pronounced.³⁵⁷ Switching to ZnS shells would change the electronic structure as it should confine both the electron and hole. Furthermore, CdSe can also be synthesized in 1D (nanorod, NR)³⁵⁸⁻³⁶⁰ or 2D (nanoplatelet, NPL)³⁶¹⁻³⁶² structures. Of the two, the latter is particularly interesting since CdSe NPLs are atomically precise in one dimension. This would, in principle, reduce the inhomogeneity that QDs are prone to and could reduce distributed kinetics and narrow linewidths.

There are also many parameters of the technique itself that can be changed to probe these systems further. Using circularly polarized light may excite a majority of spin-up or spin-down electrons due to optical selection rules in semiconductors.³⁶³⁻³⁶⁵ This may manifest as spectral changes by TCW. Anisotropic NCs such as NRs and NPLs can be oriented using Langmuir-

Blodgett methods and polymers^{62, 366-367}; this directionality coupled with linearly polarized light could produce interesting results. While chapter seven covered some brief forays into changing the wavelength and temperature expansion of this could help understand how the electronic states of the QDs is structured and determine limits to these experiments. Moving from liquid helium experiments to liquid nitrogen would reduce cost and prove more feasible for devices; room temperature spin coherence would be even better. The Hahn echo sequence used in chapter eight is just one type of pulsed-EPR experiment; given the T_2 lifetimes, these samples could be manipulated further with microwave radiation. Although less related to QIS, a 5-pulse RIDME experiment could quantify the distance between the radicals.³⁶⁸⁻³⁶⁹ This is particularly intriguing for cases like these given the hole may be delocalized over the entirety of the CdSe core.

Appendix A: Supporting Information for Chapter 3

A.1 Experimental Details

Details of our femtosecond stimulated Raman spectroscopy experiment have been detailed elsewhere.¹⁵⁸ For each sample, the actinic pump was tuned to 400 nm and focused to 250 μm . The Raman pump was tuned to the low energy FWHM of the absorption feature (see Figure 1b in main text). For the samples with radius $R = 1.3$ and 1.5 nm, the chirped continuum probe was generated with a 2 mm sapphire plate and spectra were collected using a grating with 1200 lines/mm with a 600 nm blaze. For the $R = 2.0$ nm sample the probe was generated with a 1:1 $\text{H}_2\text{O}:\text{D}_2\text{O}$ mixture in a 5 mm quartz cuvette and spectra were collected using a grating with 2400 lines/mm with a 400 nm blaze. Chirped probe pulses were not compressed for experimental simplicity and owing to observations that such does not affect time-resolution particularly since the spectral range probed is small.³⁷⁰ All spectra were collected using a 1.0 mm quartz cuvette with OD around 0.2. Samples were stirred during data acquisition to minimize sample degradation and the effects of local heating. The CdSe NCs were dispersed in hexanes for both stability and to ensure that the ligands and solvent are thermally similar.

A.2 LO Phonon Mode

In order to aid visualization of the LO phonon mode studied, we provide an illustration (Figure A.1). Phonon frequencies and vectors were obtained from the referenced website³⁷¹ and are displayed using the VESTA visualization package.³⁷²

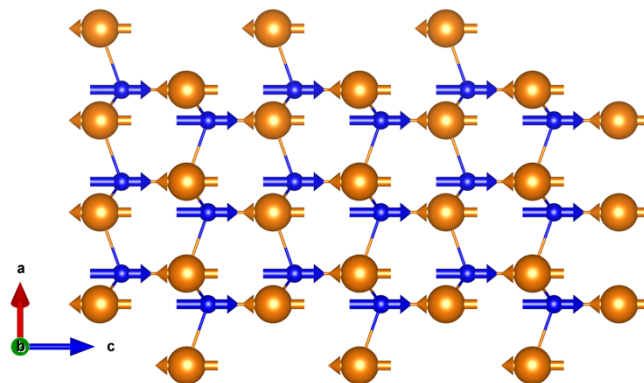


Figure A.1: Lattice motion corresponding to the LO phonon. Cd^{2+} are shown in blue and Se^{2-} in orange.

A.3 Background Subtraction Process

In order to monitor the dynamics of only the LO phonons, the Raman features and background were fit to a sum of two Gaussians (for the LO and SO phonon modes) and a polynomial, respectively. Both were fit simultaneously in a MATLAB script before the polynomial was subtracted. An example of a fit is given in Figure A.2.

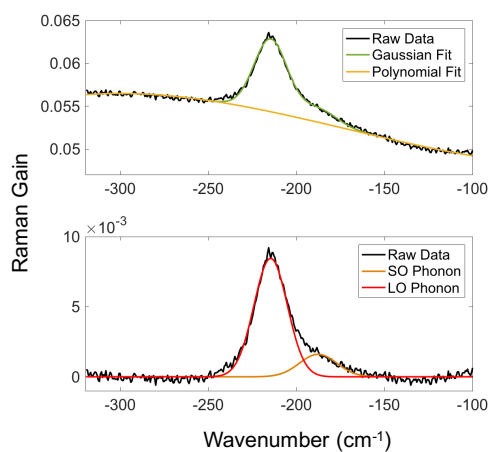


Figure A.2: anti-Stokes LO phonon mode for the $R = 2.0$ nm CdSe. (Top) Raw data along with the fit and polynomial baseline. (Bottom) Spectrum shows the baseline-subtracted data with Gaussians.

A.4 Normalized Spectrum

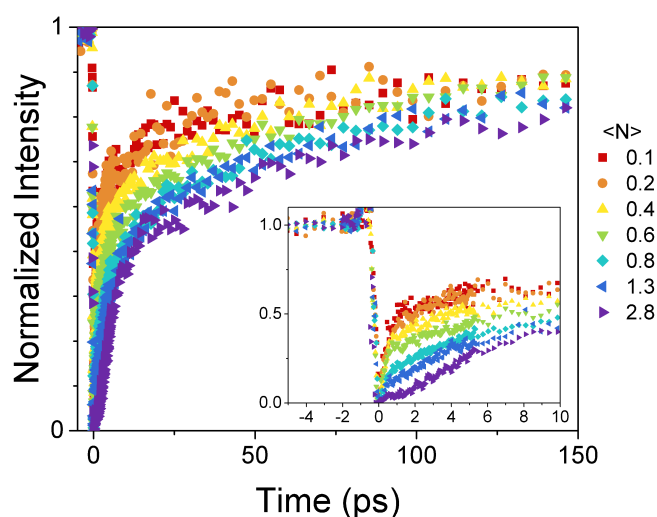


Figure A.3. Data presented in Figure 3.2b with all spectra normalized to the same value allowing better comparison of lifetimes. Inset shows the same data with a smaller time range.

A.5 Multiexciton Fitting Process

In order to determine the lifetimes due to Auger heating, all data was fit to both the single exciton component (determined from fits of the lowest pump fluence for each sample) and one or two more exponentials. As pump fluence is increased not only do the population of multiexcitons increase, but the number of NCs with single excitons decrease, so the single exciton components have fixed lifetimes and relative amplitudes but were allowed to vary collectively in amplitude. All fits were done using a MATLAB script. An example of a fit is given in Figure A.4.

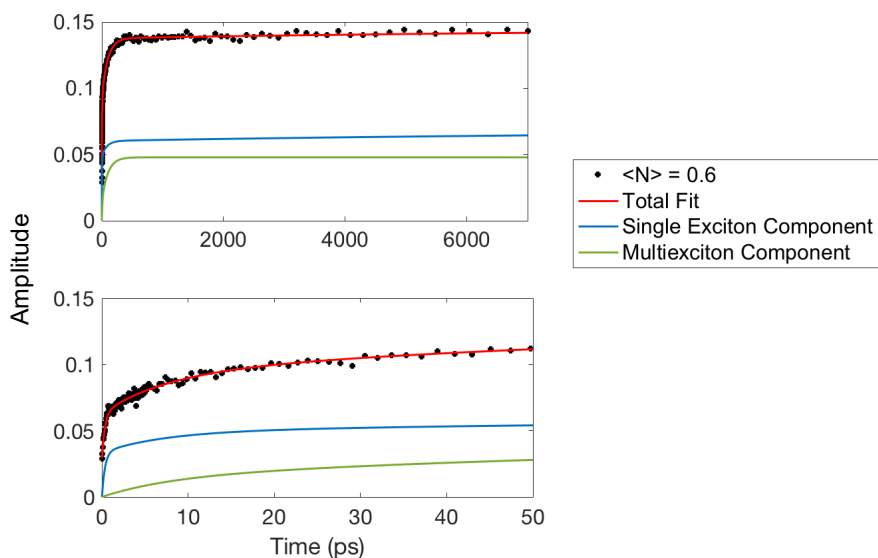


Figure A.4: Fits for the $R = 2.0$ nm CdSe NCs sample (Stokes, $\langle N \rangle = 0.6$) where the data is fit to a combination of single and multi-exciton components.

A.6 Multiexciton Fits and Errors

The average of our multiexciton fits are compared to literature values for AR in Table A.1.

Table A.1: LO Phonon Lifetimes, vs Auger Recombination Lifetimes

Sample	FSRS Lifetime (ps)	AR Lifetime (ps)
R = 1.3 nm	16	8
R = 1.5 nm	25	15
R = 2.0 nm	100	41

In order to not crowd Figure 3.3c, errors were not included. Representative errors of the different sizes, derived from the fit of a single $\langle N \rangle$ for each size are given in Table A.2 below.

Table A.2: Errors derived from multiexciton fits

Sample	FSRS Lifetime (ps)	95% Confidence Interval
R = 1.3 nm, $\langle N \rangle = 1.45$	12.7	± 0.8
R = 1.5 nm, $\langle N \rangle = 1.04$	32.7	± 5.3
R = 2.0 nm, $\langle N \rangle = 0.6$	99.3	± 12.1

A.7 Solvent Shifts

In order to ensure that our peak shifts are not due to experimental artifacts we monitored the solvent (hexanes) modes at the same actinic pump powers used for $R = 2.0$ nm CdSe NCs. We saw no change in the peak positions suggesting that any peak shifts observed for the NCs was intrinsic to the material.

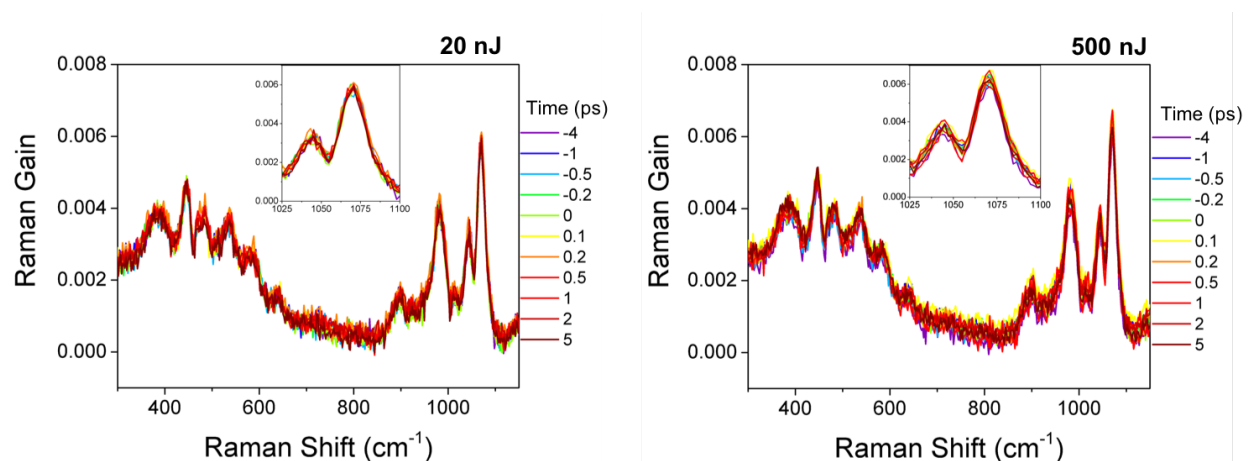


Figure A.5: Hexane Raman modes as a function of time showing no change in position upon optical excitation with the actinic pump. Actinic pump powers of 20 nJ and 500 nJ correspond to the powers used to generate $\langle N \rangle = 0.1$ and $\langle N \rangle = 2.8$ for the $R = 2.0$ nm CdSe NCs. Inset zooms in on the peaks between 1025 and 1100 cm^{-1} .

Appendix B: Supporting Information for Chapter 4

B.1 Transient X-ray Diffraction Dynamics of Samples

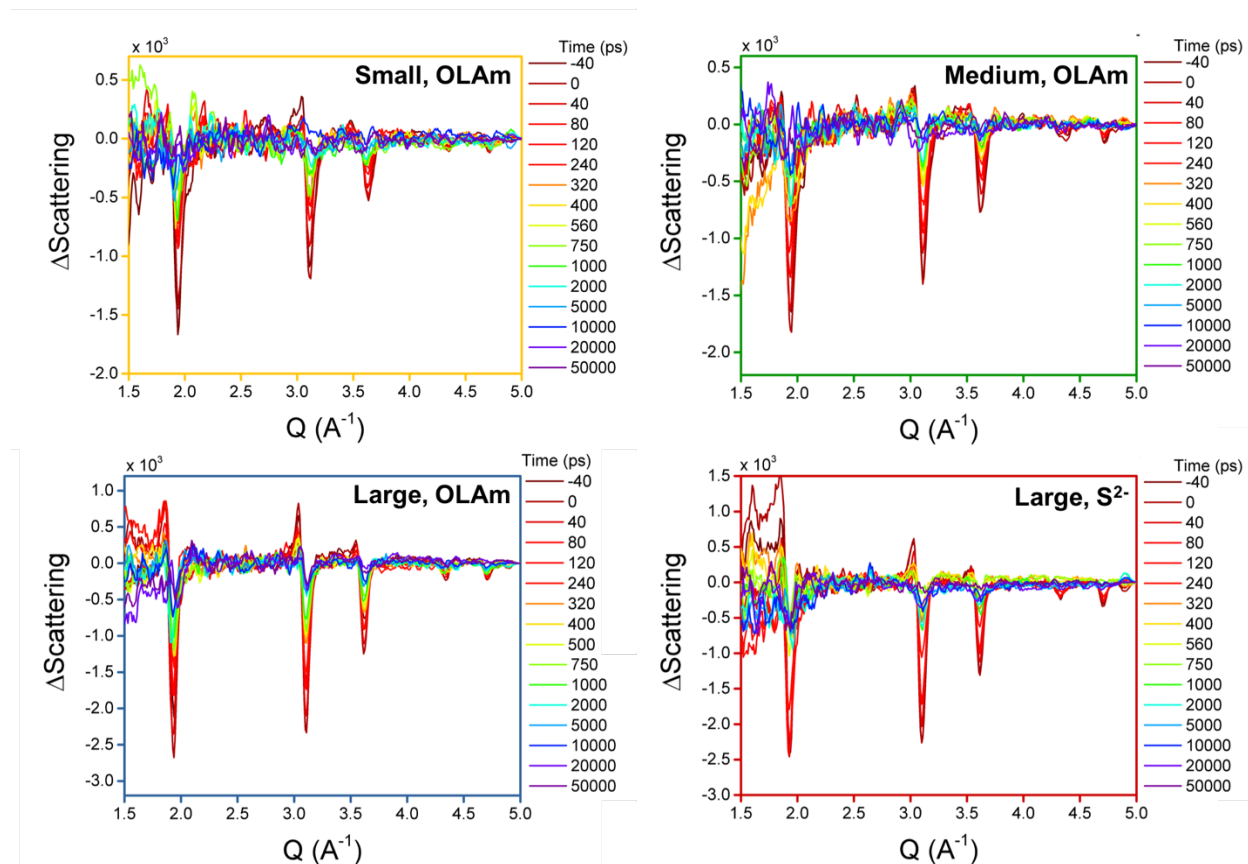


Figure B.1: Differenced X-ray diffraction as a function of delay between the 400 nm pump laser and the X-ray probe for the four samples.

B.2 Characterization of Dynamics

To increase signal to noise, only Q -values that were consistently part of the negative portion of the lineshape were included in integration. For consistency only the (204)/(220) and (116)/(312) peaks were used to determine dynamics in the main text. Kinetics were then normalized to $t = 0$ to allow easier comparison between samples. All reported error in the dynamics are due to fitting error. In the case of the S^{2-} sample, addition of a second exponential produced two identical, redundant time constants and therefore it was kept as a single exponential. In Table B.1, we give the deconvoluted time constants from our fits with an IRF of 79 ps

Table B.1: τ_1 lifetimes derived from fitting of TR-XRD differenced patterns with their corresponding instrument-response-function-deconvolved values.

Sample (Diameter, Capping Ligand)	τ_1 from fit (ps)	τ_1 deconvoluted (ps)
Small (3.4 nm, OLAm)	90	43
Medium (5.4 nm, OLAm)	136	111
Large (10.8 nm, OLAm)	201	185
Large (10.2 nm, S ²⁻)	207	191

B.3 Temperature Dependent X-Ray Diffraction of Samples

The temperature dependent XRD of the large, OLAm sample is given in Figure 4.8a and the medium, OLAm sample is given in Figure B.2 below. Unlike the large sample, the diffraction of (400)/(008) feature was not usable due to high noise. The small, OLAm sample would not fit to pseudo-Voigt lineshapes and therefore was not analyzed and the large, Na₂S sample was never attempted for this experiment.

To ensure that our samples did not sinter or degrade over the course of this experiment, three heating and cooling cycles were done. The peak shift showed clean reversibility over all cycles. Data from all these temperature points was used to calculate peak shift and volume expansion as a function of temperature.

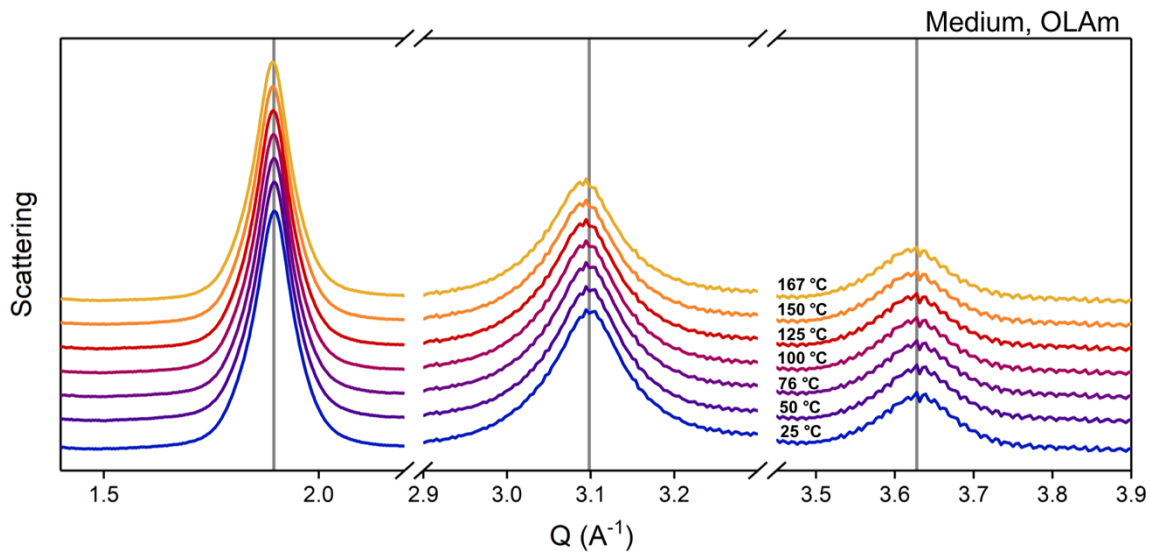


Figure B.2: Baseline-subtracted, temperature dependent static X-ray diffraction for the Medium, OLAm sample from 25 to 167 °C. Peak position at 25 °C is marked with a grey line to show how the peak shifts to lower Q with increased temperature.

B.4 Characterization of Temperature-Dependent X-ray Diffraction

The temperature dependent XRD diffraction patterns were baseline subtracted and fit to a pseudo-Voigt function (Eq. B.1) to determine peak position. Here y_0 is the y offset, ω is the FWHM of the lineshapes, μ is the weighting factor for the Gaussian and Voigt functions and x_c is the center of the peak.

$$B.1 \quad y = y_0 + A \left[(\mu) \frac{2}{\pi} \frac{\omega}{4(x-x_c)^2 + \omega^2} + (1 - \mu) \frac{\sqrt{4\ln 2}}{\sqrt{\pi}\omega} e^{\frac{-4\ln 2}{\omega^2}(x-x_c)^2} \right]$$

B.5 Temperature Estimation from TR-XRD

Following characterization of peak shifts from static temperature-dependent XRD, we applied these parameters to the TR-XRD patterns as a function of time and power. Diffraction peak parameters for the (204)/(220) and the (312)/(116) features were first determined from the

(non-differenced) static XRD at -5 ns, baseline subtracted, and then fit to pseudo-Voigt functions (Figure B.3a). These static peak parameters were then applied to the power dependence and dynamics for the large and medium NCs. To reduce the number of floating variables, the μ , w , and x_c parameters were held constant for the negative (melted NCs) peaks and the x_c parameters for both positive (heated NCs) peaks were correlated to the difference in temperature through peak shift. For example, $k_1\Delta T + x_{c2}$ replaces x_{c1} in the original equation, k_1 is derived from the temperature dependent XRD; k_1 and x_{c2} are then kept constant. The fitting equation is given in Eq. B.2 with variables marked in green being fit by a MATLAB script. Values of positive peaks μ_1 , μ_3 , w_1 , w_3 were given the corresponding values of the negative peaks (μ_2 , μ_4 , w_2 , w_4) as starting parameters. Overall, the fits were remarkably good given the large parameter space. An example of one of the fits generated from this approach for large, OLAm NCs at -40 ps and 8.8 mJ/cm² is given in Figure B.3b.

$$\begin{aligned}
 \text{B.2} \quad y = & y_0 + A_1 \left[(\mu_1) \frac{2}{\pi} \frac{\omega_1}{4(x - (k_1\Delta T + x_{c2}))^2 + \omega_1^2} + (1 - \mu_1) \frac{\sqrt{4\ln 2}}{\sqrt{\pi}\omega_1} e^{\frac{-4\ln 2}{\omega_1^2}(x - (k_1\Delta T + x_{c2}))^2} \right] \\
 & - A_2 \left[(\mu_2) \frac{2}{\pi} \frac{\omega_2}{4(x - x_{c2})^2 + \omega_2^2} + (1 - \mu_2) \frac{\sqrt{4\ln 2}}{\sqrt{\pi}\omega_2} e^{\frac{-4\ln 2}{\omega_2^2}(x - x_{c2})^2} \right] \\
 & + A_3 \left[(\mu_3) \frac{2}{\pi} \frac{\omega_3}{4(x - (k_2\Delta T + x_{c4}))^2 + \omega_3^2} + (1 - \mu_3) \frac{\sqrt{4\ln 2}}{\sqrt{\pi}\omega_3} e^{\frac{-4\ln 2}{\omega_3^2}(x - (k_2\Delta T + x_{c4}))^2} \right] \\
 & - A_4 \left[(\mu_4) \frac{2}{\pi} \frac{\omega_4}{4(x - x_{c4})^2 + \omega_4^2} + (1 - \mu_4) \frac{\sqrt{4\ln 2}}{\sqrt{\pi}\omega_4} e^{\frac{-4\ln 2}{\omega_4^2}(x - x_{c4})^2} \right]
 \end{aligned}$$

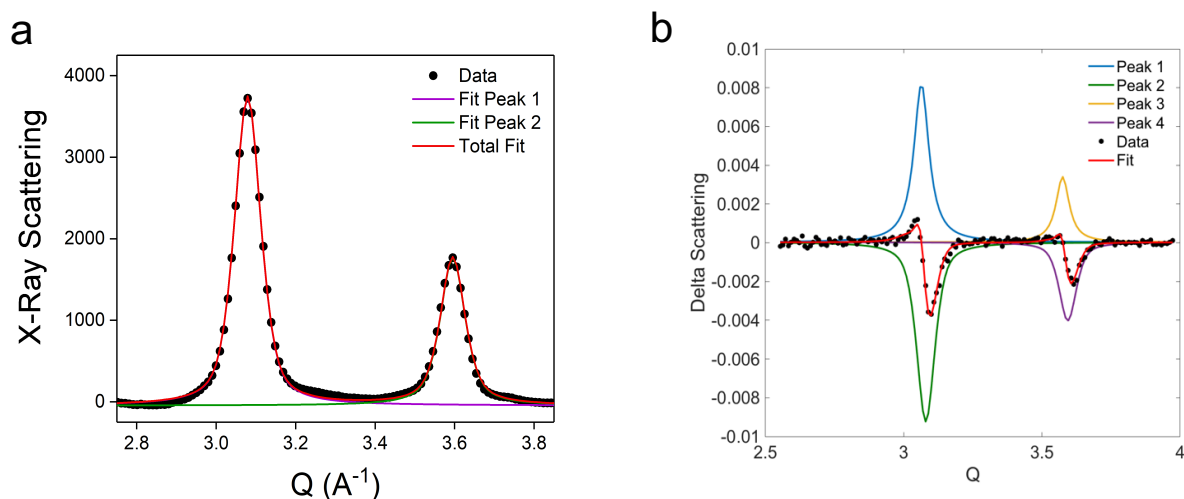


Figure B.3: (a) Pseudo-Voigt fitting of the static XRD features at -5 ns to determine starting parameters. (b) Example of the fits generated for the TR-XRD to determine temperature based on peak shift between the positive and negative features.

