

PHOTOINDUCED ELECTRON DONOR/ACCEPTOR PROCESSES IN COLLOIDAL II-VI
SEMICONDUCTOR QUANTUM DOTS AND NITROXIDE FREE RADICALS

By

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ABSTRACT

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Electron transfer (ET) processes are one of the most researched topics for applications ranging from energy conversion to catalysis. An exciting variation is utilizing colloidal semiconductor nanostructures to explore such processes. Semiconductor quantum dots (QDs) are emerging as a novel class of light harvesting, emitting and charge-separation materials for applications such as solar energy conversion. Detailed knowledge of the quantitative dissociation of the photo-generated excitons and the interfacial charge- (electron/hole) transfer is essential for optimization of the overall efficiency of many such applications. Organic free radicals are the attractive counterparts for studying ET to/from QDs because these undergo single-electron transfer steps in reversible fashion. Nitroxides are an exciting class of stable organic free radicals, which have recently been demonstrated to be efficient as redox mediators in dye-sensitized solar cells, making them even more interesting for the aforementioned studies. This dissertation investigates the interaction between nitroxide free radicals TEMPO (2,2,6,6-tetramethylpiperidine-1-oxyl), 4-amino-TEMPO (4-amino- 2,2,6,6-tetramethylpiperidine-1-oxyl) and II-VI semiconductor (CdSe and CdTe) QDs. The nature of interaction in these hybrids has been examined through ground-state UV-Vis absorbance, steady state and time-resolved photoluminescence (PL) spectroscopy, transient absorbance, upconversion photoluminescence spectroscopy and electron paramagnetic resonance (EPR). The detailed analysis of the PL quenching indicates that the intrinsic charge transfer is ultrafast however, the overall quenching is still limited by the lower binding capacities and slower diffusion related kinetics. Careful analysis of the time resolved PL

decay kinetics reveal that the decay rate constants are distributed and that the trap states are involved in the overall quenching process. The ultrafast hole transfer from CdSe QDs to 4-Amino TEMPO observed here makes this dyad a highly promising candidate for application in quantum dot sensitized solar cells.

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Dedicated to
Bapi, Maa, Didi
&
One and Only Chukra

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KEY TO ABBREVIATIONS

ALD: Atomic layer deposition

CB: Conduction band

CCD: Charge-coupled device

CdO: Cadmium oxide

CdSe: Cadmium Selenide

CT: Charge transfer

CdTe: Cadmium Telluride

CW: Continuous wave

CVD: Chemical vapor deposition

DAQ: Data Acquisition card

EPR: Electron Paramagnetic Resonance

ET: Electron transfer

E_g : Bandgap

FRET: Förster Resonance Energy-Transfer

HOMO: Highest occupied molecular orbital

HRTEM: High resolution Transmission electron microscope

HT: Hole transfer

HDA: Hexadecylamine

IR: Infrared

KWW: Kohlrausch-WilliamsWatts

LUMO: Lowest unoccupied molecular orbital

LTAQ: Low Temperature Antiquenching

MBE: Molecular beam epitaxy

NCs: Nanocrystals

ns: Nanosecond

NMR: Nuclear Magnetic Resonance

ODE: 1-Octadecene

OA: Oleic acid

OAm: Oleylamine

PL: Photoluminescence

PXRD: Powder X-ray diffraction

ps: Picosecond

PMT: Photo multiplier tube

PL: Photoluminescence

QDs: Quantum dots

QY: Quantum yield

SA: Stearic acid

Se: Selenium

TA: Transient Absorbance

TOP: Tri-n-octylphosphine

TOPO: Trioctylphosphine oxide

Te: Tellurium

TEMPO (T): 2,2,6,6-Tetramethylpiperidine 1-oxyl

TDPA: Tetradecylphosphonic acid

TCSPC: Time Correlated Single Photon Counting

TEM: Transmission Electron Microscope

TD: Time dependent

TDPL: Temperature-dependent photoluminescence

TR: Time-resolved

THz: Tera Hertz

TEM: Transmission electron microscopy

uPL: Upconversion Photoluminescence

UV-Vis: Ultraviolet-visible

VB: Valence band

λ : Wavelength of light

4-amino TEMPO (4-AT): 4-amino-2,2,6,6-tetramethylpiperidine-1-oxyl

4-carboxy TEMPO (4-CT): 4-carboxy-2,2,6,6-tetramethylpiperidine-1-oxyl

Chapter 1: Introduction

1.1: Quantum dots and their unique properties

The study of increasingly smaller materials have garnered huge interest over the past few decades, owing to the unique properties of these materials and the advancement in technology making these studies easier. Semiconductor nanocrystals (NCs) are crystalline particles with dimensions in the range of 1-100 nm that exhibit size-dependent optical and electronic properties.¹⁻³ These NCs contain approximately 100 to 10,000 atoms. Understanding the fundamental physical and optical properties of these crystalline solids has become one of the most of exciting areas of research and the advent of new technologies for production and investigation of these materials have made it more interesting to pursue.

There are two general approaches to make NCs: i) bottom-up (colloidal, plasma, solid-state, molecular self-assembly, molecular beam epitaxy (MBE), chemical vapor deposition (CVD), electro-deposition)⁴⁻⁹ and ii) top-down approach (etching, photo-lithography, electron beam lithography)¹⁰⁻¹². In this thesis, colloidal semiconductor nanocrystals have been explored. Colloidal NCs are solution-grown nanometer-sized particles that are stabilized by a layer of surfactants attached to their surface; the advantages of colloidal synthesis over other approaches have been discussed later.

The semiconductor nanocrystals with all three dimensions in nanometer range are termed as quantum dots (QDs) due to the evolution of quantum confinement effects in these nano-dots. QDs are the link between small molecules and bulk crystals, exhibiting discrete electronic transitions like isolated atoms and molecules, and enabling the exploitation of valuable properties of

crystalline materials. Bulk semiconductors are characterized by composition-dependent band gap energy (E_g), which is the minimum energy required to excite an electron from the ground state valence energy band into the vacant conduction energy band. When a photon of energy equal to the band gap is absorbed, the electron is excited to the conduction band leaving a hole in the valence band.