We attribute the difference in melting points from power dependent and time-resolved X-ray diffraction recorded in Table 4.1 to noise in the experiment and errors in the fitting procedure. Importantly both samples show reduced melting points from bulk CuInSe_2 and a size dependent trend for melting temperature.

Appendix C: Supporting Information for Chapter 5

C.1 ICP-OES

Samples were prepared for ICP-OES analysis using the following procedure. To begin, a stock solution of nitric acid was prepared by diluting fuming HNO_3 (90%) to a concentration of approximately 30% (solution changed from bright yellow to very pale or completely clear). A small amount of the dried nanocrystals were added to a vial (1-20 mg) and 6 mL of the HNO_3 solution were added. Sonication was used to dissolve as much solid material as possible and the resulting suspension changed from brownish black to red-orange. Since a large quantity of solid material remained 2 mL of HCl (37%) were added to the vials. Solution immediately become more orange-yellow. Samples were sonicated again and then left uncapped overnight to allow further dissolution. The next day the solution had turned a pale yellow and no remaining solids could be seen. 1 mL of this solution was diluted with 9 mL of deionized water in a centrifuge tube. Three tubes were prepared for each sample (CISE-OLAm, CISE-DPP, and CISE-TBP) along with three blanks that only included HNO_3 , HCl , and DI water to ensure that no trace amounts of metal impurities were detectable. Errors reported in Table 5.2 are statistically calculated. Ratios of Cu, In and Se are given in Table C.1 normalized to Se.

Table C.1: Molar ratios determined from ICP-OES

Sample	Cu	In	Se
CISE-OLAm	1.03 ± 0.01	1.10 ± 0.01	2.00
CISE-DPP	1.02 ± 0.02	1.09 ± 0.02	2.00
CISE-TBP	0.95 ± 0.02	1.18 ± 0.02	2.00

C.2 Photoluminescence Quantum Yield

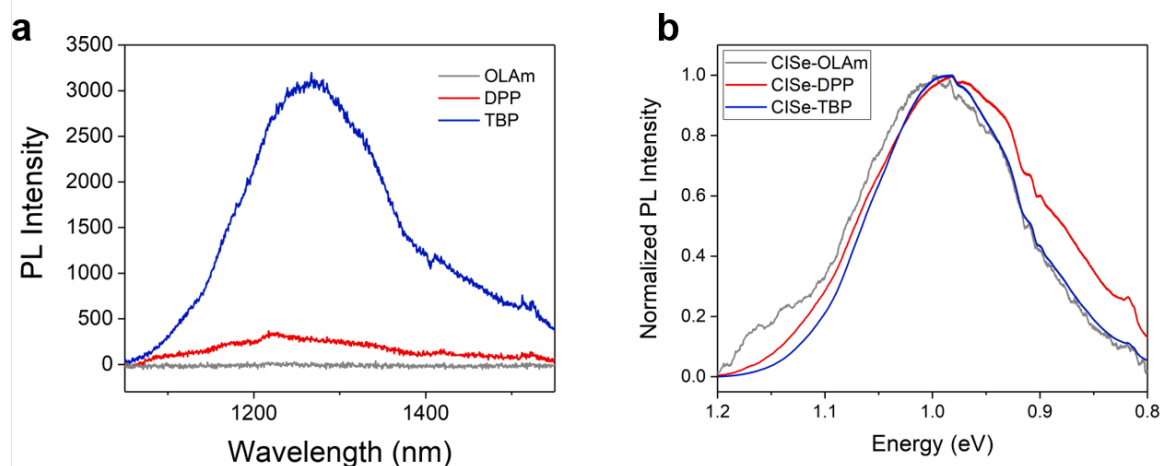


Figure C.1: PL intensity of the three samples (a) as measured and (b) normalized to peak intensity.

C.3 Determining the Bandgap Energy

Given the broad absorption linewidths in these samples it was difficult to determine the bandgap. For the values reported in the main text, we used a common technique, similar to a Tauc plot, to determine the energy of the bandgap by plotting $\alpha^{1/r}$ against photon energy (α is the absorption coefficient) and extrapolating a fitted linear region to the abscissa. In the case of CISE NCs we are monitoring a direct allowed transition and r is $1/2$.²⁶³ To determine the absorption coefficient, we used an equation from Jasieniak et. al. where α can be related to the absorption cross section (σ) and the volume of the nanocrystals (V).⁴⁰

Eq. C.1
$$\alpha = \frac{\sigma}{V}$$

Absorption cross sections for these samples were calculated for 800 nm but can easily be extrapolated to the entire wavelength range using the UV-Vis spectrum. Figure C.2 shows the resulting plot and the bandgap energy determined for each sample.

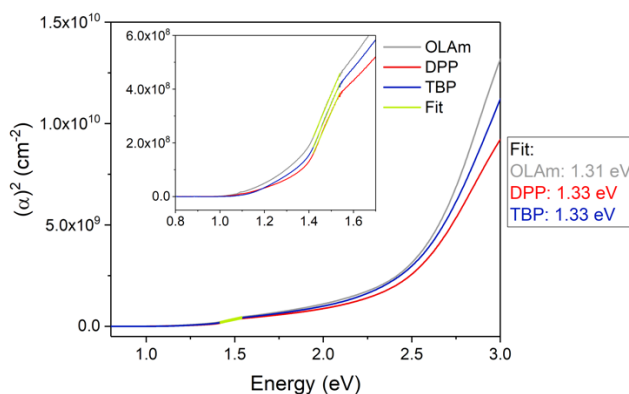


Figure C.2: Absorption coefficient squared vs. energy. A linear region around 1.5 eV was fit and then extrapolated to zero to determine the bandgap energy for each sample.

We also calculated the bandgap using a variety of other methods. We tried other Tauc plot methods (i.e. $\alpha^{1/2}$, $(\alpha h\nu)^{1/2}$, $\alpha^{1/3}$, $\alpha^{2/3}$) that correspond to amorphous, indirect transitions, or forbidden transitions. Most of these resulted in bandgap energies below that of bulk CISE (1.01 eV)¹⁸⁸ and are summarized in Table C.2. Even those that were reasonably close to the bulk bandgap are likely too low in energy since the diameter of our nanocrystals is less than the Bohr radius for this material (~ 10.6 nm) resulting in some degree of quantum confinement.²⁷⁵ Potentially these are capturing some of the midgap states.

In addition, we determined the bandgap using the second derivative of the absorption spectrum (Figure C.3). This has been used before to determine peak position in CISE NCs when the broad absorptions do not permit clear identification.²⁴⁵ The bandgaps determined using this method were higher in energy than those found above (1.48 – 1.52 eV).

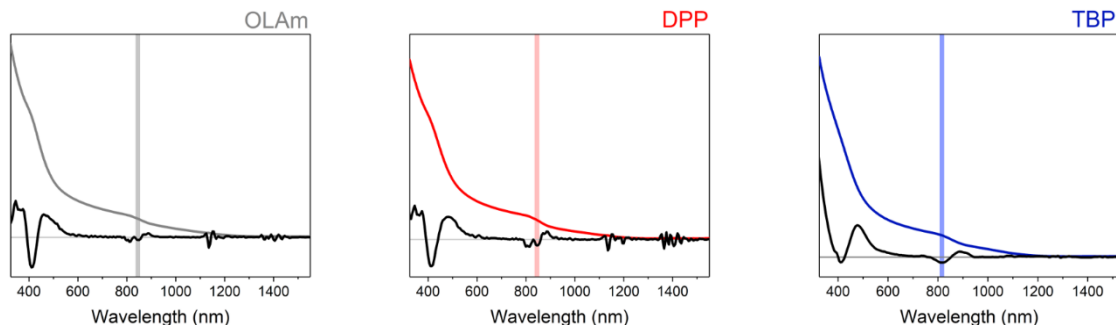


Figure C.3: The second derivative of the static absorption spectrum gives an approximation for the band edge (marked by the vertical lines).

Finally, using only the size of the nanocrystal, we calculated the bandgap using the Brus equation (Eq. C.2),¹⁵ theoretical modeling from Omata et. al.,³⁷³ and a sizing curve from Yarema et. al.²⁷⁴ These each gave numbers in the range of 1.25 – 1.46 eV suggesting that the bandgap energies found from the α^2 Tauc plot are reasonable. All bandgap energies are summarized in Table C.2.

Eq. C.2

$$E_g^{nano} = E_g^{bulk} + \frac{\hbar^2}{8r^2} \left(\frac{1}{m_e^*} + \frac{1}{m_h^*} \right) - \frac{1.8e^2}{4\pi\epsilon_0\epsilon_r r^2}$$

Table C.2: Bandgap energies for the three CISE samples found using different techniques. All values are given in units of eV.

	CISE-OLAm	CISE-DPP	CISE-TBP
α^2	1.31	1.33	1.33
$\alpha^{1/2}$	0.97, 0.99	0.98, 1.09	1.01, 1.06
$(\alpha h\nu)^{1/2}$	0.96, 1.05	0.97, 1.12	1.00, 1.10
$\alpha^{1/3}$	0.94, 0.95	1.07, 0.98	1.01, 1.00
$\alpha^{2/3}$	0.96, 1.09	0.98, 1.16	1.01, 1.14
Second Derivative of Absorption	1.47 – 1.53	1.47 – 1.53	1.51
Brus Eq.	1.4 – 1.43	1.27 – 1.3	1.34 – 1.37
Ref. 373	1.29	1.25	1.26
Ref. 274	1.46	1.38	1.43

C.4 Transient Absorption Fits

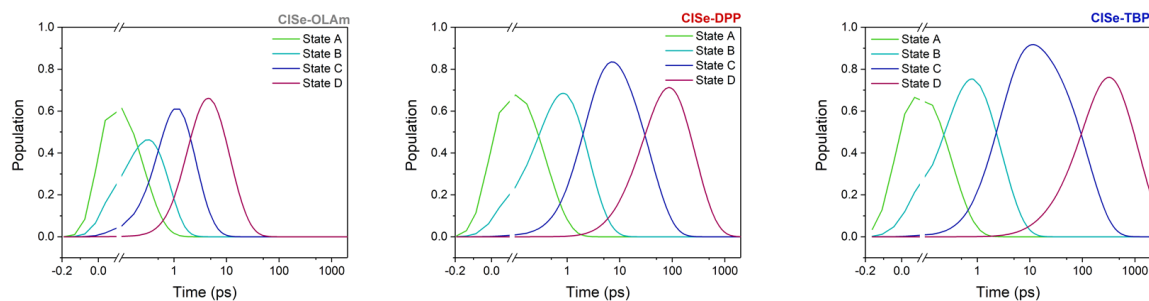


Figure C.4: Population curves generated from the fits to the TA data.

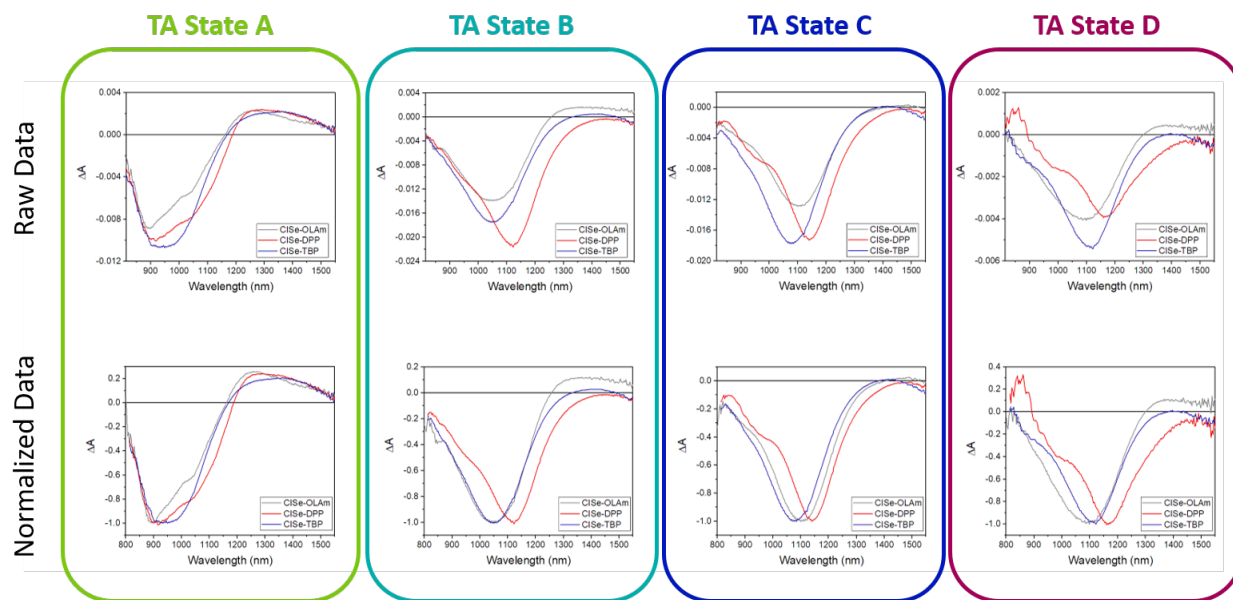


Figure C.5: Comparison of the different states generated from the TA fit for all three samples. (Top) Raw states. (Bottom) States normalized to their minimum amplitude.

Table C.3: Additional photophysical and fitting parameters

	IRF (ps)	ΔE_{AB} (meV)	ΔE_{BC} (meV)	ΔE_{CD} (meV)	ΔE_{Stokes} (meV)
CISE-OLAm	0.132 ± 0.007	202	62	10	310
CISE-DPP	0.164 ± 0.007	198 – 257	17	25	350
CISE-TBP	0.185 ± 0.005	108 – 196	30	42	350

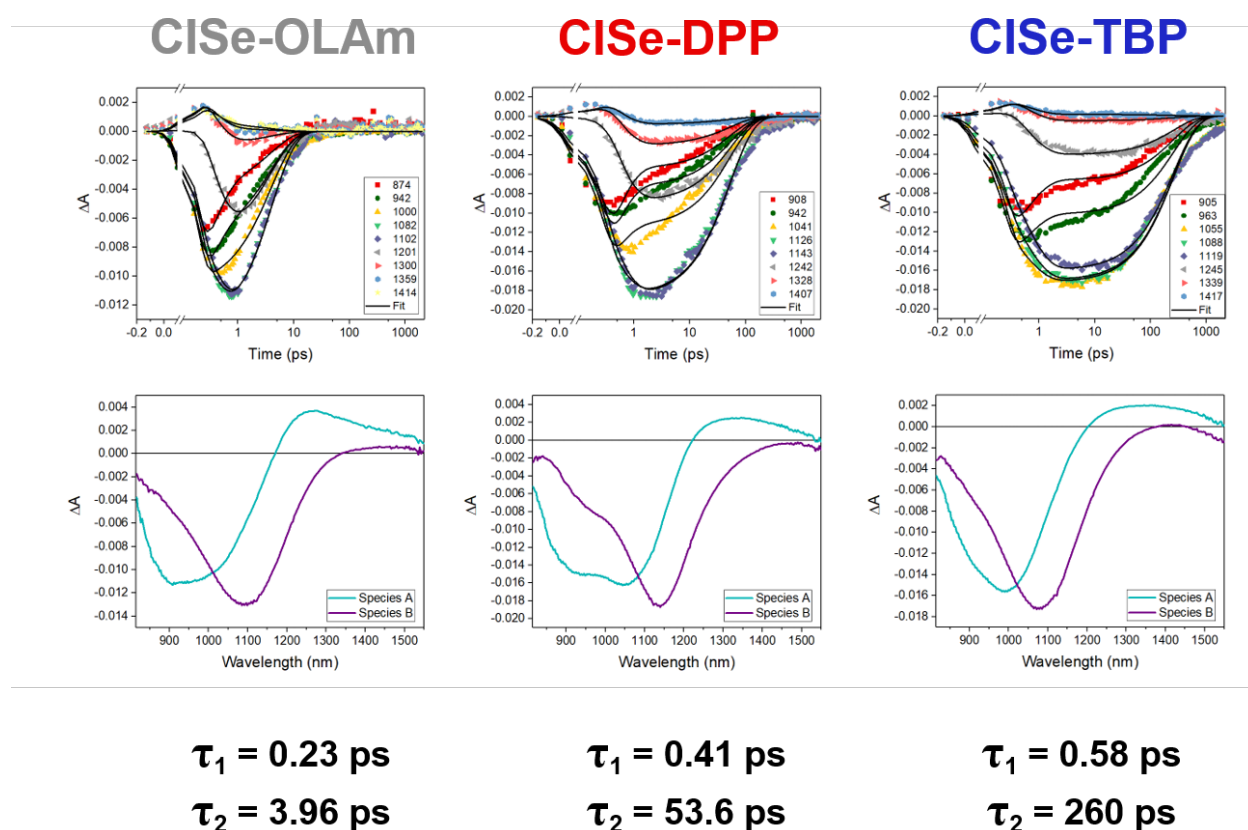
Transient Absorption Two-Species Fits

Figure C.6: Fits to the three samples presented in Ch. 5 using only two species (Model: $A \rightarrow B \rightarrow \text{Ground}$). The general trends are maintained between samples such that lifetimes increase going from OLAm to DPP to TBP, and Species A is characterized by a higher energy bleach and induced absorption that transitions to Species B with a lower energy bleach. However, the model severely underfits the data at late time delays and lower wavelengths.

Transient Absorption Three-Species Fits

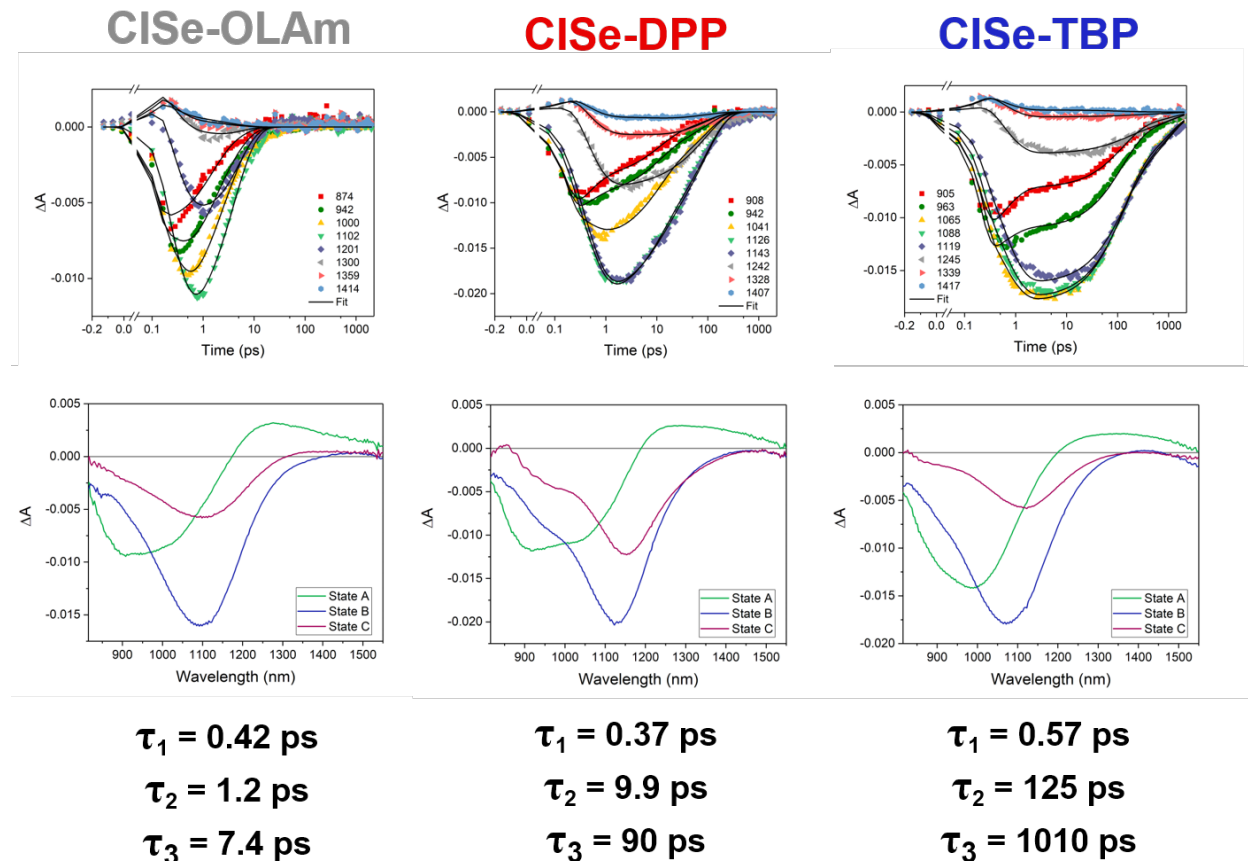


Figure C.7: Fits to the three samples presented in the Ch. 5 using three species (Model: $A \rightarrow B \rightarrow C \rightarrow \text{Ground}$). Like the two and four species fit, the general trends are maintained between samples such that lifetimes increase going from OLAm to DPP to TBP. This model still does not fully capture the kinetic components at early times, especially in **CISE-OLAm** suggesting the need for the fourth component used in the main text.

C.5 Transient Absorption at Other Powers

In addition to the laser fluence used in Ch. 5 ($76 \mu\text{J}/\text{cm}^2$) the **CISE-DPP** and **CISE-TBP** samples were run at lower fluences. The excitation wavelength was maintained at 800 nm. The lifetimes were longer in both (likely due to reduced Auger recombination). In addition, the **CISE-DPP** sample was run at a higher fluence, which caused the lifetimes to shorten. The data was fit to both a three and four species model with similar results. Importantly while the lifetimes differed

due to power, **CISE-TBP** was still consistently longer lived than **CISE-DPP** at both high and low fluence.

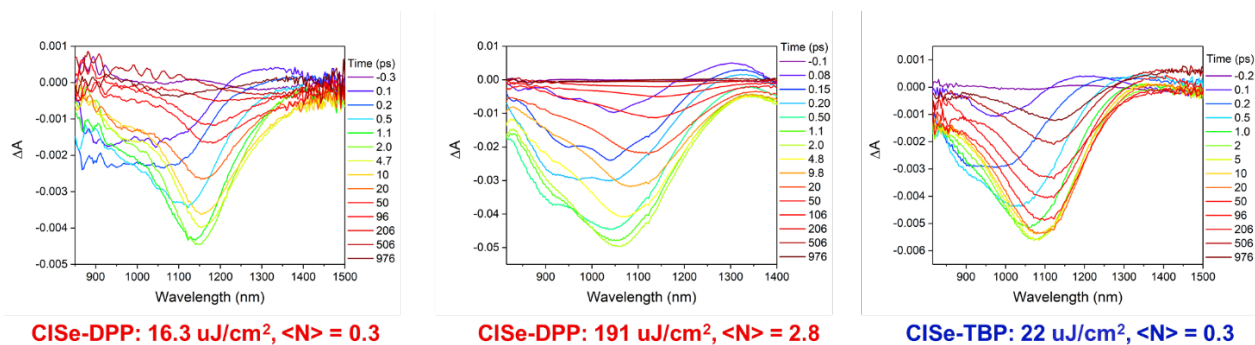


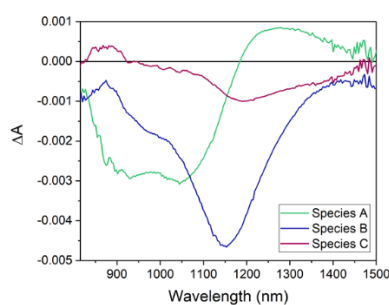
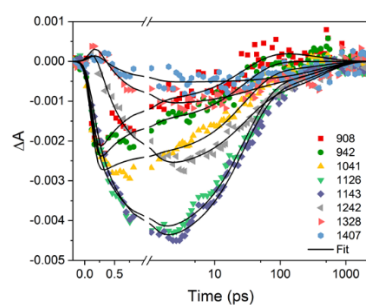
Figure C.8: Transient absorption data of the **CISE-DPP** and **CISE-TBP** samples at other laser fluences.

A $\rightarrow$ B $\rightarrow$ C $\rightarrow$ Ground

$$\tau_1 = 0.46 \pm 0.02 \text{ ps}$$

$$\tau_2 = 29 \pm 1 \text{ ps}$$

$$\tau_3 = 430 \pm 50 \text{ ps}$$



A $\rightarrow$ B $\rightarrow$ C $\rightarrow$ D $\rightarrow$ Ground

$$\tau_1 = 0.5 \pm 0.3 \text{ ps}$$

$$\tau_2 = 0.4 \pm 0.2 \text{ ps}$$

$$\tau_3 = 25 \pm 1 \text{ ps}$$

$$\tau_4 = 230 \pm 20 \text{ ps}$$

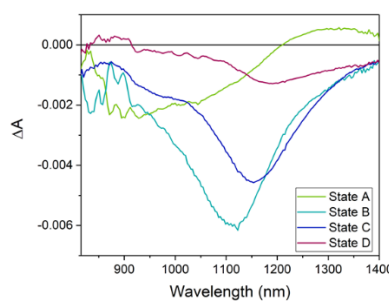
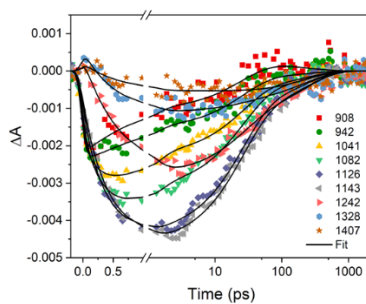


Figure C.9: Low power **CISE-DPP** ($16.3 \mu\text{J}/\text{cm}^2$, $\langle N \rangle = 0.3$) kinetic fits, evolution associated spectra, and time constants. Top row is three species fit; bottom row is four species fit.

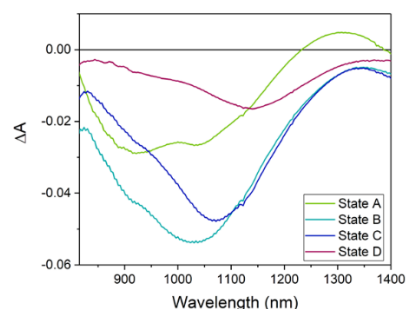
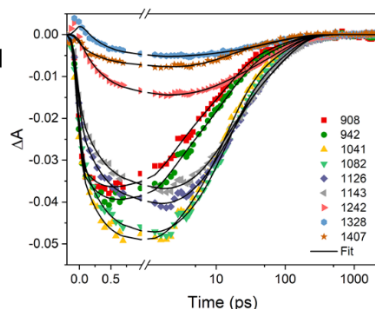
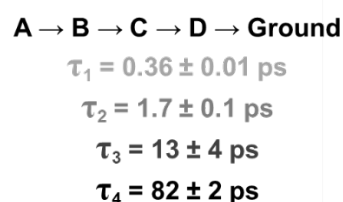
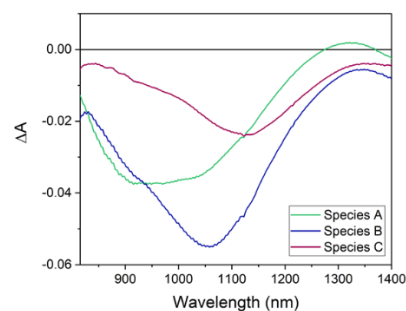
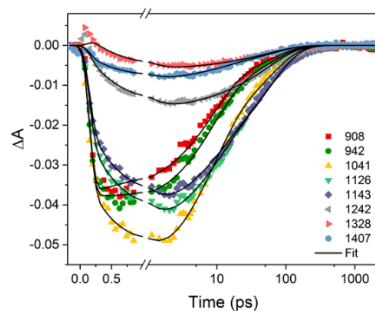
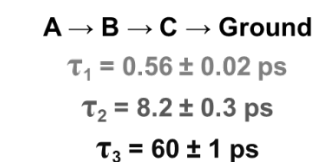


Figure C.10: High power CISE-DPP ($191 \mu\text{J}/\text{cm}^2$, $\langle N \rangle = 2.8$) kinetic fits, evolution associated spectra, and time constants. Top row is three species fit; bottom row is four species fit.

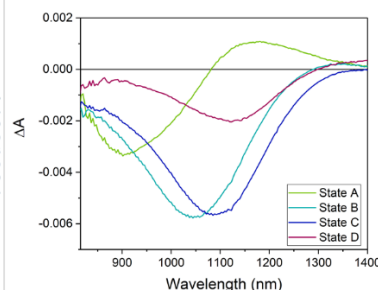
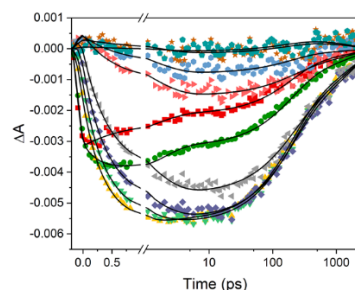
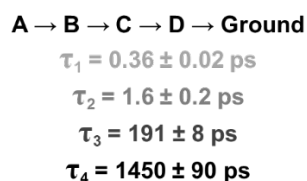
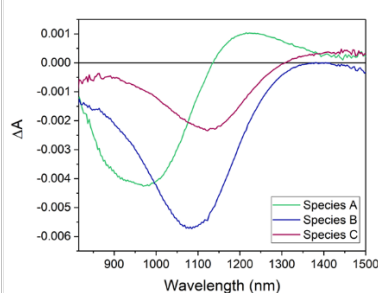
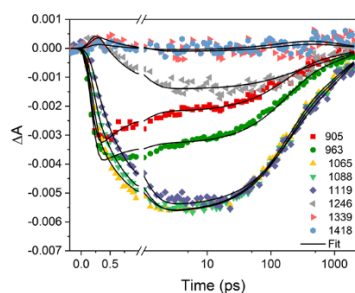
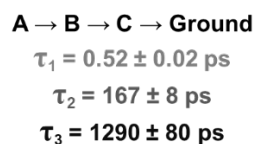


Figure C.11: Low power CISE-TBP ($22 \mu\text{J}/\text{cm}^2$, $\langle N \rangle = 0.3$) kinetic fits, evolution associated spectra, and time constants. Top row is three species fit; bottom row is four species fit.

C.6 OLAm Size Dependence

Transient absorption spectra of six **CISE-OLAm** samples are provided below. The samples were excited at 400. Small, medium, and large samples were generated by heating the reaction to different temperatures (200°C, 220°C, 240°C respectively). All samples were synthesized with OLAm ligands. In the case of Na₂S, the OLAm ligands were exchanged for S²⁻ post synthesis. Some of the samples were cleaned using the same procedure described in the synthesis section. The other samples were not precipitated/centrifuged after synthesis.

CISE-OLAm TA data was analyzed in two ways. First, the single wavelength kinetics at 4 or 5 wavelengths were fit for each sample and compared to others when relevant. This included looking at size dependence, effects of washing the NCs (precipitation) vs. not, and effects of post-synthetic ligand exchange. Second, the data was globally fit to an $A \rightarrow B \rightarrow C \rightarrow \text{Ground}$ model except for the large Na₂S sample which excluded a C state.

Important things can be derived from this data:

- In the small NCs (both washed and not), shifting of induced absorption spectral features confirms moving from a hot exciton (biexciton shift) to a cool exciton (interband transitions). See Figures S14 and S15.
- Excitation at 400 nm generally produced longer lifetimes in the lower wavelengths where induced absorption occurs (wavelengths 4 or 5). Since almost all samples saw an increase in lifetime compared to those excited at 800 nm, we can conclude that we are in fact monitoring intraband relaxation for τ_1 .
- Size dictates the energy of all spectral lineshapes with smaller nanocrystals higher in energy. This confirms that our NCs are quantum confined to some degree

- Size plays a minimal role in the dynamics. Although larger nanocrystals live longer, all the samples showed lifetimes shorter than **CISE-DPP** and **CISE-TBP** suggesting the ligand is the main contributor to differences. Furthermore, reaction temperature, which dictates the size of the NC, has little impact on dynamics such that annealing of defects is not a main contributor to differences between samples.
- Precipitation of the samples to remove excess ligand did not drastically affect lifetimes.
- Exchange for S^{2-} also did not affect dynamics drastically. This could suggest that the surface is unperturbed by ligand exchange, or that surface trapping is prevalent even when capped with OLAm.

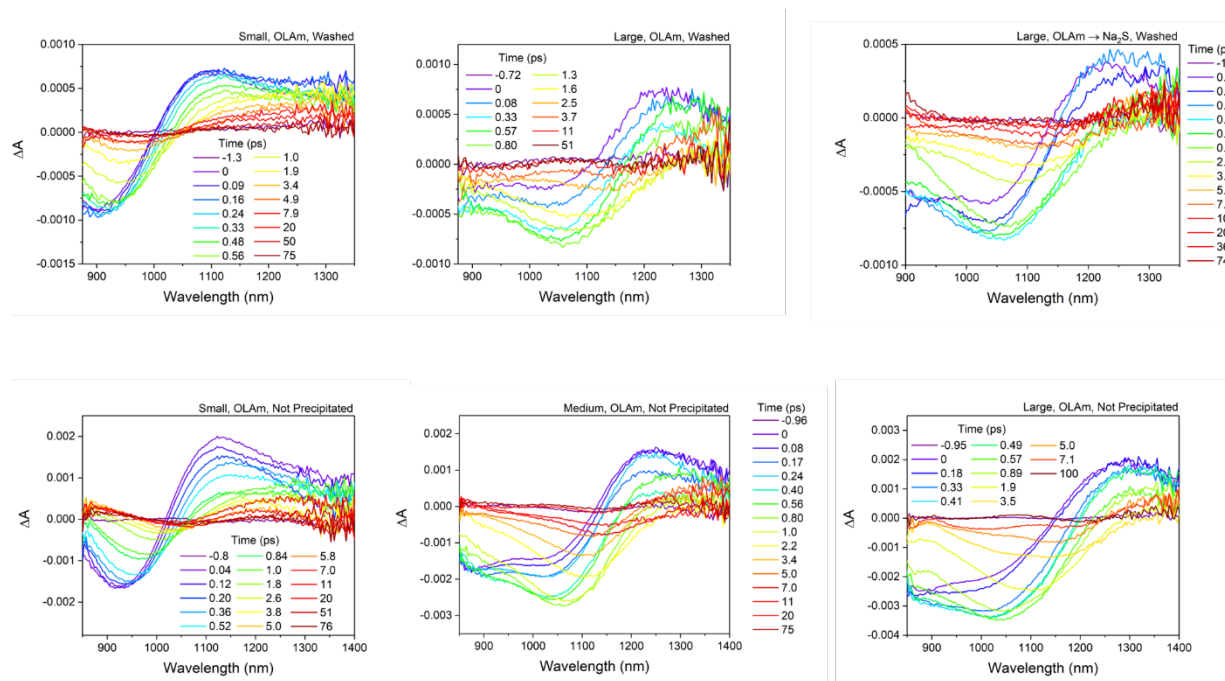


Figure C.12: Transient spectra of **CISE-OLAm** samples.

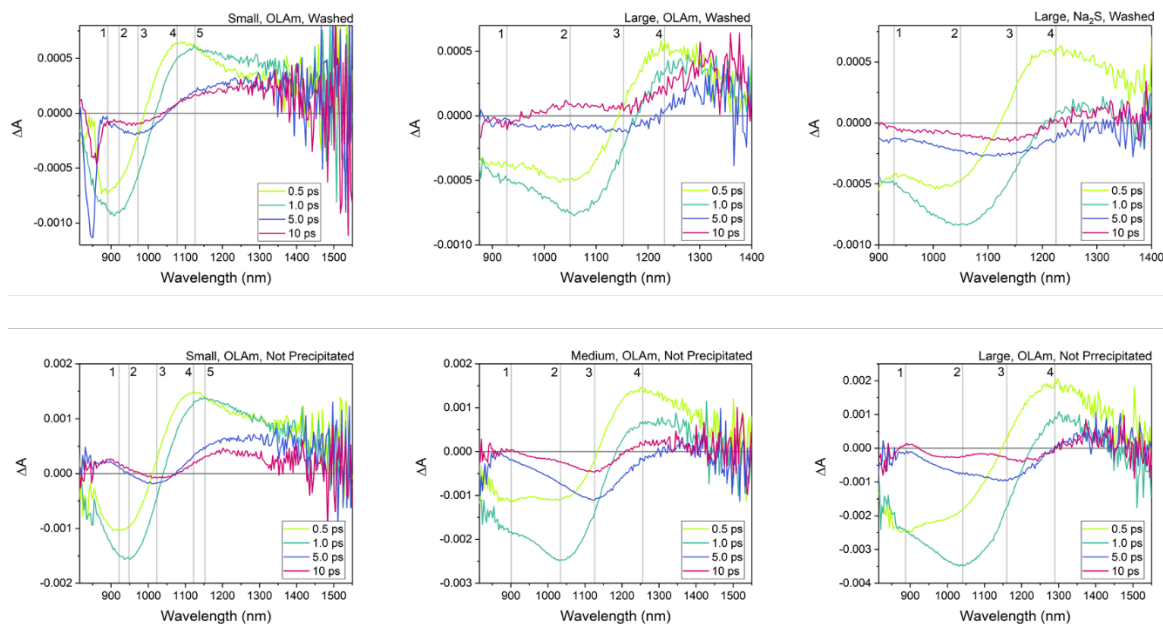


Figure C.13: Transient absorption data of CISE-OLAm samples with only 0.5 ps, 1.0 ps, 5.0 ps, and 10 ps time slices to show the similarity in spectral lineshape and decay in amplitude. Wavelengths for kinetic fitting are highlighted by the vertical grey lines and numbers. Wavelengths were chosen to occur at main bleach features (1, 2, and 3) and induced absorption features (4, 5).

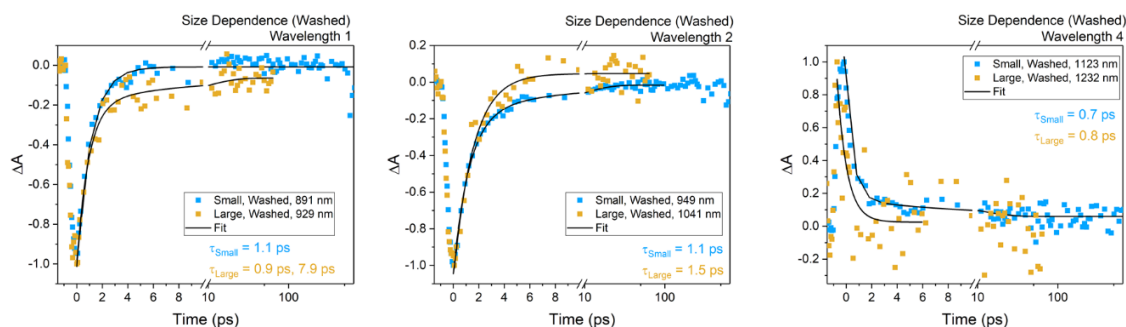


Figure C.14: Comparison of size (small vs. large). Samples were washed according to the synthetic protocols.

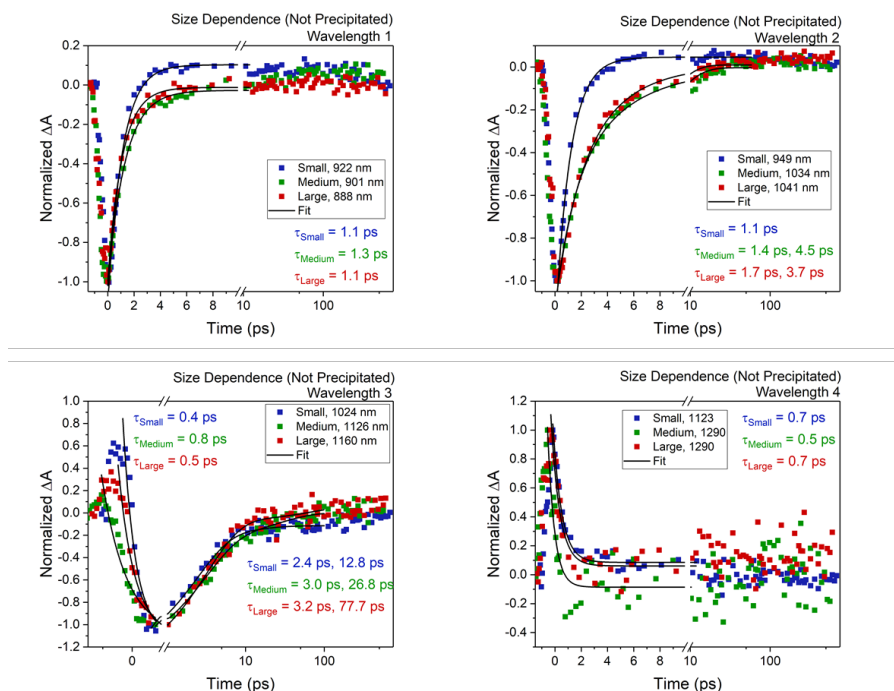


Figure C.15: Comparison of size (small vs. medium vs. large). Samples were not precipitated or cleaned in any way.

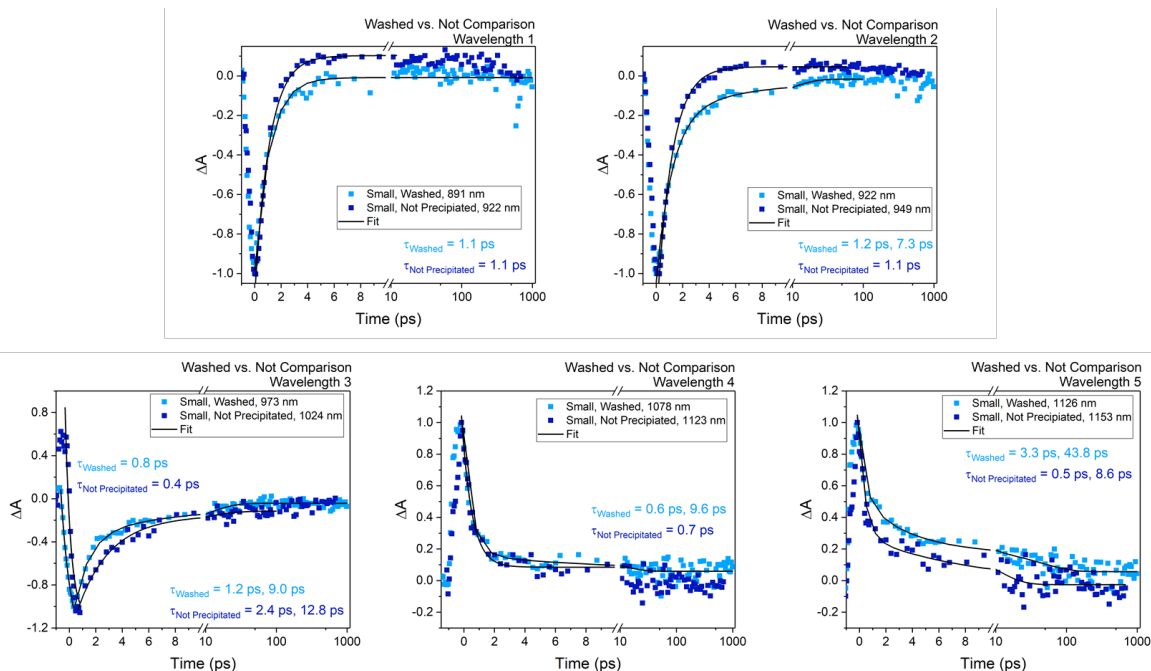


Figure C.16: Effects of precipitation on lifetimes for the small samples.

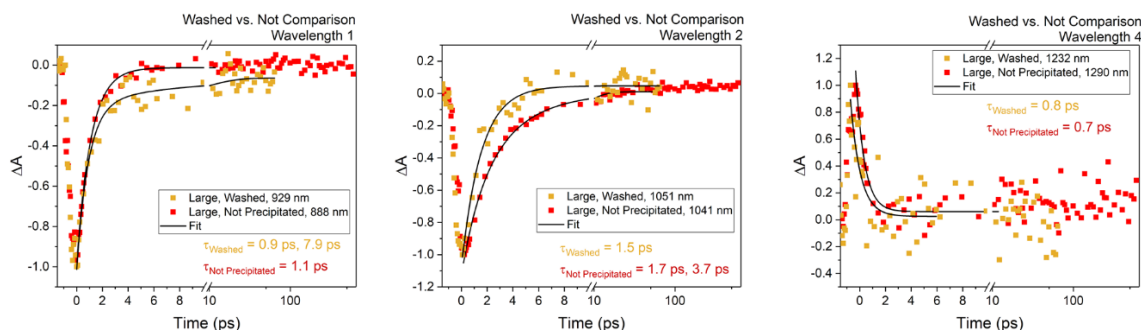


Figure C.17: Effects of precipitation on lifetimes for the large samples.

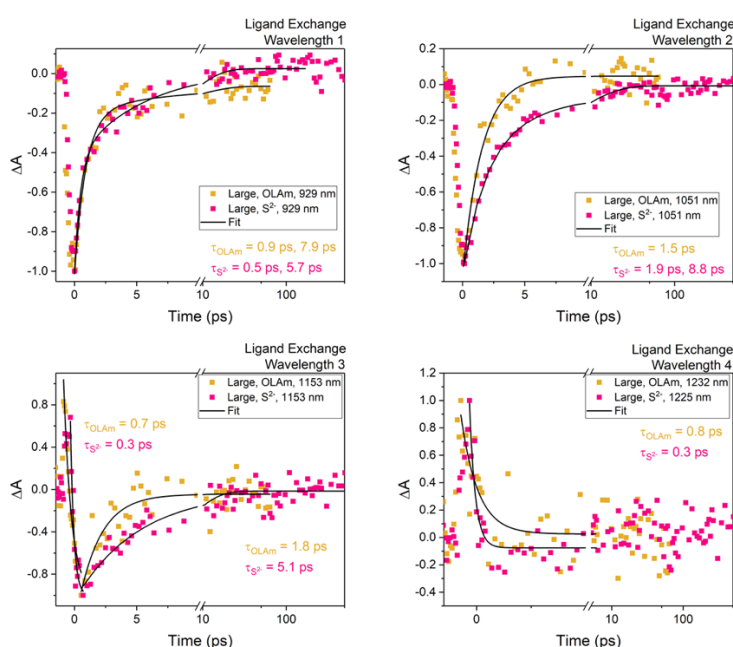


Figure C.18: Effects of post-synthetic ligand exchange from OLAm to S^{2-} .