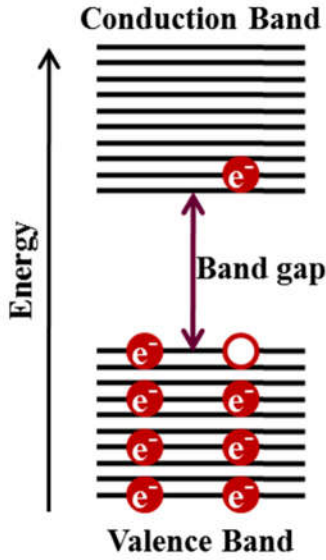


Figure 1.1: Creation of an excited electron and a hole in a semiconductor QD

The negatively charged electron and positively charged hole constitute an electro-statically bound electron-hole pair, known as the exciton. The excited electron can relax back to the valence band by emitting a photon, a process known as radiative recombination or by non-radiative processes. In a bulk semiconductor, the exciton is a Coulomb-bound state of the electron in the conduction band and the hole in the valence band. The exciton has a finite size within the crystal defined by the Bohr exciton radius (a_{exc}), which can vary from 1 nm to 50 nm¹³ depending on the nature of the material. The natural length scale of electronic excitations in bulk semiconductors is given by

the exciton Bohr radius (a_{exc}), which is determined by the strength of the electron-hole (e-h) Coulomb interaction. The exciton Bohr radius is given by the following expression and resembles the Bohr radius of the hydrogen atom.¹⁴

$$a_{exc} = \frac{4\pi \epsilon_r \epsilon_0 \hbar^2}{e^2} \left(\frac{1}{m_e^*} + \frac{1}{m_h^*} \right) = \frac{4\pi \epsilon_r \epsilon_0 \hbar^2}{\mu e^2} \dots\dots\dots \text{Eq. (1.1)}$$

The reduced mass μ is calculated from the effective masses of electron (m_e^*) and hole (m_h^*).

ϵ_r = relative dielectric constant of the material

ϵ_0 = vacuum permittivity

$\hbar$ = reduced Planck's constant

m_0 = mass of the free electron

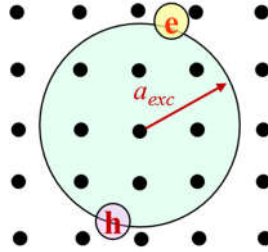


Figure 1.2: Spatial Representation of an exciton in a crystal. (For sake of representation, the electrons/holes are depicted as localized in the diagram, in reality there are electron clouds)

Thus the Bohr exciton radius depends on the dielectric constant and the effective masses which can be calculated if these parameters for a particular material are known. In NCs with sizes smaller than a_{exc} , the dimensions of the nanoparticle define the spatial extent of the e-h pair state (and not the strength of the e-h Coulomb coupling). So, here the electronic energies depend on the degree of spatial confinement of electronic wave functions and hence dimensions of the NCs (quantum size effect).

The exciton size demarcates the transition between the regime of bulk crystalline properties and quantum confinement regime. In this regime, the nanocrystals demonstrate size-dependent optical properties. NCs exhibit markedly different chemical and physical properties as compared to the bulk crystalline solids.¹⁵ Altering the size of bulk materials has no effect on their optical and electronic properties,¹⁶ which are described as intensive functions (i.e. size-independent). However, as the size of the crystals are decreased to the nanoscale regime, their optical, electronic and mechanical properties can change significantly. As mentioned above, colloidal semiconductor nanocrystals or quantum dots (QDs) have opto-electronic properties that strongly depend on their size, structure, shape, and composition.¹⁷⁻¹⁹ Additionally, since these colloidal particles are sterically stabilized by organic ligands, wet chemical techniques can be easily used to functionalize them through ligand exchange²⁰, and formation of QD monolayers or thin films is possible by various wet-processing techniques such as spin coating, drop casting and layer-by-layer assembly.²¹ This unique combination of tunable optoelectronic properties and ease of solution processability results in a remarkably wide range of applications, extending from opto-electronic devices such as photodetectors,²² LEDs,²³ and solar cells²⁴ to bio-labeling²⁵ and sensing.²⁶ In addition to the size-tunability of the QD band gaps,^{27,28} their band gaps can also be tuned via the nature and extent of surface coverage of certain strongly coupled organic ligands.^{29,30} QDs also have extraordinarily high extinction coefficients ($10^4 - 10^6 \text{ M}^{-1}\text{cm}^{-1}$)^{27,28} and greater photo-stability compared to many organic dyes with comparable extinction coefficients.³¹ Additionally, QD cores have the unique capability to accommodate multiple delocalized excitonic states, formed through either carrier multiplication or multi-photon absorption. These interesting properties make QDs excellent candidates as light harvesting,³² light emitting³³ and charge-separation materials.³⁴

1.2: Nanomaterials: Intermediate between Molecules and Bulk materials

Nanomaterials depict behavior intermediate to macroscopic crystals and molecules. The property of a crystal composed of few hundred atoms will be different from a single atom as well as a bulk solid. For nanocrystals, the surface plays a very important role because a significant fraction of the total number of atoms are on the crystal's surface. This generally leads to higher chemical reactivity of these nanocrystals as compared to the corresponding bulk solid.

The basic building blocks of matter are atoms and the simplest case is a hydrogen atom where one electron orbits around a proton and the electronic states can be derived analytically.³⁵ For many electron systems, electron-electron interactions have to be accounted for; in the simplest approximation, each electron can be ascribed to an atomic orbital, associated with a discrete energy level. For molecules, electrons cannot be ascribed to individual atoms, but are shared between the atoms and the electronic energy of the molecular orbitals (formed by linear combination of the atomic orbitals) are discrete. For very large polyatomic systems, electronic structure calculations through combination of localized atomic orbitals become unrealistic.³⁶ The system becomes simplified when the system under study is a periodic infinite crystal, and the electronic structure of the crystalline solids can be described in terms of Bloch functions (periodic combinations of atomic orbitals that rely on the translational invariance of the wavefunction).³⁷ Electrons in these solids are thus described generally by a superposition of infinite plane waves extended through the infinite crystals modulated by periodic wavefunctions. The energy structure of the solid consists of broad energy levels rather than the discrete energy levels that characterize the atoms and molecules.

For QDs (nanometer dimension semiconductor crystals), the assumption that the crystal has an infinite size is not valid, and the translational symmetry invariance cannot be used to build the wavefunction. The electronic structure of the NCs should be at the intersection between the discrete levels of the atomic system and the band structure of the bulk solids.

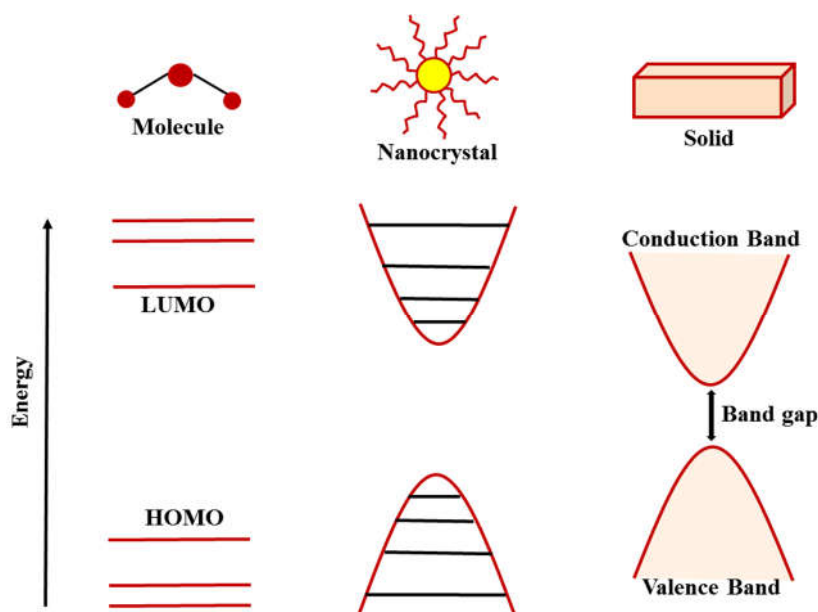


Figure 1.3: Quantum size effect in semiconductors. Molecular orbitals formed by linear combination of atomic orbitals (left), the discrete energy levels in a semiconductor nanocrystals (middle), combination of atomic orbitals from a large number of atoms yields quasi continuous energy bands in bulk solids (right)

In practice, the approximate spherical symmetry of QDs allows the description of their wavefunction in terms of their angular momentum. In absence of band-mixing effects, each bulk band should give rise to an independent series of quantized states that can be classified using two quantum numbers; “ L ” (determines the angular momentum/symmetry of the wave function that describes the carrier motion in the NC confinement potential), and “ n ” (defines the particular state of a given symmetry).³⁸ In typical notation, the momentum of NC quantized states is indicated by

a letter (S, P, D for $L = 0, 1$ and 2 respectively), with the value of n as the prefix as. Thus, the three lowest energy states would be 1S, 1P, and 1D (in the order of increasing energy). The “e” and “h” denotes the electron and the holes. These states are symmetrically equivalent to the wavefunctions of a particle-in-a-spherical-box, i.e. pure eigen functions of the kinetic energy operator. The role of coulombic potential energy in NCs is then treated as a perturbation, as described in the next section.

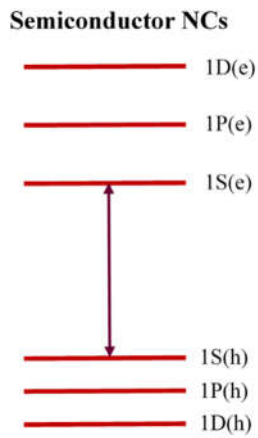


Figure 1.4: The NC energy structures are shown for a two-band semiconductor with single parabolic conduction band and a single parabolic valence band

1.3: Energy levels in Nanomaterials

When the size of a system is comparable to the wavelength of particles, quantum mechanics is needed to describe their behavior;³⁹ in 1st approximation a free carrier confined in a NC structures behaves as a particle in a spherical-box.⁴⁰ The solutions to the Schrodinger equation would represent the physical states of these particles and are standing waves confined in the potential well. In absence of degeneracy, the energies associated with two distinct wavefunctions are different and discontinuous and the system exhibits discrete energy levels with discrete peaks in

the optical spectra. This is the origin of the term “quantum confinement” and when all three dimensions of a semiconductor crystal are reduced to few nanometers, the resulting system is a “quantum dot”. An intuitive method to understanding the properties of quantum dots by utilizing particle-in-a-box approach was first demonstrated by L.E. Brus.⁴¹ The particle-in-a-box model gives an insight into the behavior of the electrons in QDs and also a quantum mechanical description of the size dependent electronic structure of QDs.

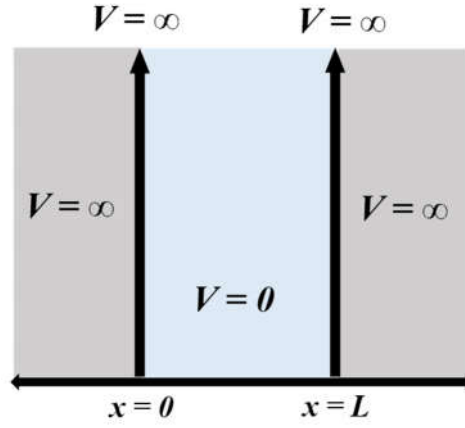


Figure 1.5: Schematic representation of a particle in a box

The simplest form of the particle in-a-box model considers a one-dimensional system where the potential energy (V) is described as:

$$V(x) = 0, \quad 0 < x < L$$

$$V(x) = \infty, \quad \text{outside the box}$$

where : L = length of box and x = position of particle within the box.

The kinetic energy E of each allowed states n for the electron can be computed as:

$$E_n = \frac{n^2 h^2}{8mL^2} \dots\dots\dots \text{Eq. (1.2)}$$

The energy E_n of the electron states is inversely proportional to the square of the length of the box.

As the length of the box decreases, the energies of the states increase.

In QDs, the charge carriers are confined in all three dimensions, and can be described as an infinite 3-dimensional potential box (infinite spherical well)¹⁴. The potential energy is zero inside the sphere ($V(x) = 0, x < R$) but is infinite on its walls ($V(x) = \infty, x > R$ R = Radius of sphere).

The Schrodinger equation can be solved to obtain the energy of the lowest energy level⁴²:

$$E_{nl} = \frac{n^2 h^2}{8mR^2} \quad (n=1, 2, 3\dots l=0) \dots\dots\dots \text{Eq. (1.3 a)}$$

The wavefunctions are given by:

$$\psi_{n00} = \frac{1}{\sqrt{2\pi R}} \frac{\sin(n\pi x / R)}{x} \dots\dots\dots \text{Eq. (1.3 b)}$$

For $l > 0$, the allowed energies are:

$$E_{nl} = \frac{h^2}{8mR^2} \beta_{nl}^2 \quad (l > 0) \dots\dots\dots \text{Eq. (1.3 c)}$$

And the wavefunctions are:

$$\psi_{nlm}(r, \theta, \phi) = A_{nl} j_{nl}(\beta_{nl} x / a) Y_l^m(\theta, \phi) \dots\dots\dots \text{Eq. (1.3 d)}$$

where the constant A_{nl} has to be determined from normalization, $j_l(x)$ is the spherical Bessel function of order l , and $n_l(x)$ is the spherical Neumann function of order l .