Table C.4: Time Constants and IRF from global fitting of CISE-OLAm TA

Reaction Temperature, Ligand, Washing Procedure*	τ_1 (ps)	τ_2 (ps)	τ_3 (ps)	IRF (ps)
200, OLAm, P	0.30 ± 0.02	1.2 ± 0.1	35 ± 4	0.56 ± 0.04
240, OLAm, P	0.6 ± 0.2	1.0 ± 0.2	85 ± 53	0.24 ± 0.04
240, S^{2-} , P	0.18 ± 0.05	3.1 ± 0.2		0.52 ± 0.04
200, OLAm, NP	0.23 ± 0.08	1.3 ± 0.1	45 ± 6	0.68 ± 0.06
220, OLAm, NP	0.5 ± 0.2	0.9 ± 0.2	8.2 ± 0.6	0.80 ± 0.05
240, OLAm, NP	0.2 ± 0.1	0.7 ± 0.1	3.6 ± 0.2	0.93 ± 0.07

*Some of the samples were cleaned using the same procedure described in the synthesis section and are marked with a P. The other samples were not precipitated/centrifuged after synthesis and are marked with by NP.

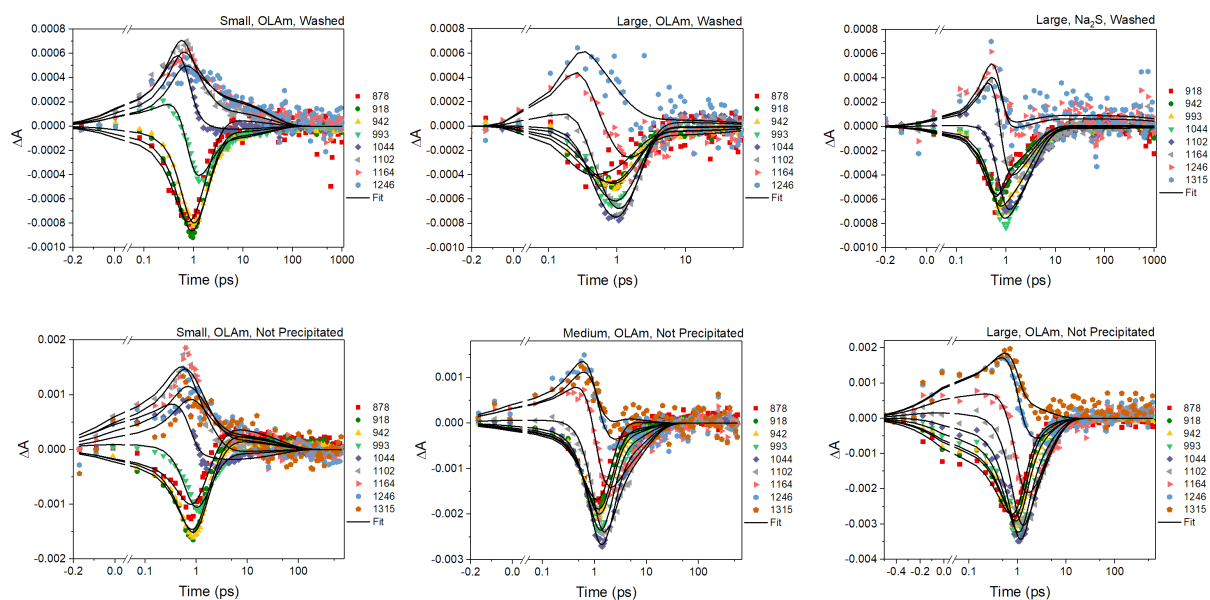


Figure C.19: Kinetic fits for CISE-OLAm samples

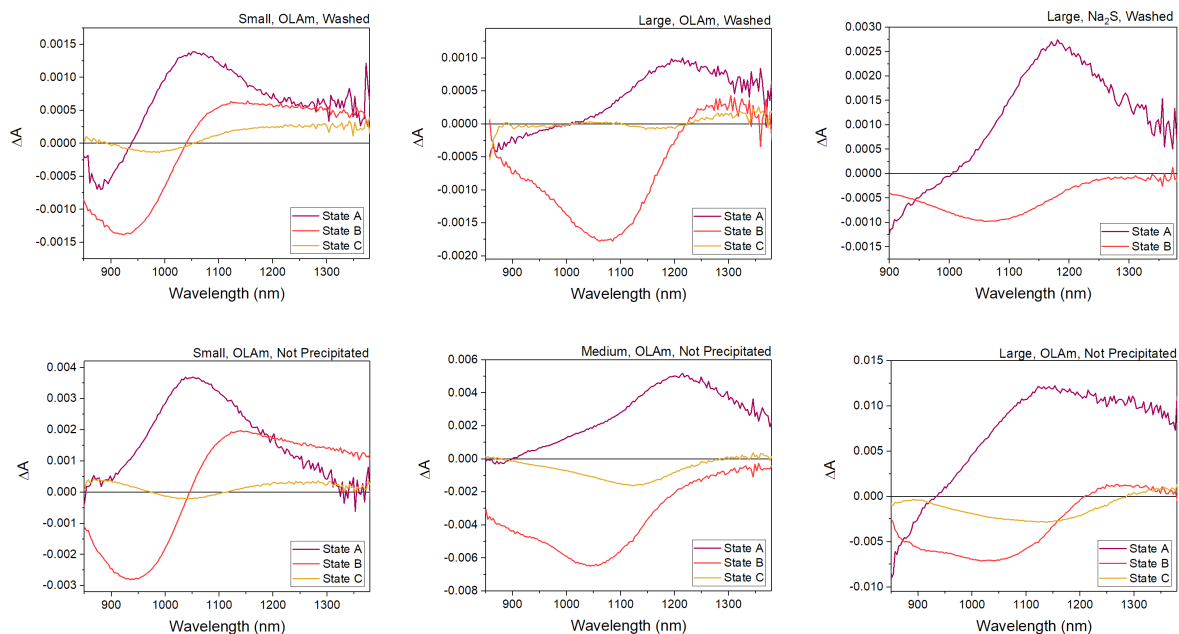


Figure C.20: Evolution associated spectra for CISE-OLAm samples

C.7 Temperature Dependent PL

PL intensity as a function of temperature as well as spectra before and after heating are given in Figure 5.9. For the **CISe-OLAm** NCs, due to low PL QY and losses from the experimental setup, a PL spectrum was only detectable at low temperatures. (The PL measurements in Figure 1b and the PLQY cited in Table 1 were performed in solution and without the use of a fiber optic allowing higher signal to noise). Upon warming to room temperature, the PL intensity was lost in the noise and extended averaging did not increase signal. Ramping to 600K did not increase the PL appreciably; if it had shifted or lowered in intensity it would be impossible to discern. The **CISe-TBP** sample showed increased PL at lower temperatures (relative to 298K) that diminished as the temperature was raised. At 550K an increase in PL intensity was observed, but upon heating to 600K the signal diminished. After cooling to room temperature, the PL was found to have redshifted and broadened suggesting sintering of the sample. The **CISe-DPP** sample similarly showed higher PL at low temperatures. Upon heating the sample, it began to brighten, a trend that continued with rising temperature. After returning to 290K the sample remained brighter. To ensure that this increase was not due to photobrightening from the laser, the sample was moved to fresh spots. While PL intensities differ due to film thickness, all showed at least twice the PL intensity found before heating (Figure 5.10).

Temperature Dependent Transient Absorption

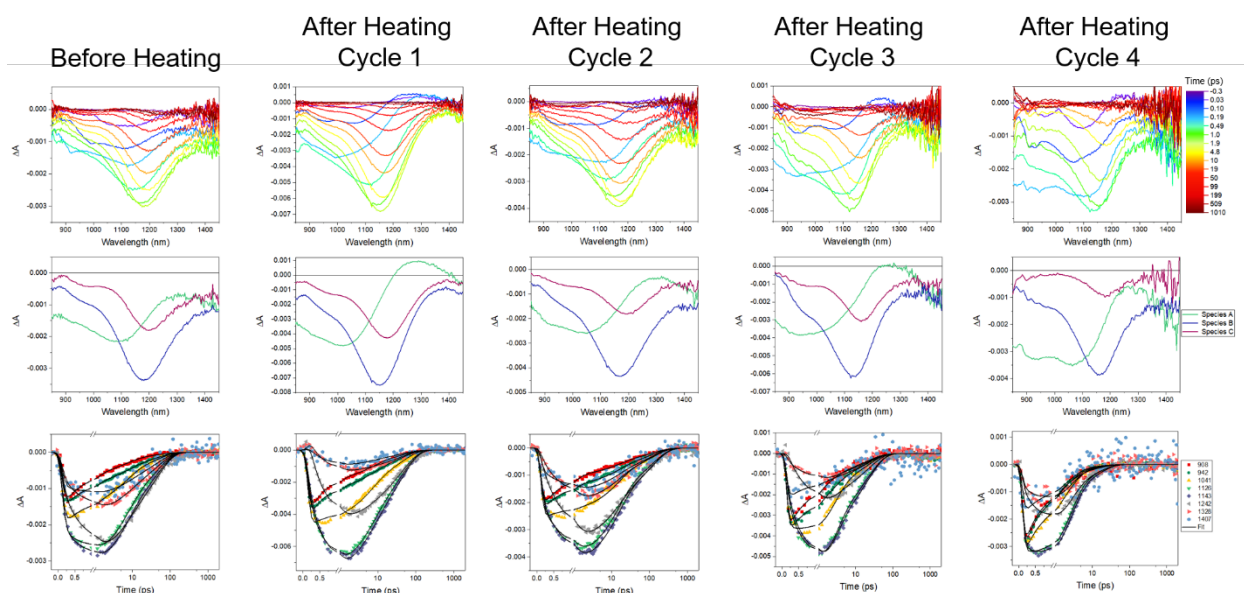


Figure C.21: Transient absorption spectra, evolution associated spectra, and kinetic fits for the film samples used in the pendulum heating experiment.

Table C.5: Time constants from the temperature dependent TA

Sample	τ_1 (ps)	τ_2 (ps)	τ_3 (ps)
No Heating	0.62 ± 0.04	6.6 ± 0.5	46 ± 2
After Heating Cycle 1	0.43 ± 0.01	6.3 ± 0.3	45 ± 1
After Heating Cycle 2	0.63 ± 0.03	14.2 ± 0.6	125 ± 5
After Heating Cycle 3	0.59 ± 0.05	2.4 ± 0.3	23 ± 1
After Heating Cycle 4	0.49 ± 0.06	2.3 ± 0.2	15 ± 3

C.8 NMR Fits

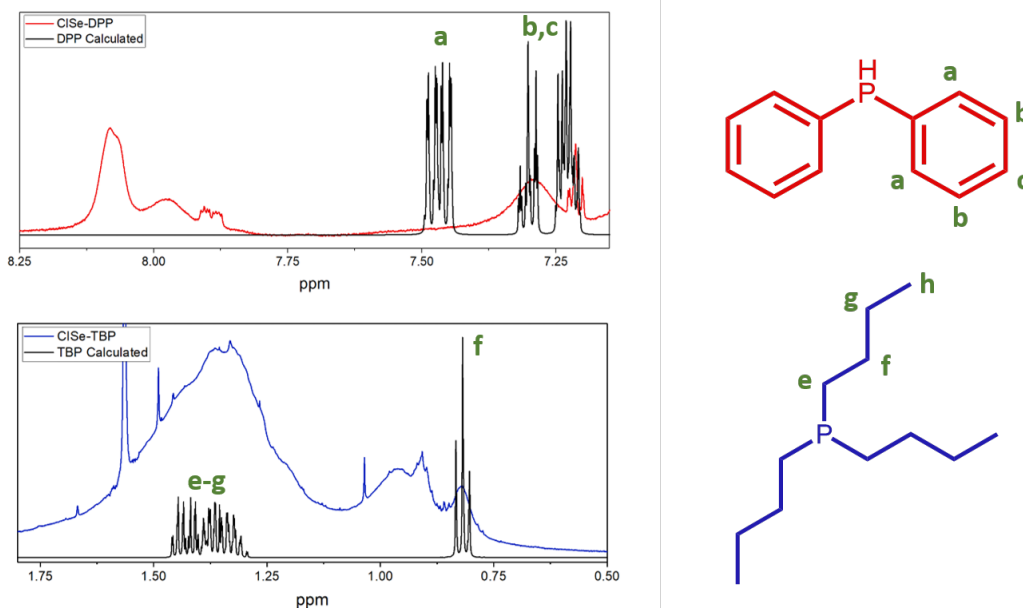


Figure C.22: NMR spectra of **CISE-DPP** (top) and **CISE-TBP** (bottom) plotted against calculated NMR spectra. The hydrogens corresponding to the features are delineated. We note that the calculated spectra were used for identification of features, but in the case of DPP are not 100% accurate since the solvent is not taken into account and molecule is likely Ph_2HPSe^+ . There is literature precedence for the **a** hydrogens being closer to ~ 8.0 ppm, which matches more with the features seen in our samples.²⁰⁵ Importantly the sharp features between 7.5 and 7.75 ppm are a ddd, which match expected splitting.

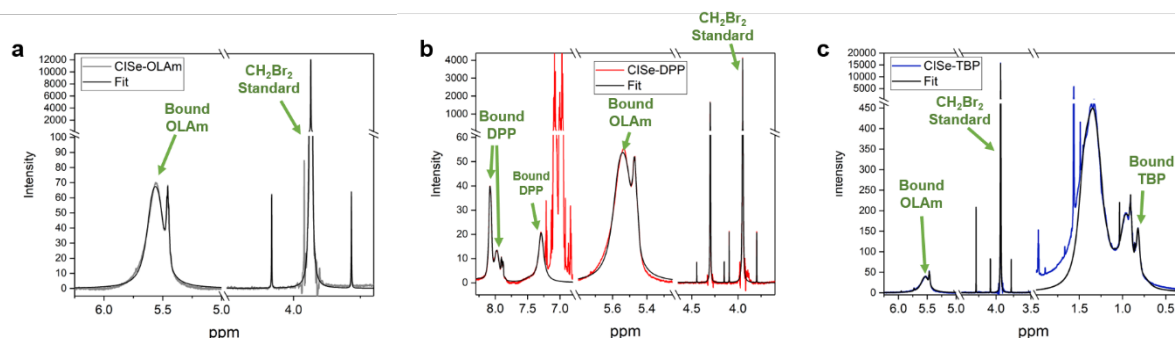


Figure C.23: Selected regions of the NMR spectra of (a) **CISE-OLAm**, (b) **CISE-DPP**, and (c) **CISE-TBP** along with their corresponding fits. For all three samples the region between 5 and 6 ppm was used to calculate the number of OLAm molecules bound. In addition, the feature at 3.9 ppm and its satellite peaks correspond to CH_2Br_2 the standard used to calculate moles of ligands. For **CISE-DPP**, the features above 7.5 ppm were used to calculate the number of DPP molecules bound. Although features around 7.25 ppm were fit, they were too convoluted with solvent features to be accurate. For **CISE-TBP** a large portion of the features upfield of 1.5 ppm were fit, however only the feature highlighted by the arrow was used to calculate the number of TBP molecules bound.

C.9 Raman Spectra

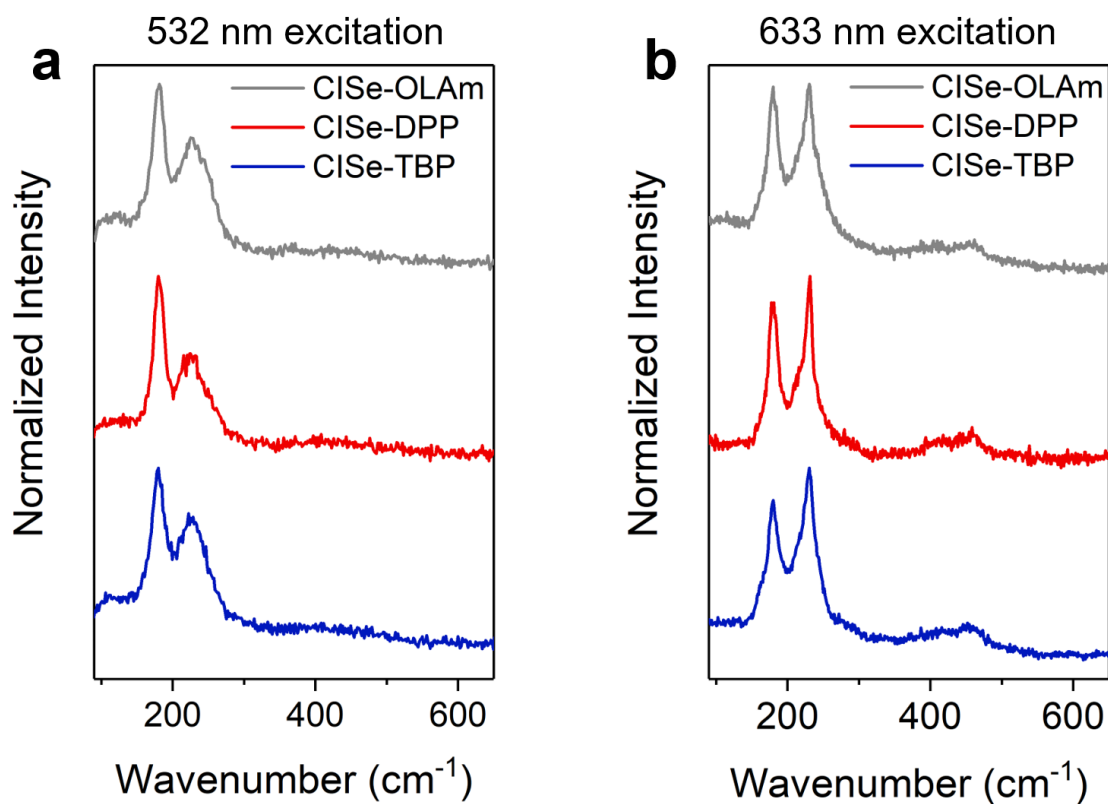


Figure C.24: Raman spectra of the samples with two different laser excitations.

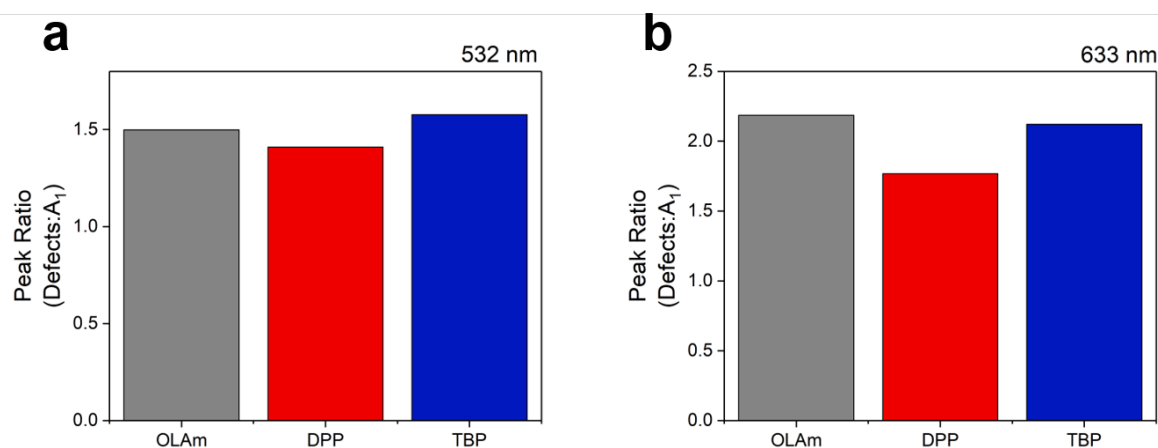


Figure C.25: Peak area ratio determined by fitting the Raman modes to Lorentzian functions. All samples show a larger proportion of the defect states at 115 and 230 cm^{-1} compared to the A_1 mode at 180 cm^{-1} . CISE-OLAm and CISE-TBP show a higher volume of defects than CISE-DPP.

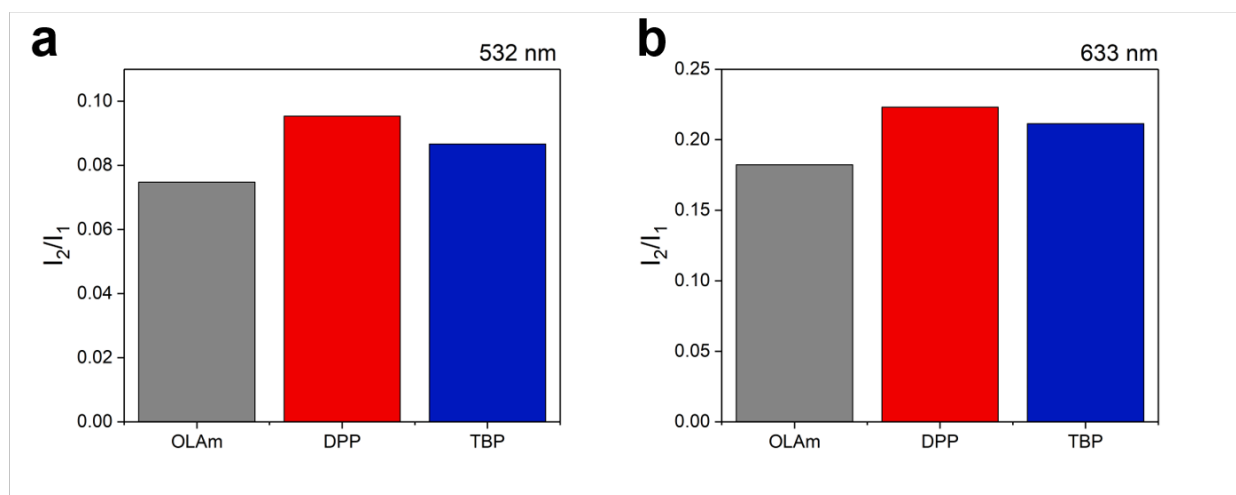


Figure C.26: Ratio of second order Raman features to first order by peak area. **CiSe-DPP** shows the largest intensity of second order modes.

C.10 Device Data

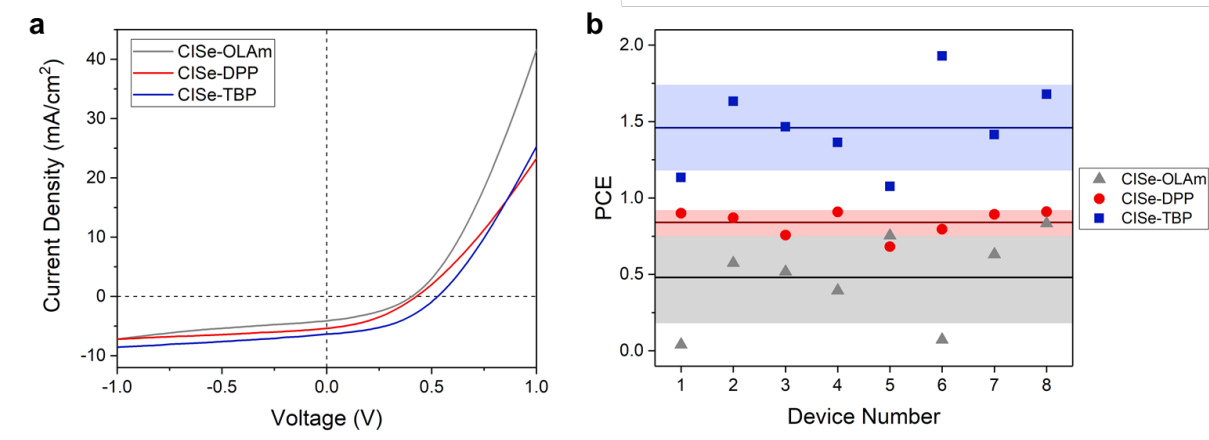


Figure C.27: Device data (a) Representative J-V curves for each sample (numbers given in Table SX). (b) All PCEs for the devices along with mean (line) and standard deviation (shaded area).

Table C.6: Device data for one device for each sample

	V _{oc} (V)	J _{sc} (mA/cm ²)	Fill Factor	PCE (%)
CiSe-OLAm	0.41	-4.10	0.380	0.63
CiSe-DPP	0.43	-5.38	0.378	0.87
CiSe-TBP	0.53	-6.35	0.436	1.47

Appendix D: Supporting Information for Chapter 6

D.1 Transmission Electron Microscopy

NC solutions were heavily diluted and dropcast on a copper grid. Multiple TEM images were taken of each sample (Tubes 1-4 and control). Diameters and particle-to-particle distances were measured using ImageJ.

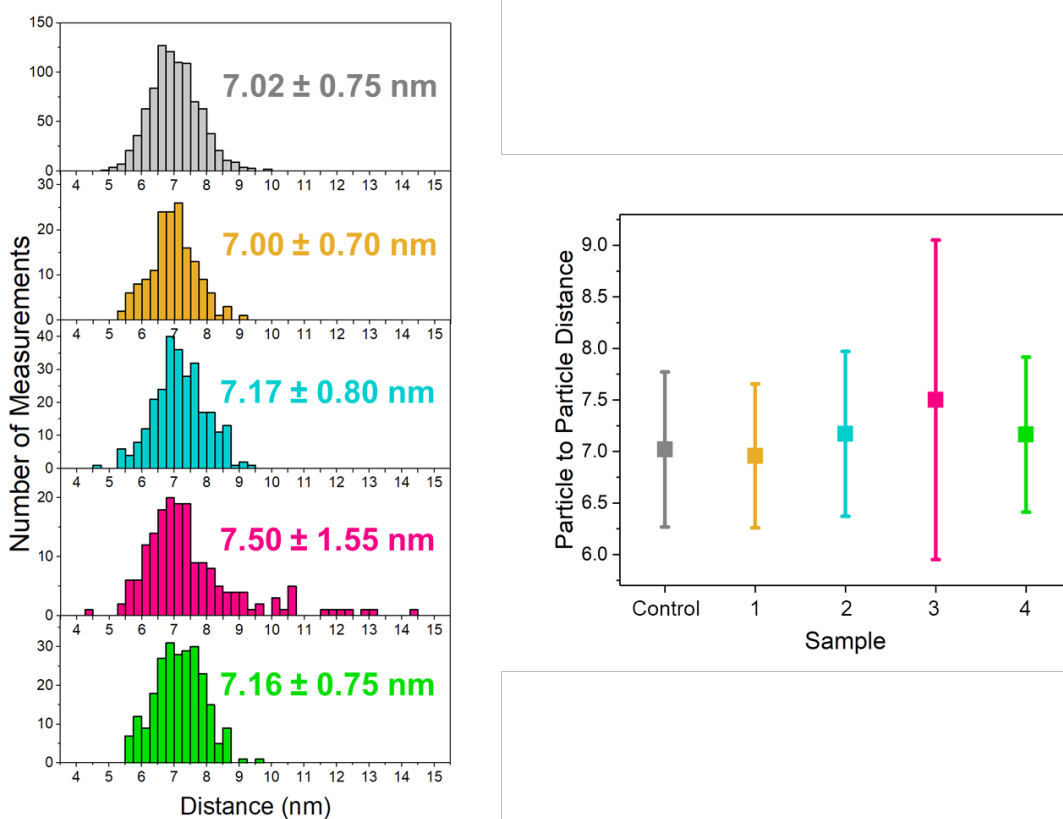


Figure D.1: Particle to particle measurement histograms for the control and Tubes 1-4. Importantly only nanocrystals that were packed in a hexagonal fashion (implying they are as close as their ligands would allow) were measured. Measurements were done from center to center, thus increased size (as in the case of Tube 3) results in larger distances. For the most part the distance did not differ between the NCs except due to size.

D.2 X-ray Diffraction FWHM

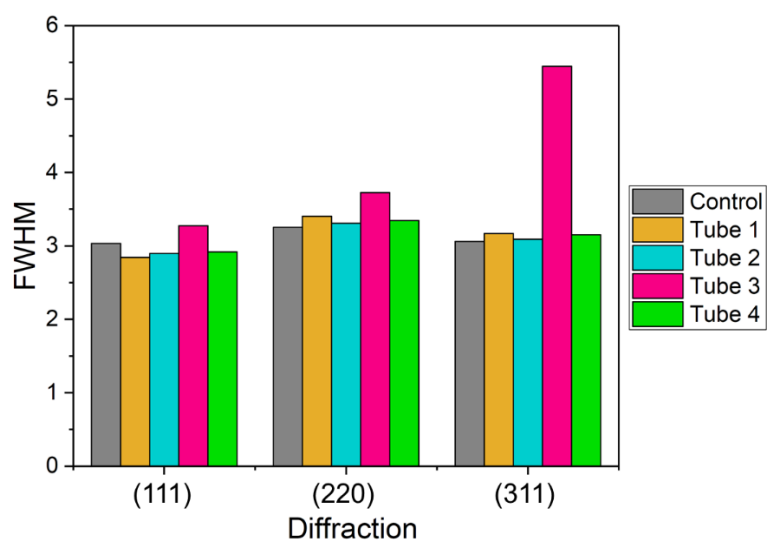


Figure D.2: Full-width half-maximums for the control and Tubes 1-4 derived from X-ray diffraction data.

D.3 NMR Data and Analysis

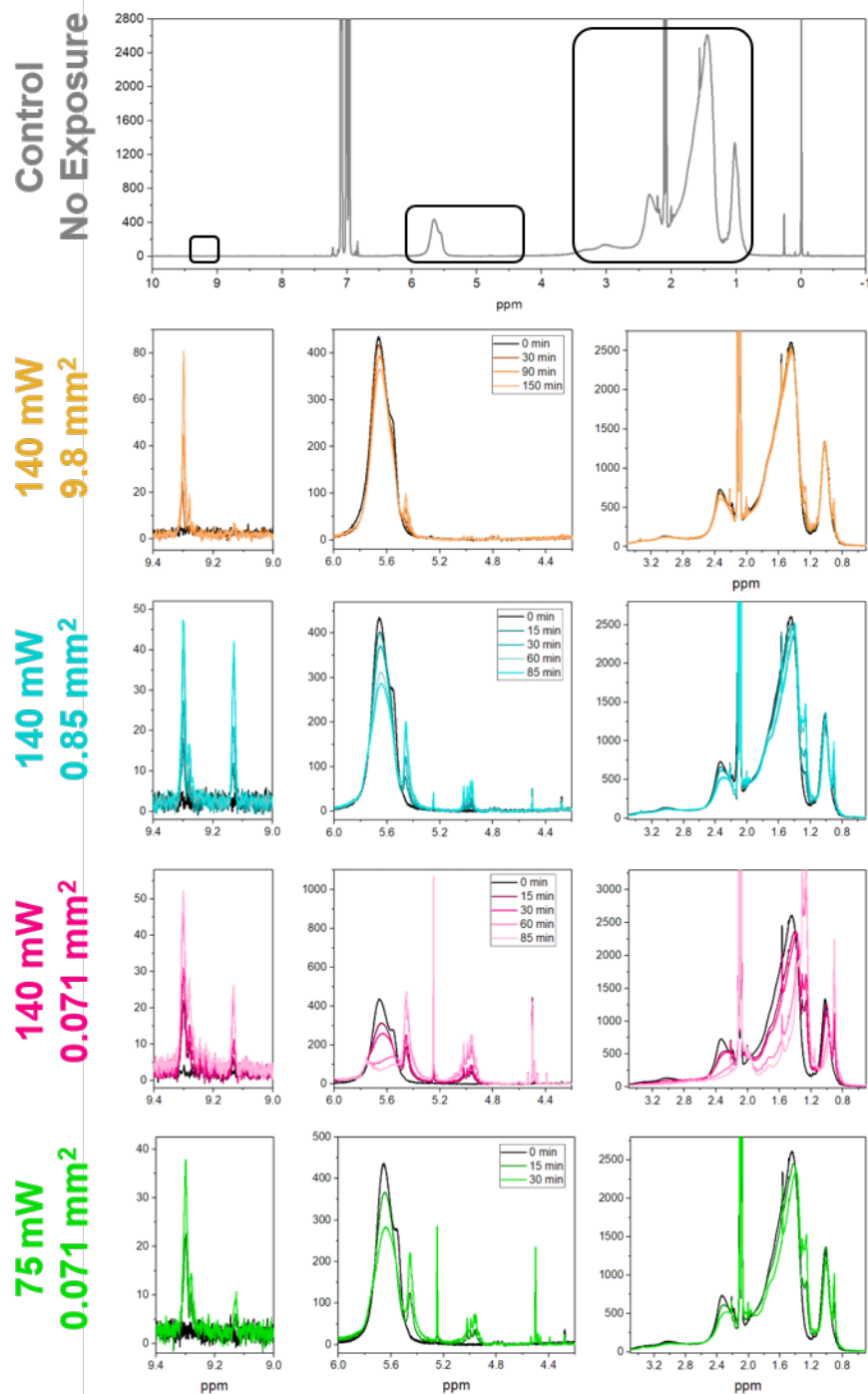


Figure D.3: NMR spectra of the control (top) and all photoexcited samples. Areas not shown are dominated by toluene features or show no features at all.

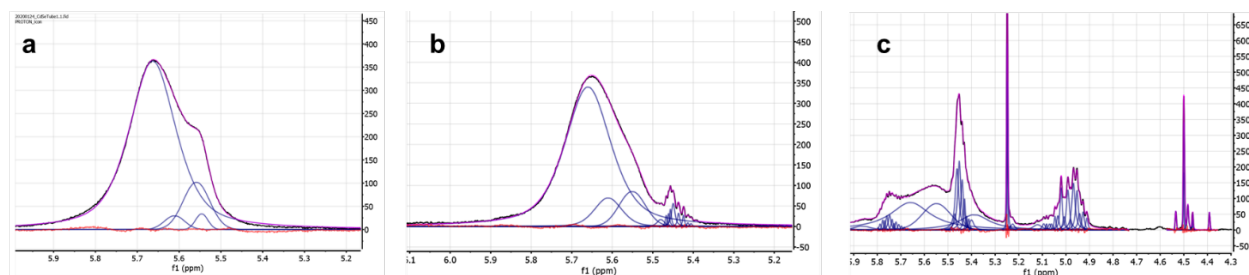


Figure D.4 Examples of fitting in MNOVA. (a) Tube 1, 0 minutes. (b) Tube 1, 150 minutes. (c) Tube 3, 60 minutes.

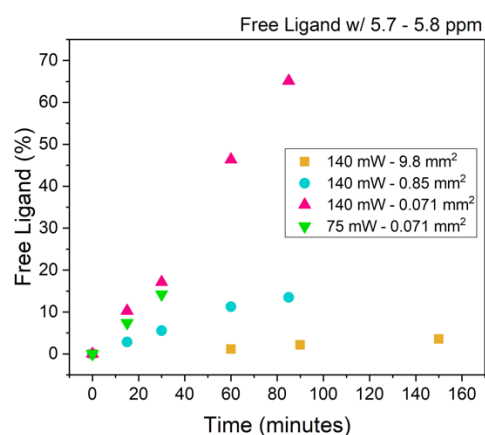


Figure D.5: Ratio of free ligand calculated if the undecane/undecanoic acid features between 5.7 – 5.8 ppm are free ligand that arose from oleic acid.

D.4 Static Photoluminescence

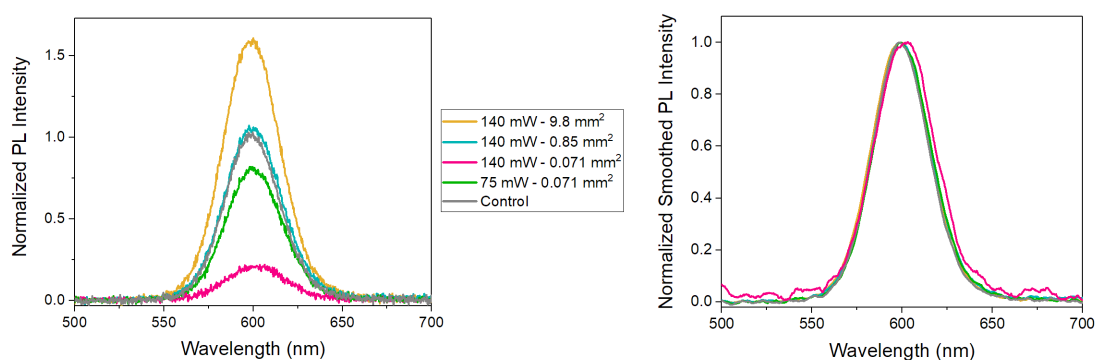


Figure D.6: Static PL (a) normalized such that the control is 1 and (b) all datasets normalized (and smoothed).

D.5 Streak Camera Data

All samples were diluted in toluene to an OD of ~ 0.1 for measurements. Streak camera data was taken using 400 nm excitation. All samples were taken using the 5 ns and 50 ns time window. The control and Tube 3 were also studied using a 1.5 ns time window for higher resolution. Data is cut off around 400 nm using a bandpass filter to remove scatter.

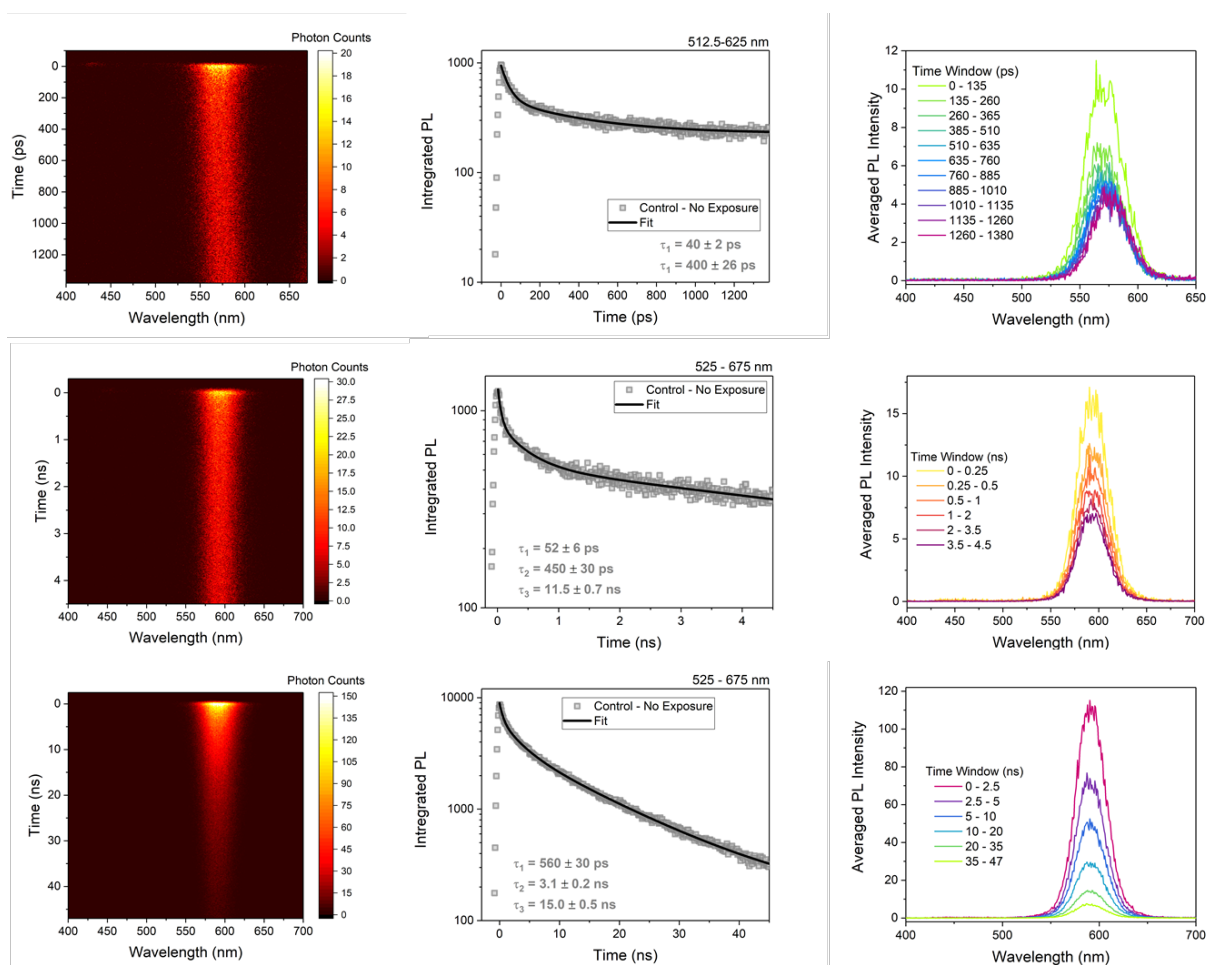


Figure D.7: Control sample with increasing time range (top to bottom). (Left) 2D plots, (center) kinetic at specified wavelengths along with fit, (right) spectral evolution.

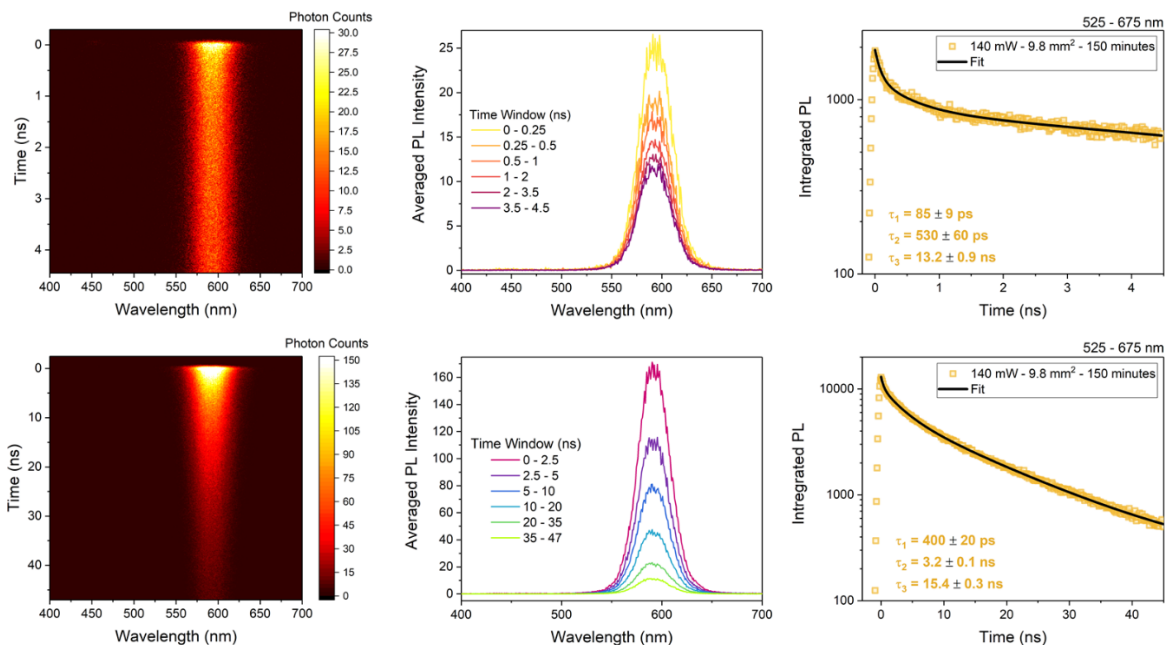


Figure D.8: Tube 1 (140 mW, 9.8 mm², 150 minutes) with increasing time range (top to bottom). (Left) 2D plots, (center) kinetic at specified wavelengths along with fit, (right) spectral evolution.

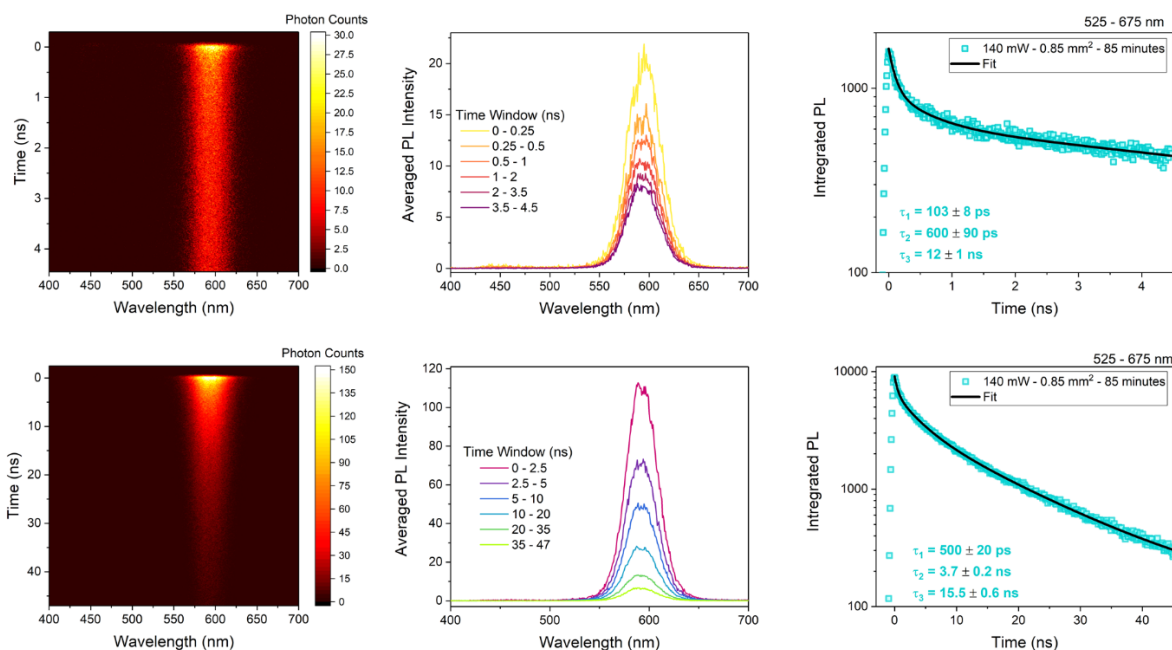


Figure D.9: Tube 2 (140 mW, 0.85 mm², 85 minutes) with increasing time range (top to bottom). (Left) 2D plots, (center) kinetic at specified wavelengths along with fit, (right) spectral evolution.