The minimum energy required to create an electron-hole pair in a quantum dot has several contributions, a) the bulk band gap energy $E_g(bulk)$, b) confinement energy of the carriers and c) the Coulomb energy which accounts for the mutual attraction between electrons and holes and the screening of the carriers by the crystal (the strength of which depends on the dielectric constant of the material (epsilon)). The size-dependent energy gap of a semiconductor QD $E_g(dot)$ is given by the Brus Equation⁴¹ :

$$E_g(dot) = E_g(bulk) + \frac{h^2}{8R^2} \left[\frac{1}{m_e^*} + \frac{1}{m_h^*} \right] - \frac{1.8e^2}{4\pi\epsilon_0\epsilon_r R} \dots\dots\dots \text{Eq. (1.4)}$$

where R : radius of the QD

ϵ_0 = permittivity of vacuum

ϵ_r = relative permittivity

e : charge of an electron

There are two size-dependent terms in the equation above: the confinement energy (second term) which is inversely proportional to the square of the radius and the Coulomb interaction (third term) which has an inverse dependence on the radius. The confinement energy is a positive term, so the energy of the lowest level in a QD is raised compared to the bulk owing to this term. However, the Coulomb interaction is attractive in nature for the electron-hole pair and thus lowers the energy. As the size of a QD reaches the Bohr exciton radius (a_{exc}), quantum confinement effects dominate and the apparent band gap (of the confined QDs) increases with decreasing QD size and a blue shift in the absorption spectrum is observed.

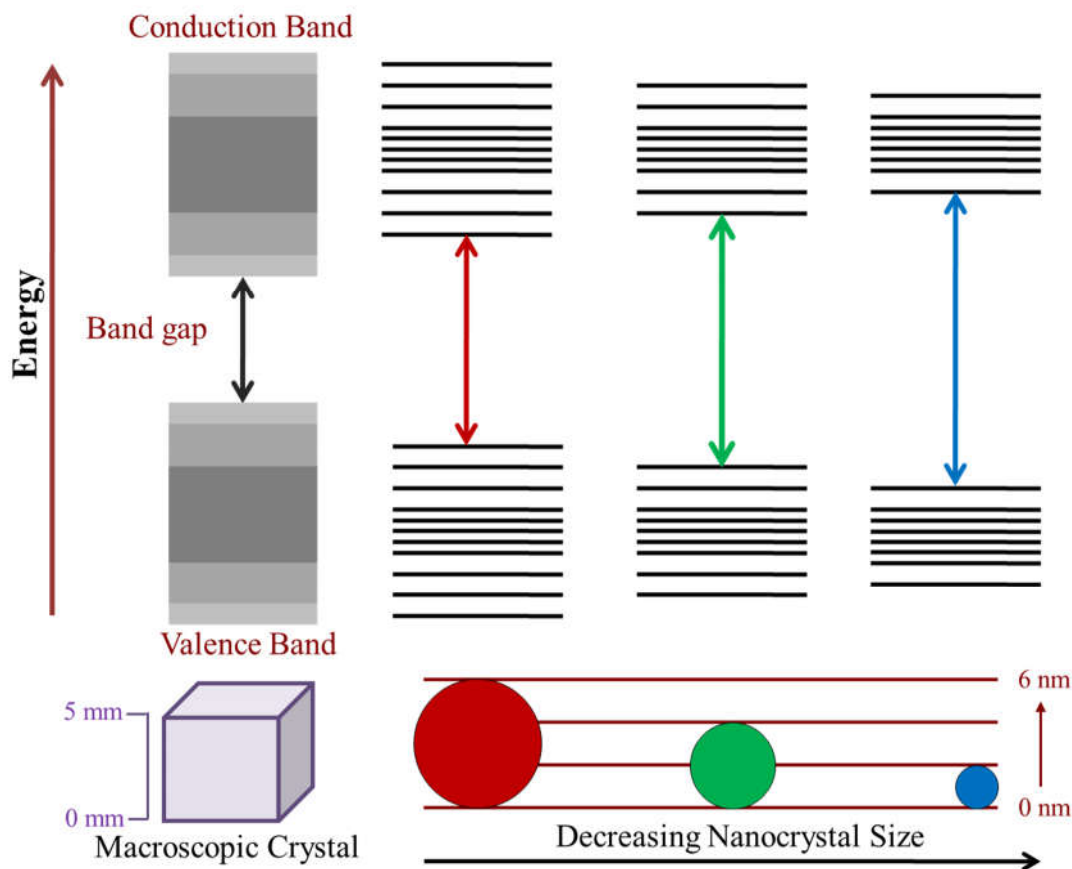


Figure 1.6: Bulk band structure in a macroscopic crystal vs. discrete energy levels in a nanocrystal. The figure also demonstrates the size dependent band gap in semiconductor nanocrystals

The Brus equation allows us to calculate the change in energetics between the bulk material and QDs. In light of this unique size-dependent absorption and emission property of the QDs, significant research has been dedicated to understand and control the physical and optical behavior of QDs for use in novel applications as mentioned previously. Figure 1.7 shows the E_g (eV) predicted by the Brus equation for some of the CdSe QDs used in this work. This figure also includes the experimentally observed band gap energies, where the values were obtained by Mulvaney and co-workers by recording the absorption spectra of CdSe QDs of different size and

determining their size from transmission electron microscopy.⁴³ Though the Brus equation gives an intuitive approach towards understanding the size-dependent optical properties in QDs, it differs significantly from the experimentally observed values (especially for smaller sizes). Therefore, empirical equation developed from the E_g vs. size spectrum (sizing curve) is used to calculate the size of QDs from the absorbance spectrum. The same has been done for all the QDs used in this work.

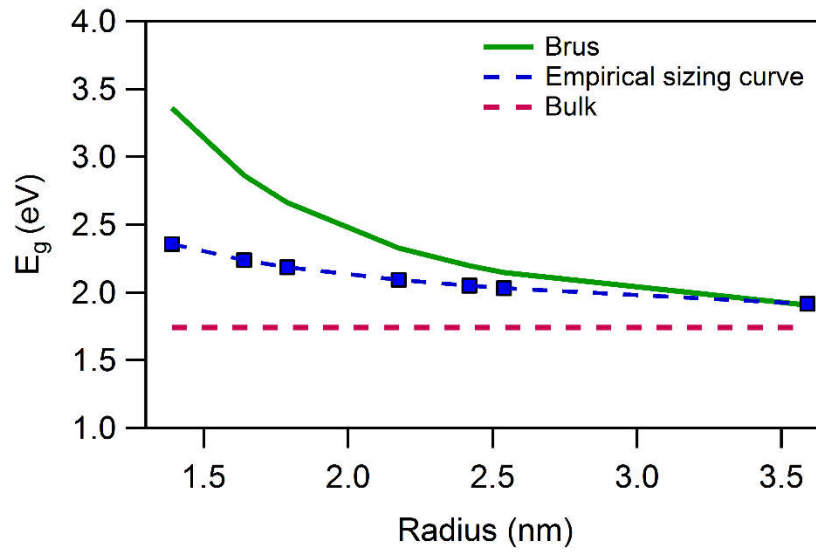


Figure 1.7: Size dependence of the energy gap E_g for colloidal CdSe QDs

The bulk value of E_g is 1.74 eV,⁴⁴ the theoretical curve was obtained using Eq. 1.4 with the following parameters: $m_e^* = 0.13m_0$, $m_h^* = 0.4m_0$,⁴⁴ m_0 = mass of free electrons, $\epsilon_r(\text{CdSe}) = 5.8$,⁴⁵ $\epsilon_0 = 8.854 \cdot 10^{-12} \text{ C}^2 \text{ N}^{-1} \text{ m}^{-2}$, $h = 6.63 \cdot 10^{-34} \text{ Js}$, $1 \text{ eV} = 1.6 \cdot 10^{-19} \text{ J}$.

The experimental curve was obtained using the empirical curve developed by Mulvaney⁴³ $D(\text{nm}) = 59.6082 - 0.5474\lambda + 1.8873 \times 10^{-3} \lambda^2 - 2.8574 \times 10^{-6} \lambda^3 + 1.6297 \times 10^{-9} \lambda^4$ where D = QD diameter and λ = Wavelength (nm) of the 1st Exciton peak.]

1.4: Semiconductor QDs and their Classification

The exceptional optical and electronic properties of nanocrystalline semiconductors were discovered in 1981 by Alexey Ekimov, who first synthesized nanocrystals embedded in a glass matrix.⁴⁶ The first colloidal semiconductor nanocrystallite solution was synthesized in 1983 by Louis Brus⁴⁷ and the phrase “quantum dots” was coined by Mark Reed for these zero-dimensional crystalline materials.⁴⁸ In accordance to the type of material structures, QDs can be classified as single-core, core-shells (where a shell of another semiconductor is grown on the core QD) and alloy structured QDs. Semiconductor materials are generally classified on the basis of the periodic table group that their constituent elements belong to. Some of the commonly studied nanocrystals are listed in Table 1.1.

Table 1.1: General classification of semiconductor QDs

Core QDs	II-VI	CdS, CdSe, CdTe, ZnSe
Core QDs	III-V	InN, InP, InAs, GaN, GaP, GaAs
Core QDs	IV-VI	PbS, PbSe
Core QDs	IV	Ge, Si
Core-shell QD heterostructures	Type I	CdSe/ZnS, CdSe/CdS/ZnS, InP/ZnS
Core-shell QD heterostructures	Type II	CdTe/CdSe, CdSe/ZnTe, ZnSe/CdS

1.5: Fabrication of QDs

A wide variety of methods have been developed for fabrication of QDs in different media including organic solvents,⁴⁹ aqueous solution⁵⁰ and molecular films deposited on solid substrates.⁵¹ In a

broad sense, the synthetic approaches are divided into two categories: top-down and bottom-up approach. In the first approach, QDs are fabricated through epitaxial growth⁵² and/or nanoscale patterning using technologies like lithography,⁵³ vacuum deposition (atomic layer deposition, ALD)⁵⁴, and electrochemical methods are used to reduce the bulk semiconductor to nanometer size. The second approach is the bottom-up approach, e.g. reverse micellar synthesis,⁵⁵ arrested precipitation method,⁵⁶ and the more popular colloidal synthesis approach⁵⁷ where molecular or ionic precursors are reacted together in a solvent media to produce colloidal QDs. Over the years, QDs have been fabricated by lithography, molecular beam epitaxy, microwave-assisted methods⁵⁸ as well as colloidal synthetic methods. However, the ultimate technique for synthesis of QDs would be the one that produces significant amounts of sample with control over the QD size, shape, monodispersity and can be scaled up easily. The colloidal synthesis of QDs have become very popular over the years owing to the ease of synthesis, solution-processability and the high-quality (crystallinity and mono-dispersity) of the QDs produced by this method.

1.6: Colloidal QDs

In the fabrication of colloidal QDs, the atomic species that are required for the NC growth are introduced into the reaction media in the form of precursors. The precursors decompose into reactive species (monomers) as the solvent reaches the required temperature.^{59,60} These monomers lead to nucleation and growth of the NCs. The key parameter in the controlled growth of NCs in the colloidal synthesis approach is the inclusion of long chain organic ligands, more commonly known as the surfactants. The surfactants are dynamically adsorbed on to the QD surface during the reaction. These ligands prevent aggregation of the individual NCs and hence provide the stability to the colloidal QDs. By adjusting the mixture of surfactant molecules used in the QD synthesis, excellent control can be obtained on the size, shape and size-distribution of the QDs.^{18,61}

1.7: Optical properties of QDs

1.7 A: UV-visible absorbance

The minimum energy required to create an exciton is defined by the band gap of the material, i.e., the energy required to excite an electron from the highest level of valence energy states to the lowest level of the conduction energy states. For a quantum dots, since the band gap depends on the size of the particles, the optical properties are size-dependent as well. For a smaller particle, the energy required for an electron to get excited is higher. Since, energy is inversely proportional to wavelength, a smaller QD absorbs at a lower wavelength compared to a larger one (blue shift observed as the size decreases). For II-VI QDs the band gap energy falls in the UV-visible range; i.e. UV or visible light source can be used to excite an electron from the ground valence states to the excited conduction states. In the bulk semiconductor the band gap is fixed, and the energy states are continuous. This results in a rather uniform absorption spectrum however, as described above the QDs have a size-dependent absorption with discrete energy peaks.

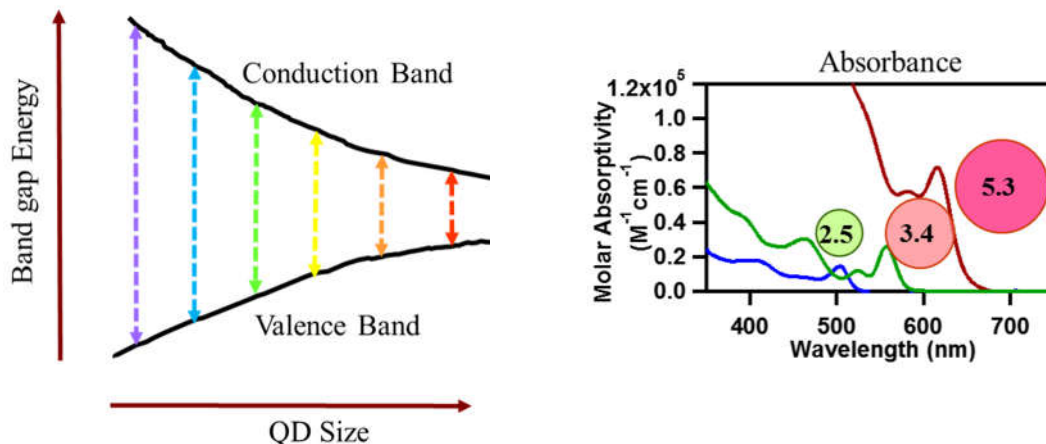


Figure 1.8: Size-dependent band gap in QDs (left); Absorption spectra of 2.5 nm, 3.4 nm and 5.3 nm (diameter) CdSe QDs (right) depicting the effect of QD size on the optical property of QDs

The peaks seen in the absorption spectrum correspond to the optical transitions between the conduction band and the valence bands. The minimum energy and thus the maximum wavelength peak corresponds to the first exciton peak or the energy for an electron to get excited from the highest valence state to the lowest conduction state.