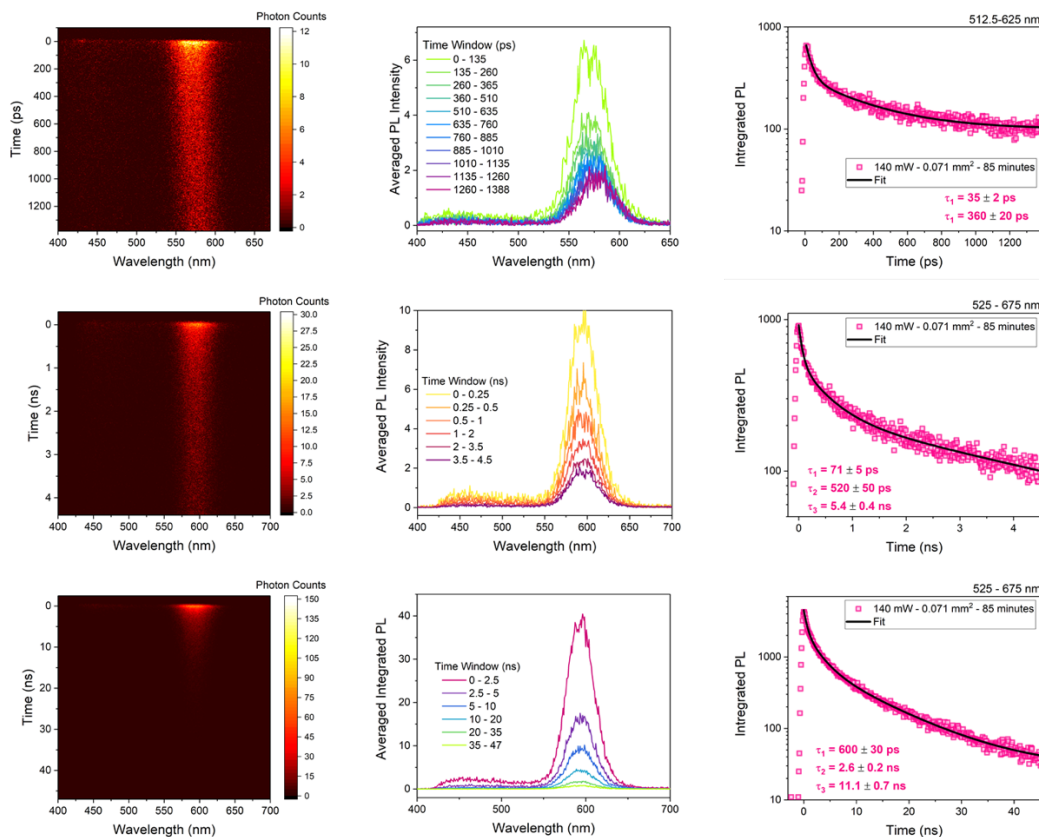


Figure D.10: Tube 3 (140 mW, 0.071 mm², 85 minutes) with increasing time range (top to bottom). (Left) 2D plots, (center) kinetic at specified wavelengths along with fit, (right) spectral evolution.

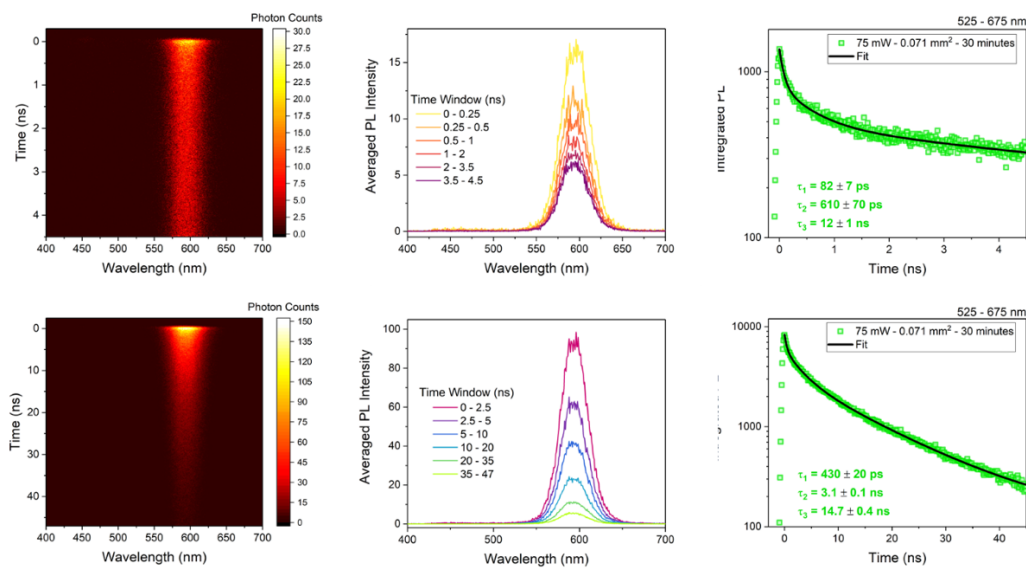


Figure D.11: Tube 4 (75 mW, 0.071 mm², 85 minutes) with increasing time range (top to bottom). (Left) 2D plots, (center) kinetic at specified wavelengths along with fit, (right) spectral evolution.

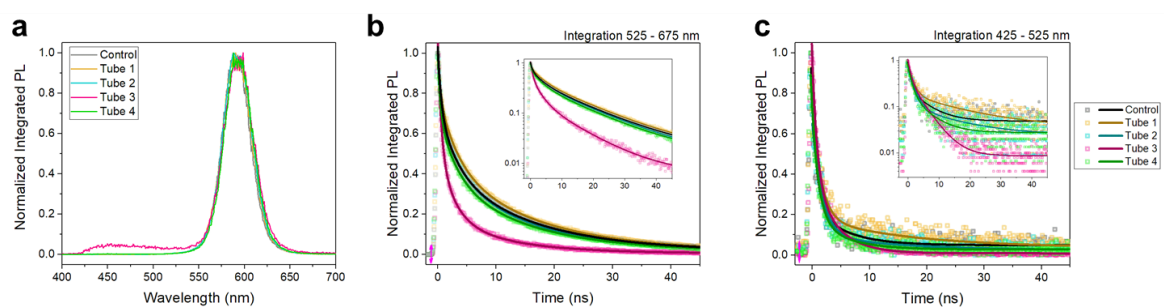


Figure D.12: Comparison between samples in the 50ns time range. (a) Average of entire spectrum, normalized. (b) Kinetic over 525 – 675 nm range along with fit, normalized. Inset is the same data using a log scale for the y axis. (c) Kinetic over 425 - 525 nm range along with fit, normalized. Inset is the same data using a log scale for the y axis.

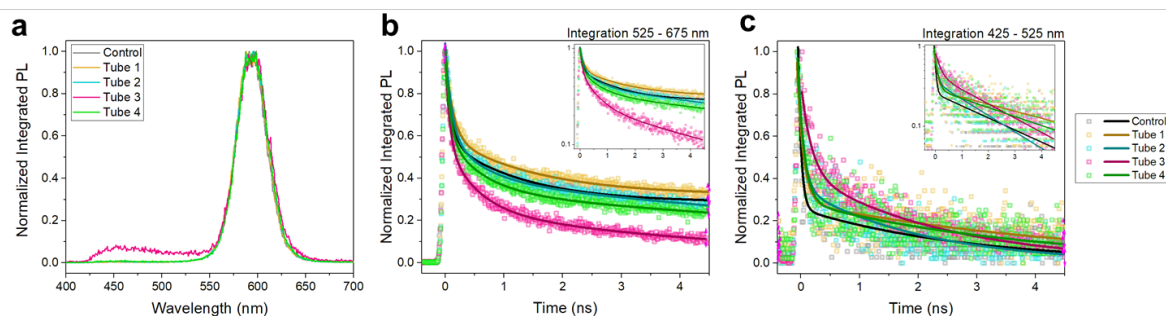


Figure D.13: Comparison between samples in the 5ns time range. (a) Average of entire spectrum, normalized. (b) Kinetic over 525 – 675 nm range along with fit, normalized. Inset is the same data using a log scale for the y axis. (c) Kinetic over 425 - 525 nm range along with fit, normalized. Inset is the same data using a log scale for the y axis.

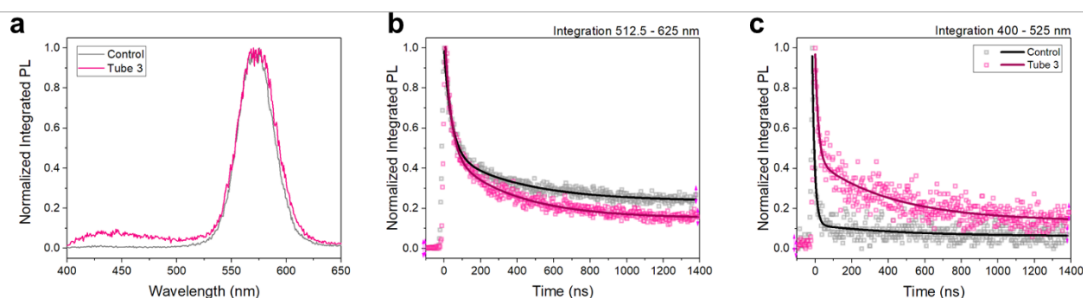


Figure D.14: Comparison between control and Tube 3 in the 1.5ns time range. (a) Average of entire spectrum, normalized. (b) Kinetic over 512.5 – 625 nm range along with fit, normalized. (c) Kinetic over 425 - 525 nm range along with fit, normalized.

Table D.1: Lifetimes from fits of streak camera data measured with a 1.5 ns time window

Sample	τ_1 (ps)	τ_2 (ps)	$\langle\tau\rangle$ (ps)
Control	40 ± 2	400 ± 26	160 ± 10
140 mW - 0.071 mm ²	35 ± 2	360 ± 20	158 ± 9

Table D.2: Lifetimes from fits of streak camera data measured with a 5 ns time window

Sample	τ_1 (ps)	τ_2 (ps)	τ_3 (ns)	$\langle\tau\rangle$ (ns)
Control	52 ± 6	450 ± 30	11.5 ± 0.7	4.9 ± 0.3
140 mW - 9.8 mm ²	85 ± 9	530 ± 60	13.3 ± 0.9	6.1 ± 0.5
140 mW - 0.85 mm ²	103 ± 8	600 ± 90	12 ± 1	4.6 ± 0.5
140 mW - 0.071 mm ²	71 ± 5	520 ± 50	5.4 ± 0.4	1.6 ± 0.1
75 mW - 0.071 mm ²	82 ± 7	610 ± 70	12 ± 1	4.4 ± 0.5

Table D.3: Lifetimes from fits of streak camera data measured with a 50 ns time window

Sample	τ_1 (ps)	τ_2 (ns)	τ_3 (ns)	$\langle\tau\rangle$ (ns)
Control	560 ± 30	3.1 ± 0.2	15.0 ± 0.5	7.4 ± 0.4
140 mW - 9.8 mm ²	400 ± 20	3.2 ± 0.1	15.4 ± 0.3	8.3 ± 0.3
140 mW - 0.85 mm ²	500 ± 20	3.7 ± 0.2	15.5 ± 0.6	7.4 ± 0.4
140 mW - 0.071 mm ²	600 ± 30	2.6 ± 0.2	11.1 ± 0.7	3.1 ± 0.3
75 mW - 0.071 mm ²	430 ± 20	3.1 ± 0.1	14.7 ± 0.4	6.8 ± 0.3

D.6 Temperature Dependence Experiment

As a control experiment the same sample and concentration of CdSe NCs were exposed to temperatures up to 100°C to determine if static heating can cause ligand loss similar to what was observed upon photoexcitation. We were only able to ramp to 100°C due to the boiling point of d8 toluene. The NCs were frozen and pumped under vacuum before being flame sealed in the NMR tube for variable temperature experiments. Figure D.15 shows NMR spectra during heating, prolonged exposure to 100°C, and the room temperature spectra before and after heating. Loss in NMR intensity and chemical shift downfield upon heating has been reported previously and is expected.¹²⁸ The temperature experiments caused a reduction of shoulder at 5.55 ppm and increase in the main peak at 5.65 ppm. No dissociated oleic acid was seen at any point during the experiments. Figure D.16 shows streak camera data averaged over 500 – 700 ppm for the sample after heating. The control sample is the same NCs as the photoexcitation experiments but was

measured at the same time as the temperature dependence sample, both experiments occurred much later than initial experiments so any discrepancy in lifetime between the control here and the control in previous streak camera experiments is purely due to this.

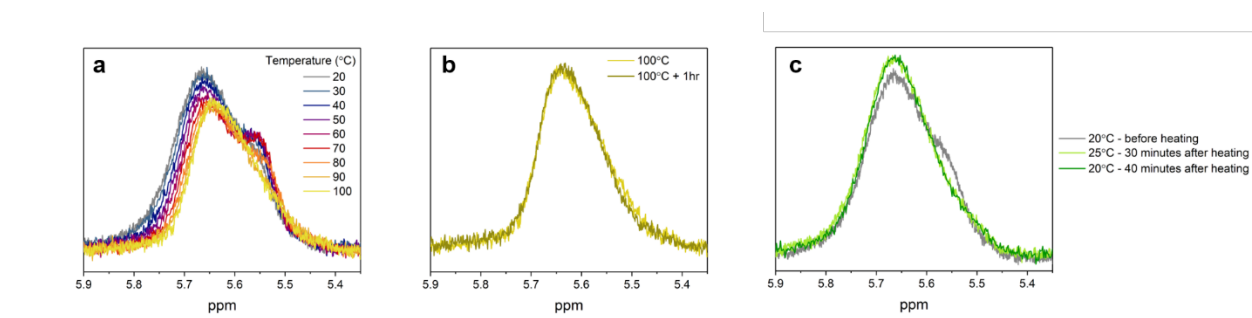


Figure D.15: NMR spectra of the alkenyl region of oleic acid for variable temperature experiment. (a) Temperature ramping from 20°C to 100°C. (b) Sample at 100°C initially and after one hour. (c) Before and after heating.

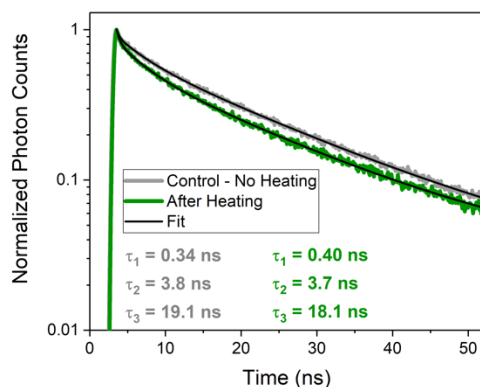


Figure D.16: Streak camera data averaged over 500 – 700 nm for sample before and after heating along with triexponential fit.

Appendix E: Supporting Information for Chapter 7

E.1 UV-Vis spectroscopy

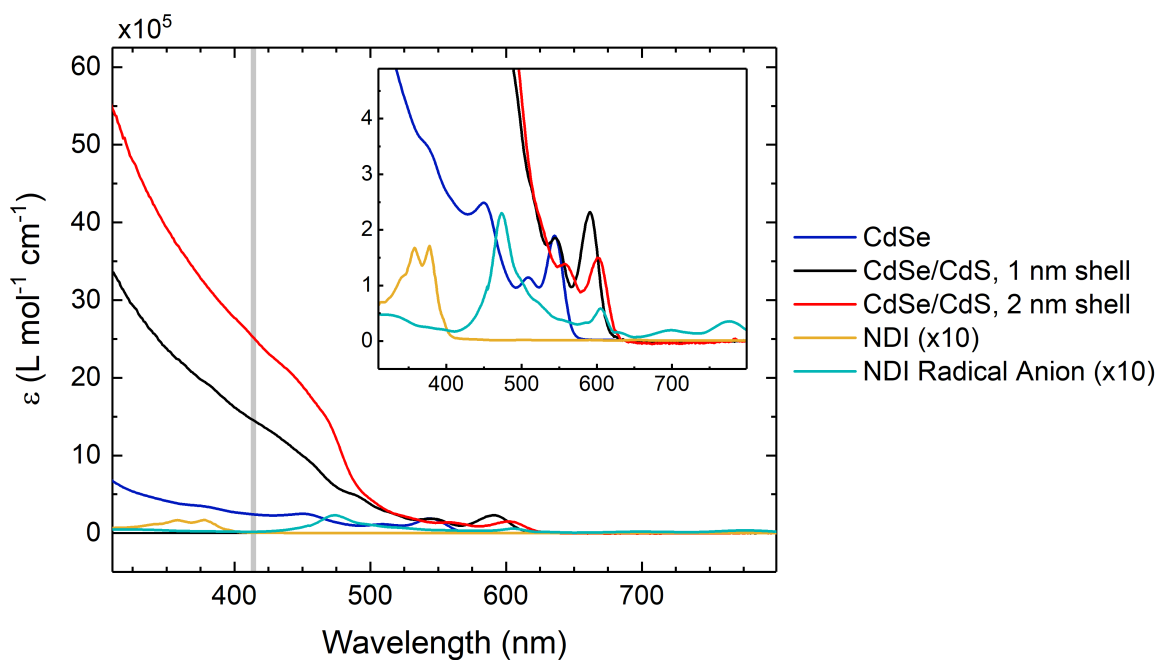


Figure E.1: Comparing the extinction of the three QD samples with those for NDI as well as the NDI anion.¹⁰³

E.2 Fluorescence spectroscopy

Table E.1: Wavelength dependence of photoluminescence quantum yield (Q.Y.) of the core/shell CdSe/CdS QDs as determined with an integrating sphere

Excitation wavelength	1 nm shell Q.Y. (%)	2 nm shell Q.Y. (%)
400 nm	16.0 ± 0.2	74.2 ± 0.2
425 nm	12.1 ± 0.2	64.9 ± 0.2
450 nm	13.3 ± 0.3	65.9 ± 0.3
475 nm	11.2 ± 0.4	60.9 ± 0.4

E.3 Absorption cross-section measurements

We performed pump-dependent transient absorption measurements to determine absorption cross sections for all samples. The transient absorption experiment has been described elsewhere.³⁷⁴ Samples were prepared as a very dilute solution ($\sim 0.2 - 0.3$ at 400 nm) in a 2 mm quartz cuvette and stirred. Pump wavelength was set at 400 nm to excite above band edge and for stability. The pump intensity was controlled via an automatic neutral density wheel providing 15 different pump powers. The samples were probed with a broadband white light at a pre-time zero point (-5 ps) and a late time point (2 ns) by which time all Auger processes should be complete. We subtracted the -5 ps time point from the 2 ns one to remove spontaneous fluorescence and any artifacts from white-light generation that may produce non-zero background signal. The signal at the lowest energy bleach was then plotted against laser flux (Figure S3) and fit to Eq. S1 where σ is the absorption cross section for the NCs at 400 nm, A and B are correction factors.

Eq. E.1
$$y = A - Be^{-\sigma x}$$

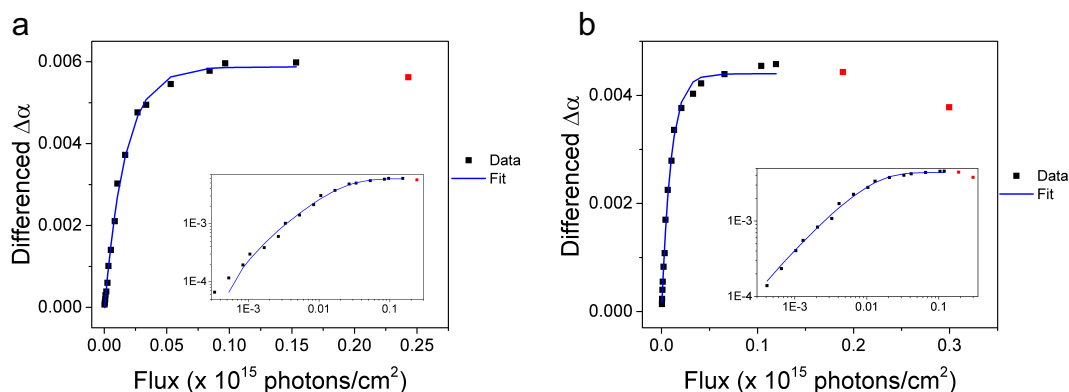


Figure E.2: Absorption cross section measurements for (a) CdSe/CdS, 1 nm shell, and (b) CdSe/CdS, 2 nm shell. All experiments were done by optical pumping at 400 nm and examining the change in the lowest energy bleach signal at 2 ns. Inset shows the data plotted on a log-log scale.

The cross section was then converted to an extinction coefficient (ϵ) via the equation:

$$\text{Eq. E.2} \quad \sigma = \frac{(2.303 \times 10^3) \epsilon}{6.202 \times 10^{23}}$$

This produced the extinction coefficient at 400 nm, which was then changed to the extinction at the lowest energy absorption feature using the static absorption spectra, allowing us to calculate the number of NCs in solution. The cross sections and extinction coefficients for each sample are summarized in Table E.2.

Table E.2: Absorption cross sections and extinction coefficients for all NC samples

Sample	Absorption Cross Section (400 nm)	Extinction Coefficient (400 nm)	Extinction Coefficient (Wavelength)
CdSe NCs (ref ³⁷⁵)	-	-	$1.9 \times 10^5 \text{ L mol}^{-1} \text{ cm}^{-1}$ (548 nm)
CdSe/CdS NCs (1 nm shell)	$6.01 \times 10^{-15} \text{ cm}^2$	$16.2 \times 10^5 \text{ L mol}^{-1} \text{ cm}^{-1}$	$2.5 \times 10^5 \text{ L mol}^{-1} \text{ cm}^{-1}$ (590 nm)
CdSe/CdS NCs (2 nm shell)	$1.03 \times 10^{-14} \text{ cm}^2$	$27.7 \times 10^5 \text{ L mol}^{-1} \text{ cm}^{-1}$	$1.4 \times 10^5 \text{ L mol}^{-1} \text{ cm}^{-1}$ (602 nm)

E.4 Ultrafast transient absorption characterization

The transient absorption setup has been described elsewhere.³⁷⁶ In this experiment we used a 414 nm pump at magic angle relative to the broadband probe. This wavelength was chosen for stability as it is the second harmonic generation output of the Ti:sapphire system. Above band-gap excitation should not interfere with the charge separation and recombination dynamics as intraband relaxation is expected to occur rapidly (< 1 ps)³⁷⁷. Samples were prepared to have an absorption between 0.2 and 0.3 at the excitation wavelength. Experiments were performed under inert nitrogen atmosphere in a 2 mm quartz cuvette. Pump power was kept around 50 nJ, with a spot size diameter of ~ 300 μm resulting in a fluence of ~ 70 $\mu\text{J}/\text{cm}^2$. This power was not in the single exciton regime, but Auger recombination is expected to outcompete most charge transfer processes observed.¹⁴⁶ In the case where it does not, we would not see multiple NDI molecules being reduced suggesting that only one electron transfer event was occurring per nanocrystal.

Core QD TA data

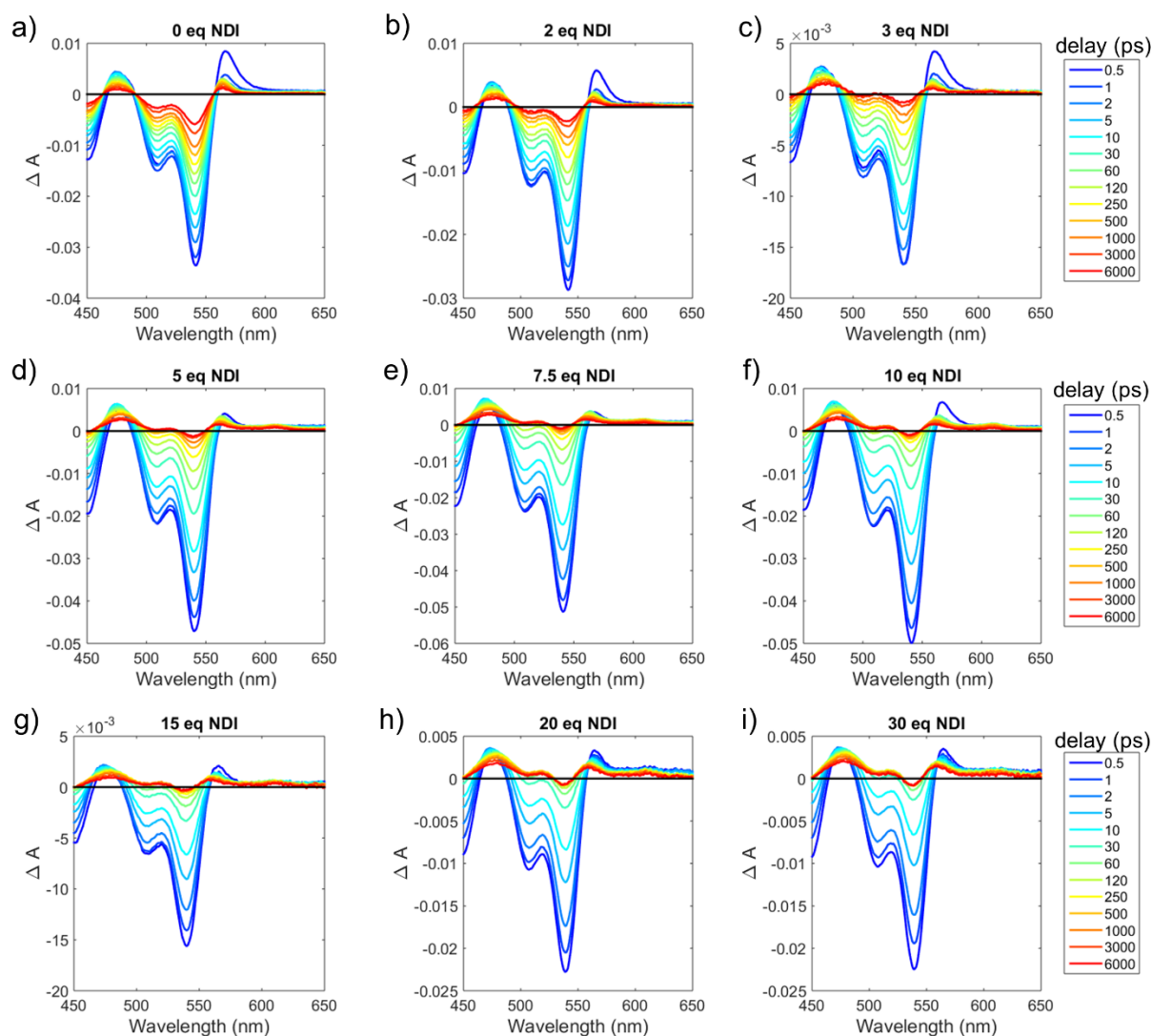


Figure E.3. Femtosecond transient absorption spectra at varying delay times of core CdSe QDs with different equivalents of the NDI ligand. a) 0 equivalents, b) 2 equivalents, c) 3 equivalents, d) 5 equivalents, e) 7.5 equivalents, f) 10 equivalents, g) 15 equivalents, h) 20 equivalents, i) 30 equivalents. Conspicuously, the QD bleach recovers faster with more equivalents of NDI, indicative of faster electron transfer with more acceptors.