The simplified model of NC electronic states discussed in Section 1.3 provides a reasonable description of the NC conduction band. However, the valence band for many semiconductors have a complex, multi-sub band character and confinement-induced mixing between different sub-bands have to be considered to explain the NC valence-band structure.^{62,63} The better representation for the quantum number would then be the total angular momentum, $\vec{F}$, which is a sum of the angular momentum, $\vec{J}$, and the orbital momentum, $\vec{L}$ ($\vec{F} = \vec{J} + \vec{L}$) and the valence-band states would usually be denoted as nL_F .⁶⁴ Ekimov et al.⁶³ calculated size-dependent hole

energies in CdSe NCs, taking into account the mixing between heavy, light, and spin-orbit split-off valence sub-bands. From these calculations, the lowest hole states were found: $1S_{3/2}$, $1P_{3/2}$, and $2S_{3/2}$ (Figure 1.9 a). Optical transitions involving these states can be resolved in the absorption spectrum of good-quality colloidal CdSe NCs (Figure 1.9 b).

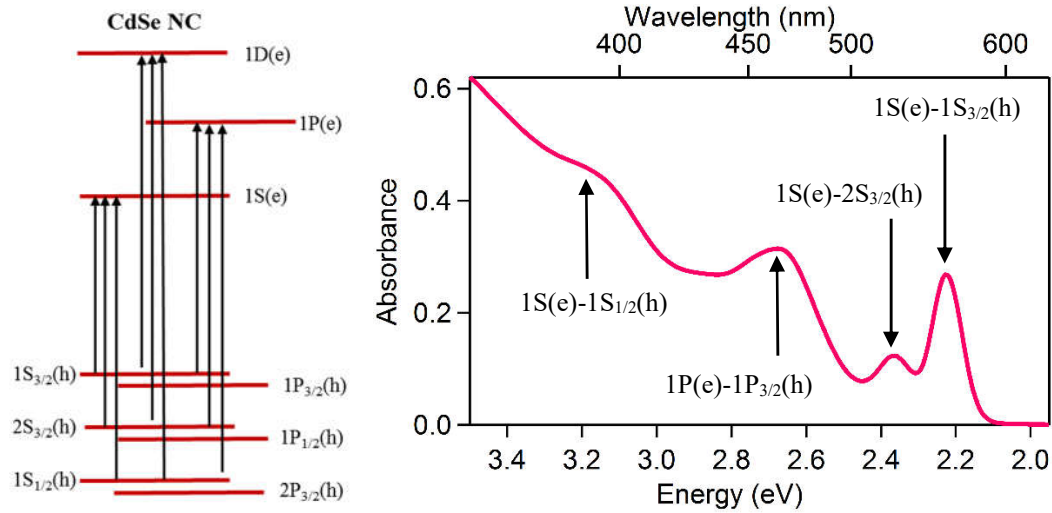


Figure 1.9: (a) In CdSe NCs, quantum confinement leads to mixing between different valence sub-bands, leading to a more complex structure of hole quantized states compared with those shown in Figure 1.4. The arrows depict the allowed interband optical transitions.⁶⁴ (b) The ground-state absorption spectrum of one of the CdSe NCs used in this thesis (diameter 3.4 nm). Arrows depict the positions of four well-resolved transitions

1.7 B: Photoluminescence

Photoluminescence (PL) is the emission of electromagnetic radiation in the form of light by a material that has absorbed a photon. When a QD absorbs a photon/energy equal to or greater than its band gap, the electrons in the QD's get excited to the conduction state. This excited state however has a short lifetime, so the electron relaxes back to its ground state by radiative decay or non-radiative decay. Radiative decay is the loss of energy through the emission of a photon or

radiation where as non-radiative decay involves the loss of energy (heat) through lattice vibrations. Usually the electron relaxes to the ground state through a combination of both radiative and non-radiative decays. As in organic flurophores, the energy emitted from a QD after photo-excitation, is lower than that required to excite the sample, or the wavelength of the PL is longer than the absorption. This shift between the lowest energy peak in the absorption spectrum and the corresponding emission peak is known as the Stokes shift ⁶⁵ and is explained by investigating the complex excitonic fine structures in QDs ^{66,67} which is discussed next. The commonly observed stokes shift value in CdSe QDs is $\sim 10\text{-}20\text{ meV}$.⁶⁶

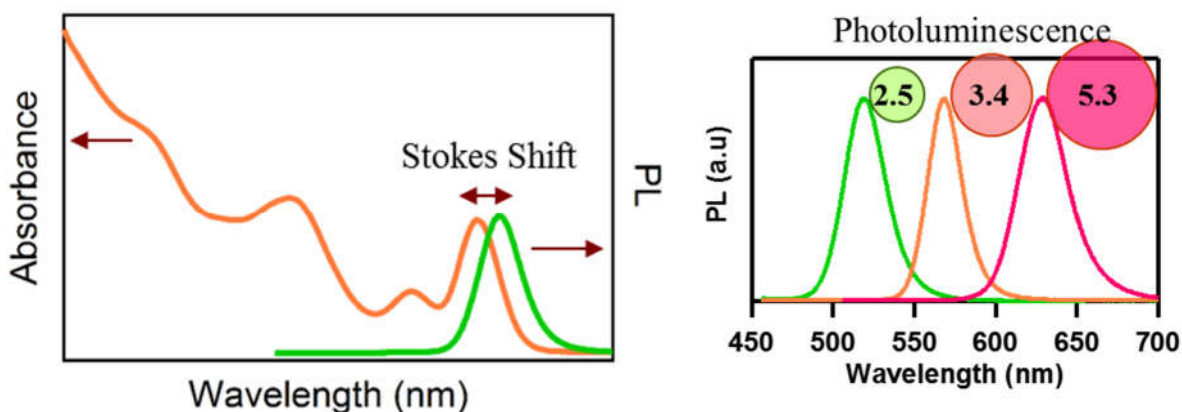


Figure 1.10: Depiction of Stokes shift in CdSe QDs (left), PL spectra of 2.5 nm, 3.4 nm and 5.3 nm CdSe QDs (right)