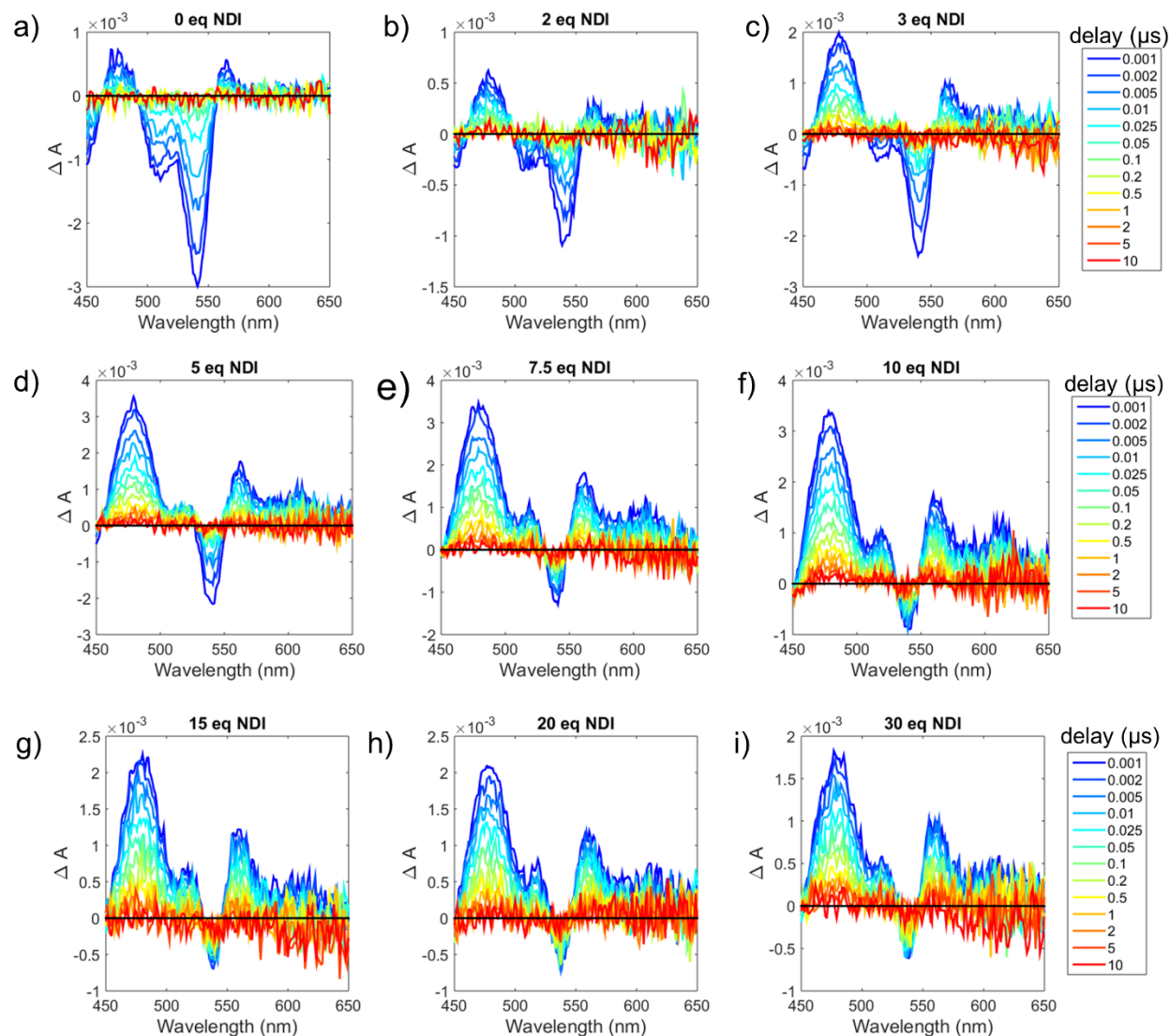


Figure E.4. Nanosecond transient absorption spectra at varying delay times of core CdSe QDs with different equivalents of the NDI ligand. a) 0 equivalents, b) 2 equivalents, c) 3 equivalents, d) 5 equivalents, e) 7.5 equivalents, f) 10 equivalents, g) 15 equivalents, h) 20 equivalents, i) 30 equivalents. The peak at ~ 480 nm is assigned to $\text{NDI}^{\cdot-}$, while the derivative like feature at ~ 560 nm is a result of Stark-shifted QD absorption caused by the presence of the hole.

Core/shell QD TA data (1 nm shell)

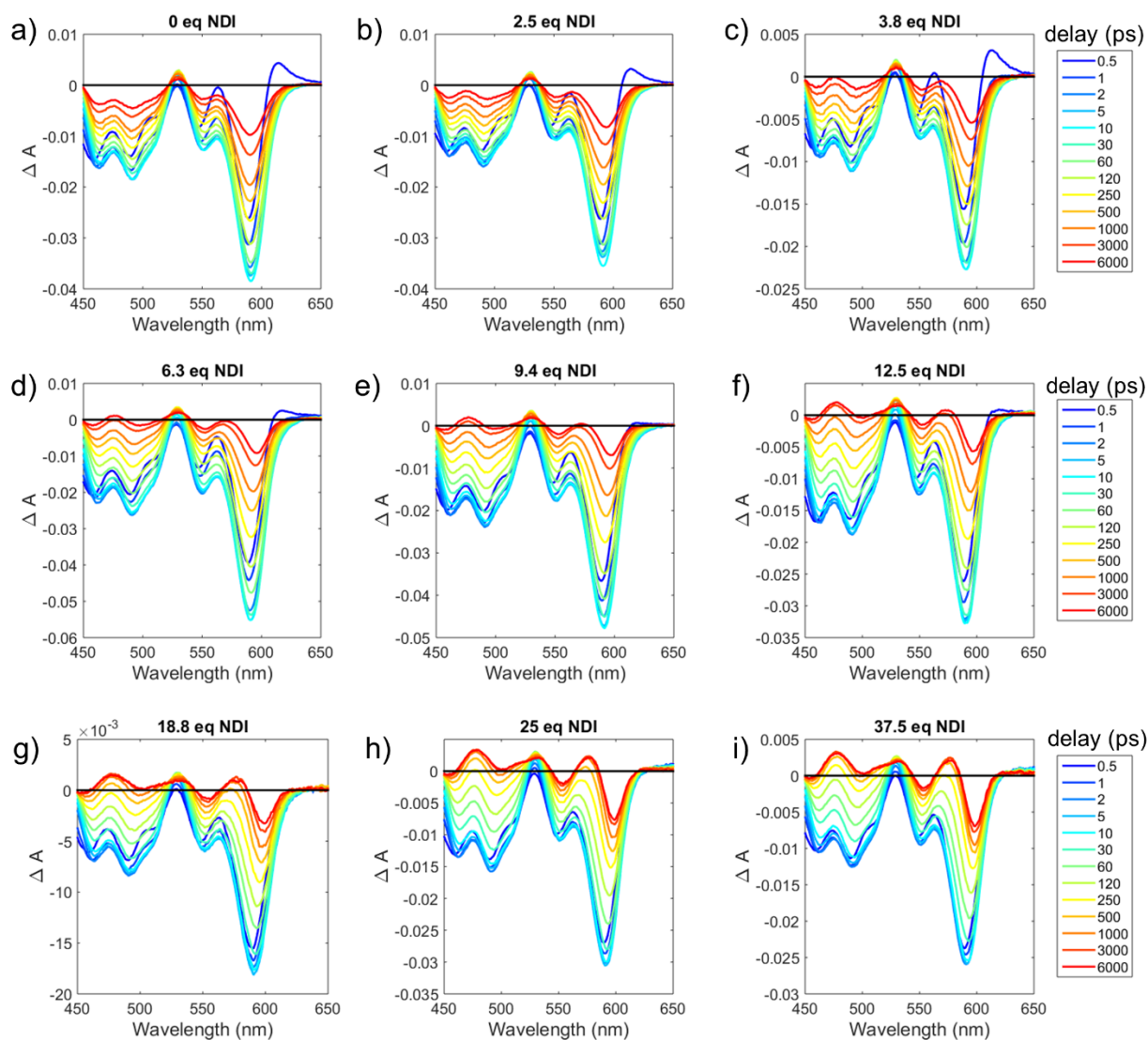


Figure E.5. Femtosecond transient absorption spectra at varying delay times of core/shell CdSe/CdS QDs (~ 1 nm shell) with different equivalents of the NDI ligand. a) 0 equivalents, b) 2.5 equivalents, c) 3.8 equivalents, d) 6.3 equivalents, e) 9.4 equivalents, f) 12.5 equivalents, g) 18.8 equivalents, h) 25 equivalents, i) 37.5 equivalents.

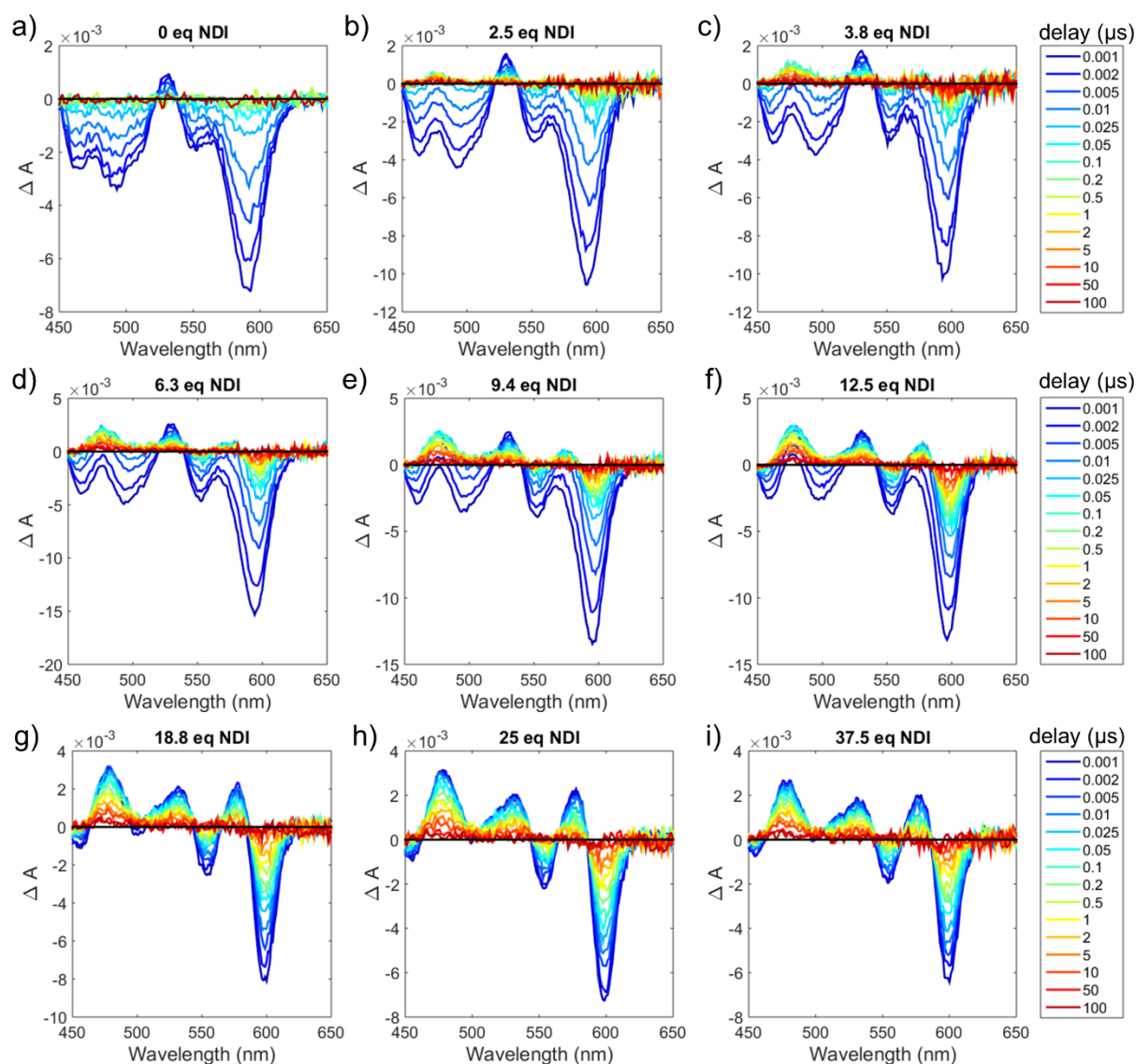


Figure E.6: Nanosecond transient absorption spectra at varying delay times of core/shell CdSe/CdS QDs (~1 nm shell) with different equivalents of the NDI ligand. a) 0 equivalents, b) 2.5 equivalents, c) 3.8 equivalents, d) 6.3 equivalents, e) 9.4 equivalents, f) 12.5 equivalents, g) 18.8 equivalents, h) 25 equivalents, i) 37.5 equivalents. The peak at ~480 nm is assigned to $\text{NDI}^{\cdot-}$, while the derivative like features between 520-630 nm are a result of Stark-shifted QD absorption caused by the presence of the hole.

Core/shell QD TA data (2 nm shell)

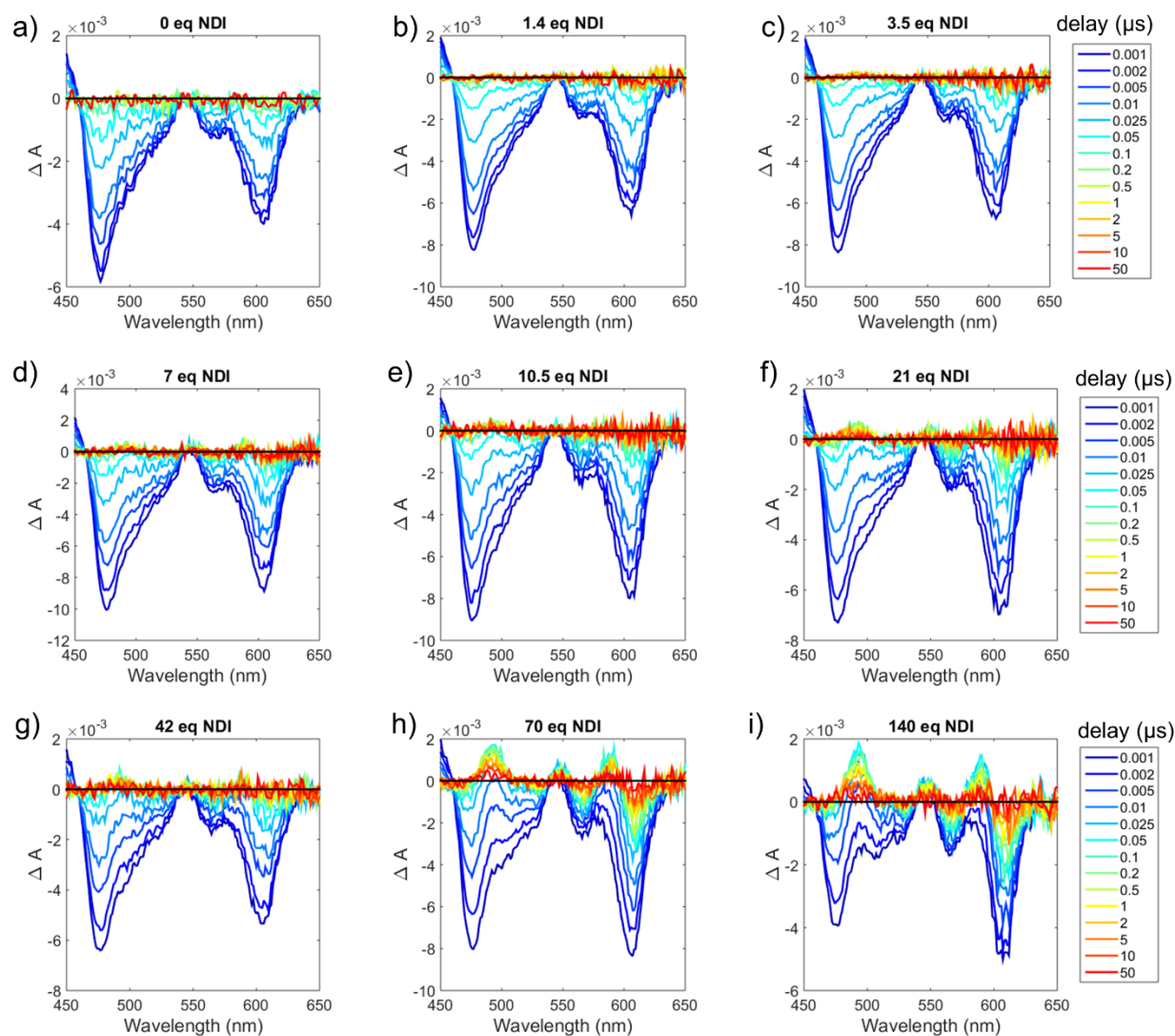


Figure E.7: Nanosecond transient absorption spectra at varying delay times of core/shell CdSe/CdS QDs (~2 nm shell) with different equivalents of the NDI ligand. a) 0 equivalents, b) 1.4 equivalents, c) 3.5 equivalents, d) 7 equivalents, e) 10.5 equivalents, f) 21 equivalents, g) 42 equivalents, h) 70 equivalents, i) 140 equivalents. The peak at ~490 nm is assigned to $\text{NDI}^{\cdot-}$, while the derivative like features between 530-630 nm are a result of Stark-shifted QD absorption caused by the presence of the hole.

E.5 Extracting charge separation and recombination rate constants

TA basis spectra deconvolution and fitting charge separation

Basis spectra were determined for the QD bleaches (core, 1 nm shell, and 2 nm shell) by analyzing the QD only TA spectra. We noted that normalized (to maximum ΔA at a given time) spectra across times past 1 ps were indistinguishable. We averaged these spectra to yield a QD bleach or QD* basis spectrum, plotted in black in Figures E.8a,d,g. Basis spectra for the charge separated state ($\text{NDI}^{\bullet-} - \text{QD}^+$ state) were determined by analyzing late time spectra for samples with highest NDI equivalents (i.e. 42+ equivs for 2 nm shell, 18.8+ equivs for 1 nm shell, and 15+ equivs for the cores). The normalized spectra for these samples were indistinguishable past ~ 1 ns in the core/shell samples, and 300 ps in the core samples. The spectra were averaged to yield $\text{NDI}^{\bullet-} - \text{QD}^+$ basis spectra, plotted in red in Figures E.8a,d,g. Spectral deconvolution was used to generate population traces (all normalized to the maximum population amongst all NDI concentrations) (Figure E.8).

The QD* populations were fit by first fitting the QD* population of the native QD to a complex multi-exponential function we will call $QD_0(t)$. The populations at non-zero NDI equivalents were then fit to the following stretched-exponential equation:

$$\text{Eq. E.3} \quad CS \text{ population}(t) = A * \exp\left(-\left(k_{cs,tot} * t\right)^{0.6}\right) * QD_0(t)$$

Results of these fits are shown in Figure E.9 (black symbols). The $\text{NDI}^{\bullet-} - \text{QD}^+$ basis spectra were fit to multi-exponential functions. Two decays had negative pre-exponential coefficients, and two with positive pre-exponential coefficients to capture charge separation (rise) and charge

recombination (decay). Intensity weighted average rate constants for charge separation are shown in Figure E.9 (red symbols).

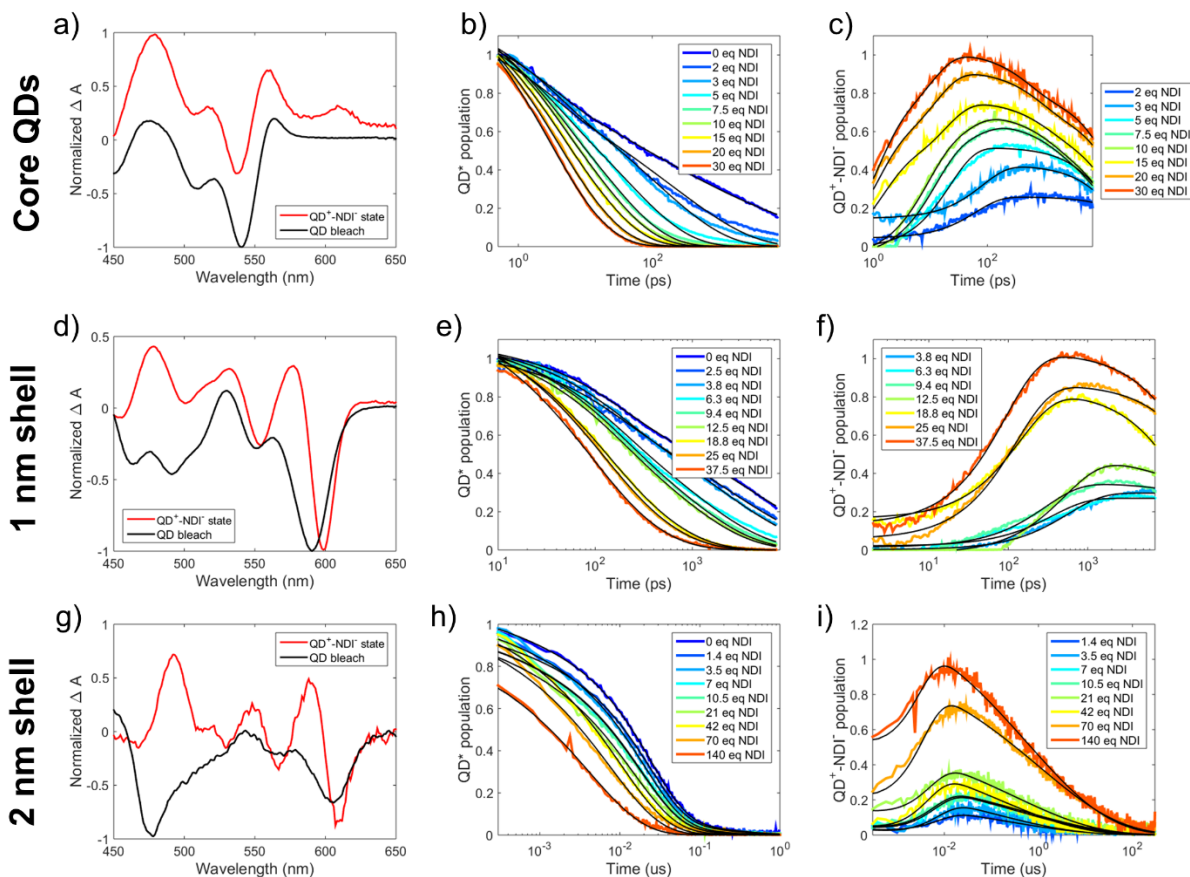


Figure E.8: Basis spectra for the QD^* state (black) and the $NDI^* - QD^+$ basis spectra state (red) (a,d,g). Extracted time dependent QD^* (or QD bleach) populations (b,e,f) and time dependent $NDI^* - QD^+$ populations (c,f,i) for varying NDI concentrations per QD . Black lines represent fits, as described above.