Whereas band mixing can be used to explain the overall structure of NC absorption spectra, the emission properties of NCs can only be understood by considering the fine structure of the band-edge $1S(e)-1S_{3/2}(h)$ transition, especially to explain the strong dependence of the exciton radiative lifetime on the sample temperature.^{66,68,69} At liquid-He temperatures, the decay constant is found

to be very long (ranging from hundreds of ns to $\sim 1 \mu\text{s}$) whereas at room temperature it is found to be ~ 20 ns. This observation has been explained by invoking the dark/bright-exciton model.^{66,67,70} This model accounts for the fine-structure splitting of the band-edge exciton owing to the strong electron-hole (e-h) exchange interactions and anisotropies associated with the crystal field and NC-shape asymmetry. The e-h exchange interaction energy is proportional to the overlap between of electron and hole wave functions; therefore, in case of NCs it is significantly enhanced ($\sim$ tens of meVs),⁶⁶ as compared to bulk materials. In the presence of strong e-h exchange, the lowest-energy $1S$ electron and $1S_{3/2}$ hole states (with angular momentum $1/2$ and $3/2$ respectively) cannot be considered independently. These have to be treated as a combined exchange-correlated exciton. These states are further split by the exchange interaction, forming a high-energy, optically active, $N = 1$ bright exciton and a lower-energy, optically passive, $N = 2$ dark exciton (Figure 1.11). These states are again split into five sublevels because of the anisotropy of the wurtzite lattice and the non-spherical NC shape (CdSe NCs are usually slightly prolate) forming two manifolds of upper and lower fine-structure states. The effect of additional level-splitting does not change the nature of the lowest-energy state, which remains optically passive (i.e., dark). It is separated from the next, higher-energy, bright state by an energy of ~ 1 meV to more than 10 meV, depending on the NC size.⁶⁶

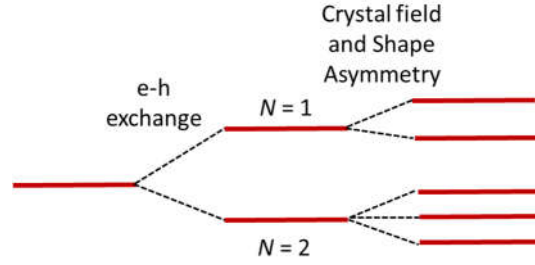


Figure 1.11: Fine-structure splitting of the band-edge $1S(e)-1S_{3/2}(h)$ transition in CdSe NCs due to the e-h exchange interaction and anisotropies associated with the crystal field in the hexagonal lattice and NC-shape asymmetry

The thermal redistribution of excitons between the lowest two states (after the crystal field splitting) is the main reason for the strong temperature dependence of the exciton recombination dynamics in CdSe NCs. At low temperatures, exciton recombination occurs primarily via the low-oscillator-strength dark state, which results in slow (sub μs to μs) PL decay. As temperature is increased, the excitons are thermally excited from the dark to the higher-oscillator-strength bright state, which produces faster PL dynamics.

The band-edge exciton fine structure also contributes to the large Stokes shift observed in NCs (as depicted in Figure 1.10). For most of the CdSe NC sizes studied, the band-edge absorption is dominated by the superposition of two upper-manifold strong optical transitions (Figure 1.11). These absorbing states are separated from the two lowest-energy emitting states by ~ 20 to ~ 80 meV, depending on the NC size.^{67,70-72} This energy, together with the effects of size dispersion leads to the large values of the Stokes shift observed for NC samples.^{71,72}

1.8: Influence of surface on optical properties of NCs

Size-dependence of optical properties is largely as a result of the internal structure of the NC. However, as the crystal becomes smaller, the number of atoms on the surface increases, which can also impact the optical properties. For example, CdSe NCs with a diameter of ~ 2.73 nm, have $\sim 53\%$ of the atoms located on the surface. The atoms on the surface of a crystal facet are incompletely bonded within the crystal lattice, thus disrupting the crystalline periodicity and leaving one or more “dangling orbital” on each atom pointed outward from the crystal. The dangling bonds of the surface atoms act as traps for the photo-generated electron or hole and affects the optical properties of nanocrystals.

During synthesis of colloidal NCs, ligands are used to solubilize the nanoparticle. Surface ligands control the colloidal stability and prevent aggregation of nanocrystals. When the NCs capped with a certain ligand is exposed to a good solvent, they disperse in that solution. Changing the nature of the solvent, by changing polarity, can induce flocculation of NCs. Generally, NCs are coated with a layer of surface-tethered hydrocarbon chains leading to sterically stabilized particles. In this case a good solvent is the one which has a negative free energy of chain-solvent mixing.⁷³ This would lead to the repulsion between the hydrocarbon chains and stabilizing NC dispersions. However, in a non-solvent, with positive chain-solvent mixing energy, the NCs try to minimize contact with the surrounding liquid, leading to contraction of ligand chains and aggregating the dispersed NCs. Typical good solvents for hydrocarbon-capped NCs are nonpolar liquids (for example hexane, toluene, chloroform) and the non-solvents are polar solvents (for example ethanol, acetone, acetonitrile).

Interaction between the NC core and ligand headgroup can be understood by using covalent bond classification,⁷⁴ which was originally used for metal coordination complexes. Eventually, this classification was adapted for NCs by Owen and co-workers.^{75,76} According to this classification, L-type ligands are neutral two-electron donors with a lone electron pair that coordinates datively with the surface metal ions. Amines (RNH_2), phosphines (R_3P) and phosphine oxides (R_3PO) are examples of L-type ligands. X-type ligands are species that possess odd number of valence-shell electrons in neutral form and need one electron from the NC surface site to form a two-electron covalent bond. X-type ligands can also be neutral radicals binding neutral surface sites or monovalent ions binding oppositely charged sites at the NC surface. Examples of X-type ligands include carboxylates (RCOO^-), thiolates (RS^-) and phosphonates. Nucleophilic L- and X-type ligands bind to electron-deficient surface sites, typically under-coordinated dangling metal ions at the NC surface. The surface of metal chalcogenides also exposes electron-rich anionic Lewis base sites. These sites can interact with Z-type ligands, such as CdCl_2 , which bind through the metal atom as two-electron acceptors.⁷⁵ The surface of oxide NCs can also bind protons (H^+), an example of positively charged, electrophilic X-type ligands.⁷⁷

For II-VI QDs, these capping ligands are Lewis bases which adsorb to the NC surface through dative ligand-metal bonds between the basic moiety on the ligand and metal atoms on the NC surface, solubilizing the NC in nonpolar solvents through lyophilic interactions with the alkyl chains on the ligands.⁶¹ In some cases, if the NCs have to be dispersed in polar solvents, polar end groups and hydrophilic polymers might be similarly used to solubilize nanocrystals in polar solvents.⁷⁸ Hole traps are generally predominant in NCs due to the nature of organic capping ligands (usually Lewis bases). These ligands passivate the metal atoms at the surface, thus passivating to a certain degree surface electron trap sites and leaving the anionic sites free to trap

the photo-generated hole. However, in most cases the passivation is never complete and surface states with energies within the band gap of the semiconductor material exists. The typical ligand coverage (surface ligand density i.e. number of ligands per unit area of the QD) for CdSe QDs is observed to be 3-5 ligand/nm²).^{75,79,80}