Charge separation rate constant vs. NDI equivalents

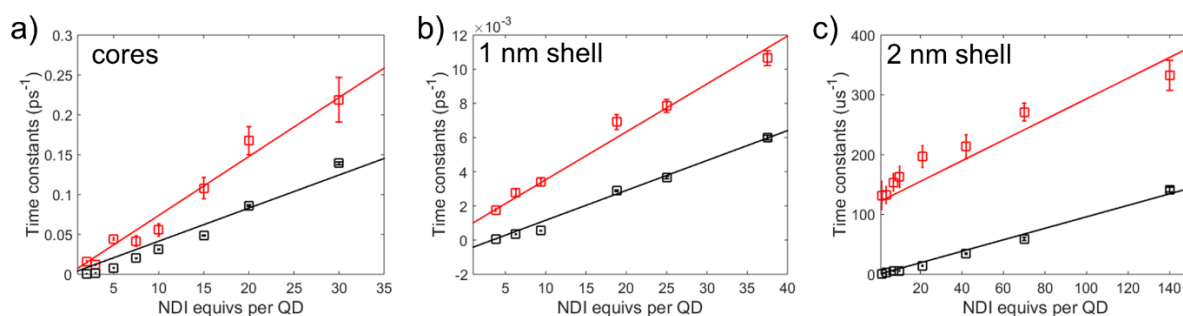


Figure E.9. Individual charge separation rate constants ($k_{cs,tot}$) for varying NDI equivs per QD as determined by the QD* population (black symbols) and the NDI^{••} - QD⁺ population (red symbols). Linear fits are also shown. In principle, these lines should intercept at the origin in accordance with the relation $k_{cs,tot} = Nk_{cs}$. The rate constants for the 2 nm shell sample analyzed with the NDI^{••} - QD⁺ population deviate significantly from this expectation, possibly a result of the lower signal to noise in the nanosecond TA, artifacts in the basis deconvolution, or the existence of an as yet unknown process.

Charge recombination

Charge recombination was analyzed by fitting the NDI^{••} - QD⁺ populations to a stretched exponential with functional form:

$$\text{Eq. E.4} \quad CS \text{ population}(t) = A * \exp(-(k_{CR} * t)^{0.25})$$

The low value of the power coefficient (0.25) indicates that a fairly broad distribution of rates is present in the charge recombination dynamics. This may be a result of inhomogeneities at the QD-ligand interface, as well as the possibility for charge migration on the QD surface prior to recombination. The raw decays as a function of NDI equivalents per QD are shown below, as well as the extracted charge recombination time constants (k_{CR}). The k_{CR} values appear relatively consistent across all NDI concentrations, consistent with bimolecular recombination resultant from a single NDI^{••} - QD⁺ pair being photogenerated. Averaging across all NDI concentrations gives k_{CR} (and std deviation) values of 50 (20), 1.5 (0.7), and 2.5 (2) μs^{-1} for cores, 1 nm shell, and 2 nm shell samples, respectively. Interestingly, both core/shell samples have indistinguishable

recombination times. This could be a result of charge migration on the surface, hole trapping, shell thickness inhomogeneities, or an as yet unknown process.

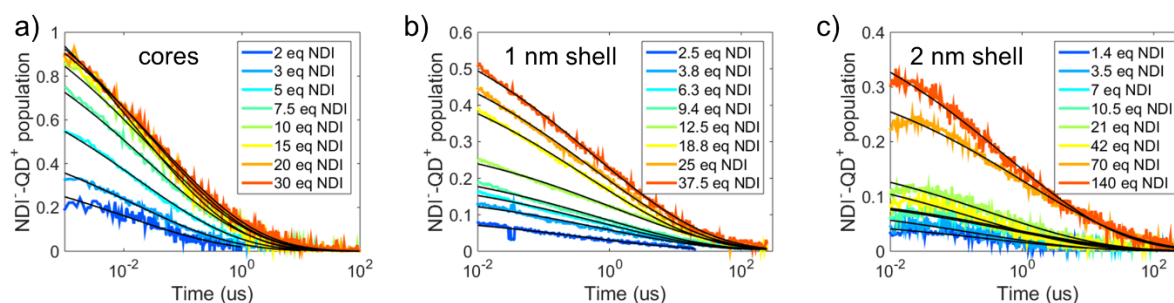


Figure E.10. $\text{NDI}^* - \text{QD}^+$ populations as a function of time and NDI equivalents as determined by basis spectra convolution in the nanosecond transient absorption data. Black lines represent best fits using equation E.4.

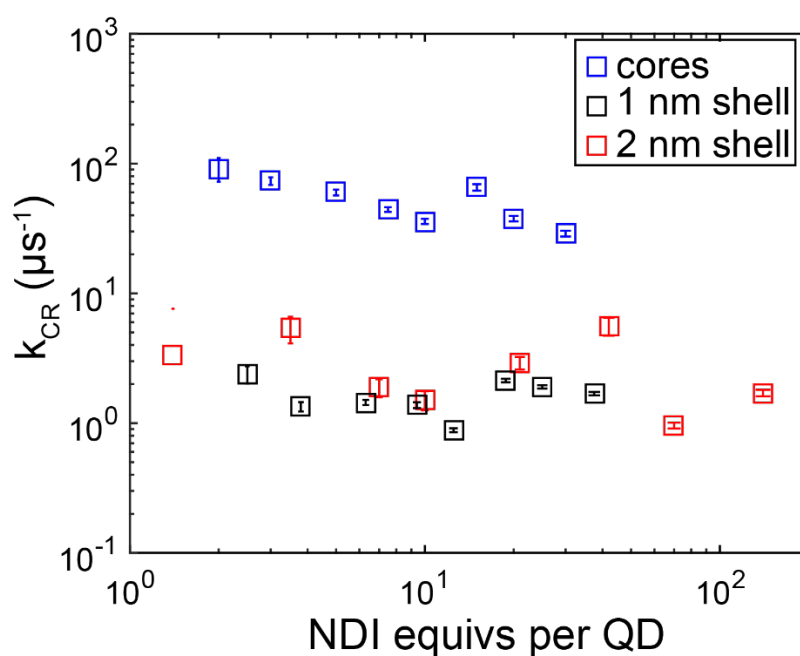


Figure E.11. $\text{NDI}^* - \text{QD}^+$ recombination rate constants from the fits shown in Figure E.10.

E.6 EPR spectroscopy experimental methods

Sample preparation. A small portion of the QD stock solutions in toluene (40 μL , ~ 0.95 nmol) were placed into small vials. To the QD solutions, 10 μL of a 0.9 mg/mL turbid solution of the

NDI ligand in toluene was added (~80 nmol of NDI) and the solution mixed by repeated pipet withdrawal and injection. As the NDI ligands bind to the QDs, they become visibly less fluorescent and the solution loses its turbidity (since the NDI ligands are insoluble in toluene, but the QD-NDI conjugate is soluble in toluene). After mixing for a few minutes, 30 uL of the QD-NDI solutions were transferred into quartz tubes for EPR (described below).

Instrumentation. Measurements were made at X-band (~9.6 GHz) on a Bruker Elexsys E680 X/W EPR spectrometer with a split ring resonator (ER4118X-MS3). The temperature was set by an Oxford Instruments CF935 continuous flow optical cryostat with liquid nitrogen. Solutions (~30 uL) were loaded into quartz tubes (2.40 mm o.d., 2.00 i.d.), subjected to three freeze-pump-thaw cycles on a vacuum line (10^{-4} Torr), and sealed with a hydrogen torch. The samples were pre-frozen before inserting into the pre-cooled instrument. Light from the pulsed laser was coupled through a fiber placed outside the cryostat window (~2 mJ/pulse), with some portion of the light passing through the coils of the resonator and exciting the sample.

Transient EPR measurements using continuous wave (CW) microwaves and direct detection were performed. Following photoexcitation, kinetic traces of transient magnetization under CW microwave irradiation were obtained in both imaginary and real channels (quadrature detection). Time traces were recorded over a range of magnetic fields to give 2D spectra. Spectra were processed by first subtracting the signal prior to the laser pulse for each kinetic trace (at a given magnetic field point), and then subtracting the signal average at off-resonance magnetic field points from the spectra obtained at a given time.

E.7 Transient continuous wave EPR spectra

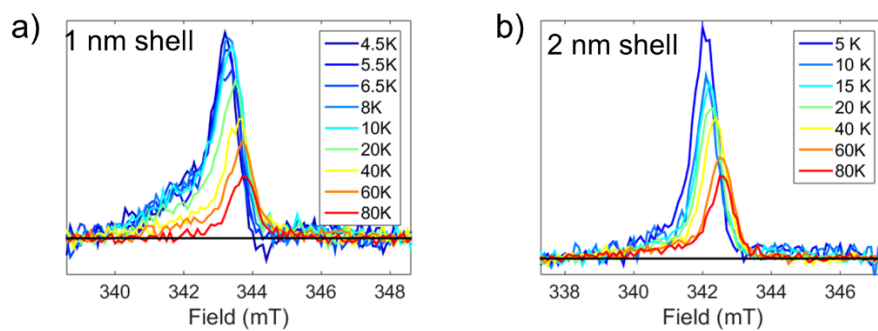


Figure E.12. Transient EPR spectra for the 1 nm shell (a) and 2 nm shell (b) samples plotted vs. magnetic field. The peak shift is entirely a result of resonance frequency shift with changing temperature. When the frequency shift is accounted for by plotting the data vs. g -value (Figure 4, main text) then the peak does not shift.

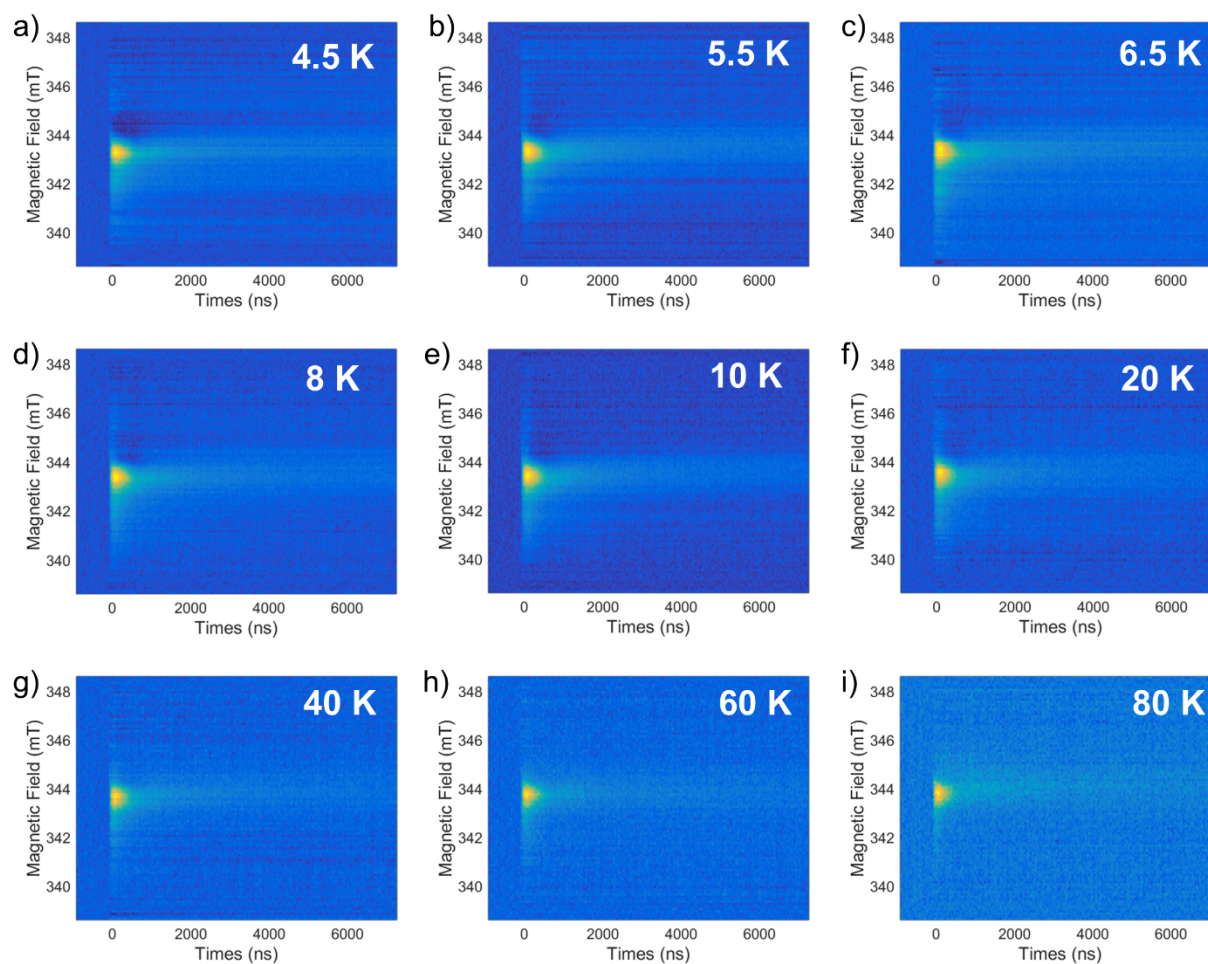


Figure E.13. Full time dependent and field dependent transient EPR signals for the 1 nm shell QD-NDI sample. Notice the emissive feature at low temperatures and higher field values, which we attribute to a spin-correlated radical pair with an A/E polarization pattern.

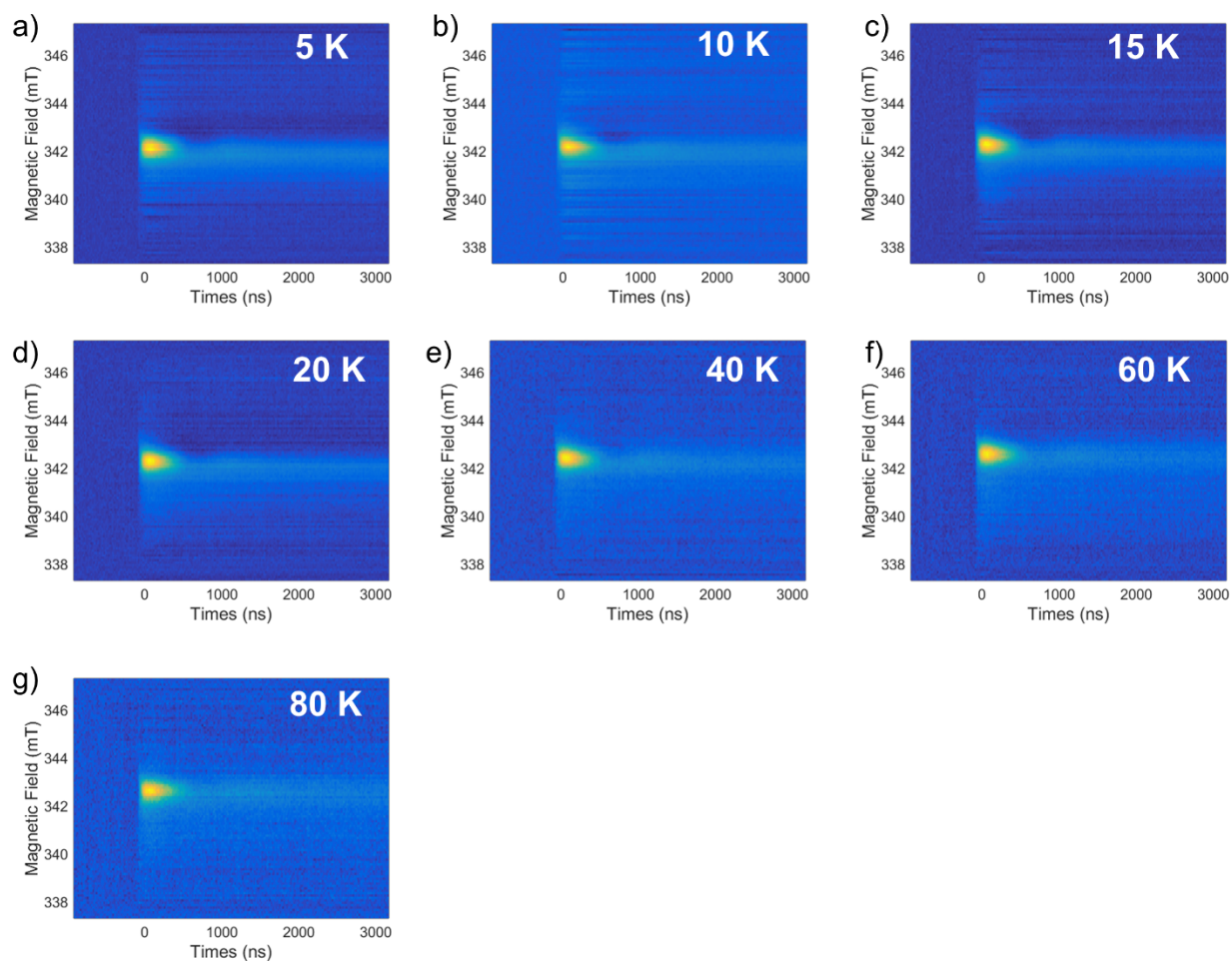


Figure E.14. Full time dependent and field dependent transient EPR signals for the 2 nm shell QD-NDI sample. Notice the emissive feature at low temperatures and higher field values, which we attribute to a spin-correlated radical pair with an A/E polarization pattern.

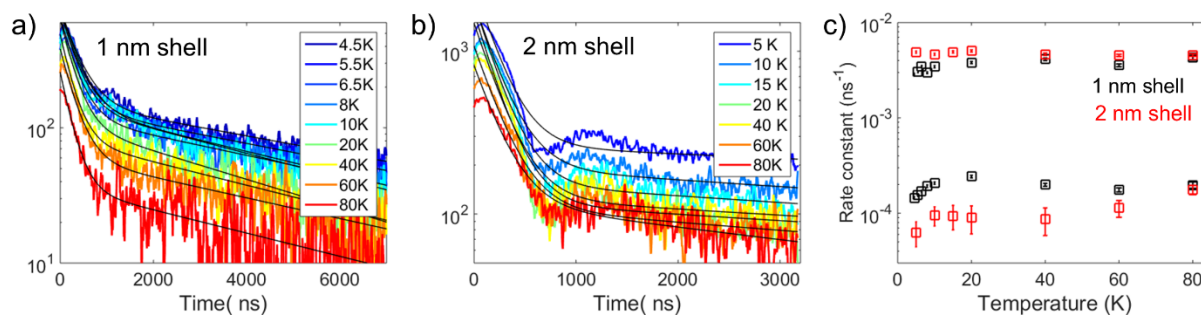


Figure E.15. Time traces of the peak EPR signal for the 1 nm shell (a) and 2 nm shell (b) samples. Data are fit to bi-exponential decays for each temperature to yield average fast time-constants of 290 ± 40 and 210 ± 10 ns for the 1 nm and 2 nm shell samples, respectively. (c). These time constants are comparable to what is obtained in spin-correlated radical pairs in entirely organic systems. They should be interpreted as an extremely low estimate for the spin relaxation time since the system is being continually excited by a microwave source. In fact, the oscillatory features in (b) are Rabi oscillations from this continual microwave source.

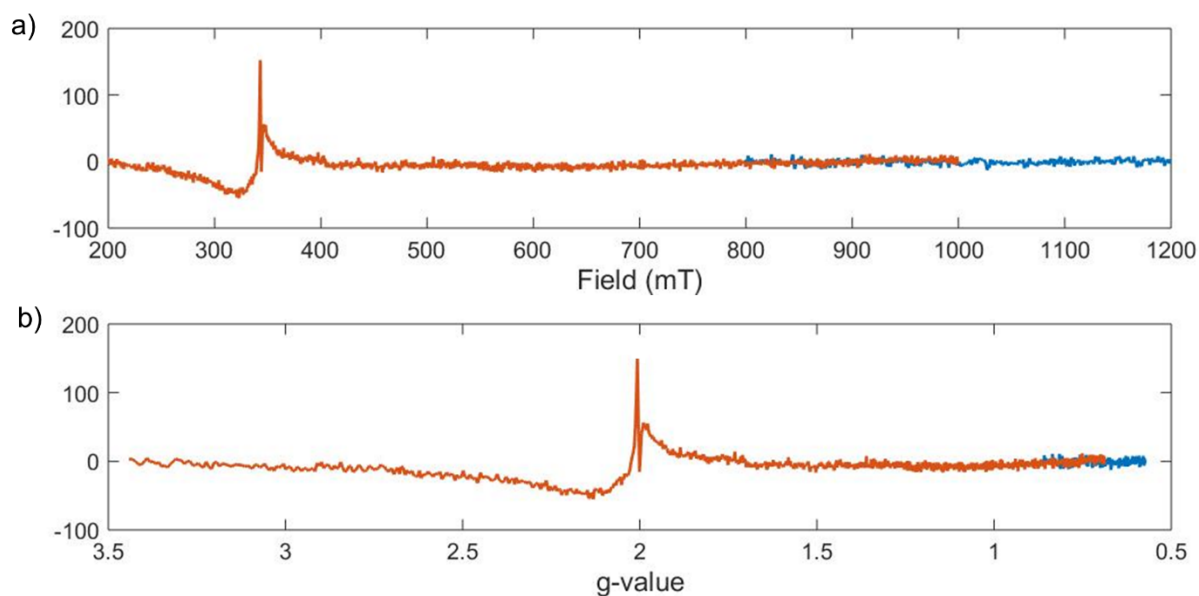
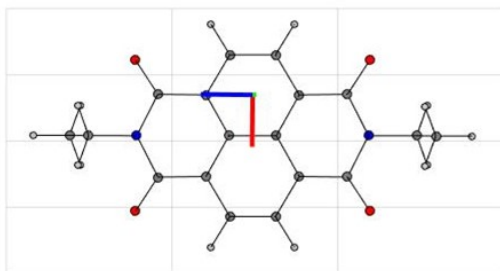


Figure E.16. Wide field TCW

E.8 Electron g -values for EPR simulation

Electron g -values for NDI $^{\bullet-}$ were computed from geometry optimized structures in ORCA³⁷⁸ using a 6-31G* basis. The computed g -values are $g_x = 2.0046$, $g_y = 2.0047$, $g_z = 2.0022$

a) $g_x = 2.0046$, $g_y = 2.0047$, $g_z = 2.0022$



b)

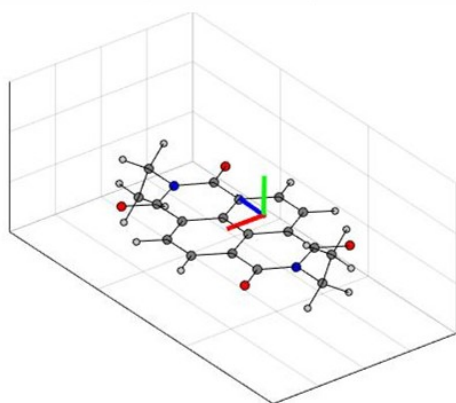


Figure E.17. Principal g -axes superimposed on structures for (a,b) NDI $^{\bullet-}$. (blue) x-axis, (red) y-axis, and (green) z-axis are shown.

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