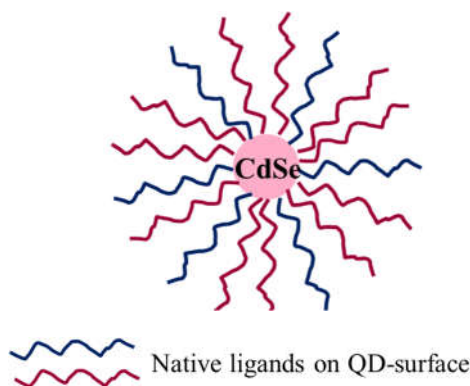


Figure 1.12: CdSe QD passivated with long-chain organic ligands. (The typical ligands used for the synthesis of CdSe QDs in this thesis are the hexadecyl amine (HDA) and tri-n-octylphosphine oxide (TOPO), the experimental details are discussed in Chapter 2, Sections 2.1 B and C)

If the energy of these surface states is within the semiconductor band gap, they can trap charge carriers at the surface, thereby reducing the overlap between the electron and hole wavefunctions, and decreasing the probability of radiative recombination. The number of surface states on a NC varies with sample preparation, and from QD to QD within an ensemble. The surface states are different for distinct members in an ensemble of particles, and often changes with time because there always exists a dynamic equilibrium where ligands constantly desorb and re-adsorb on the NC surface.⁷⁹ A trapped carrier can stay for a very long time on trap sites, and within this time scale, it may de-trap to form the exciton again and decay radiatively, or alternatively, it might

undergo non-radiative decay.⁸¹ This inhomogeneous trapping and de-trapping process is reflected in PL decays, where the traces are usually multi-exponential.

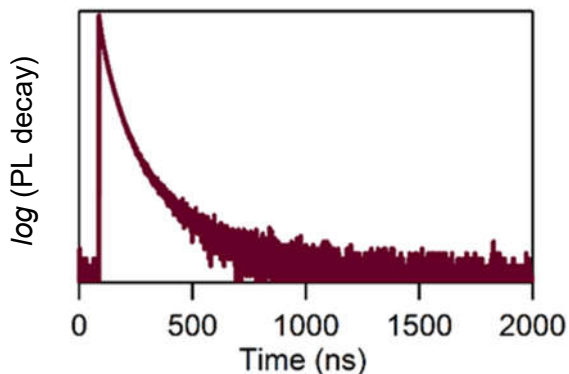


Figure 1.13: PL decay of 3.2 nm CdSe QDs (the y-axis is in log scale) showing the multi-exponential behavior

The exciton can relax back to the ground state by radiative emission but it can get trapped in the surface states. Once trapped, the exciton can relax to the ground state non-radiatively or can get de-trapped (return to the excited state) and then relax back to the ground state radiatively. The de-trapping is a thermally activated process so the exciton might be trapped in the surface states for a while before it can be emitted radiatively after de-trapping. Owing to the inhomogeneity in the QD ensemble, there are a distribution of trap state energies on the QD surface and hence the de-trapping event leads to a multi-exponential decay behavior.

1.9: Quantum Yield of PL

The energy of quantum dot exciton photoluminescence (PL) is easily controlled by varying the dot sizes; however, the factors that control the efficiency at which quantum dot excitons undergo radiative versus nonradiative decay is more difficult to manipulate. Photoluminescence quantum

yield (QY) Φ represents the ratio of number of emitted photons N_{em} to the number of absorbed photons N_{abs} .

$$\Phi = \frac{N_{em}}{N_{abs}} \dots\dots\dots \text{Eq. (1.5)}$$

High PL QY is a desirable property for applications such as multi-plexed labelling⁸² and tracking of cells or molecules in a biological environment,⁸³ solid-state lighting, illumination and displays.^{84,85} It has been found that exciton PL intensity in QDs may be altered by a variety of techniques. Capping the core CdSe QDs with a shell of higher-band-gap material such as ZnS was found to increase the luminescence QY significantly by passivating the surface traps on the QDs.⁸⁶⁻⁸⁸ Similarly, surfactant molecules bound to the CdSe QDs affect the efficiency of radiative versus nonradiative exciton decay; for example, a hole acceptor, n-butylamine, will diminish the exciton PL intensity⁸⁹ by removing core holes and rapidly trapping them at the surface of the dots. More recently, a detailed investigation of the factors governing the PL efficiency of CdSe nanocrystals during synthesis^{90,91} enabled the reproducible production of high quantum yield (50-85%) dots by selecting reaction conditions that minimized surface disorder and surface degradation and enabled good passivation of the dots. In this regard, the surface chemistry plays a crucial role in achieving high quantum yields and long term photo-stability and proper passivation of the surfaces of QDs is necessary to achieve a high PL-QY.

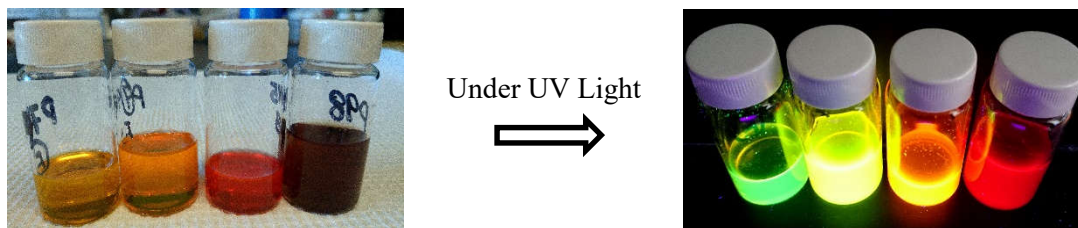


Figure 1.14: CdSe QDs (left to right arranged in increasing order of QD diameter: 2.5, 3.4, 3.8 and 5.3 nm) under room light (left) and under UV light showing the bright emission (right). The PL QYs of the samples are ~ 20-25%

1.10: Electron Transfer (ET) Processes involving QDs

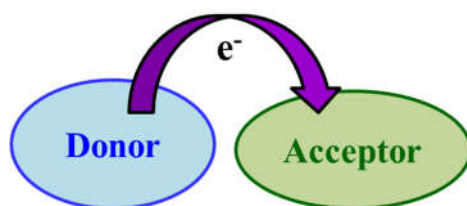


Figure 1.15: ET occurring between a donor and acceptor molecule

Electron transfer (ET) is one of the most important chemical processes occurring in nature (e.g. photosynthesis, cellular respiration). ET plays vital role in many biological, physical and chemical (both organic and inorganic) systems and is one of the most widely researched scientific areas. The interest in exploring ET reactions in QDs have grown substantially over the years owing to the number of applications involving QDs. Some of these applications are listed in Figure 1.16.

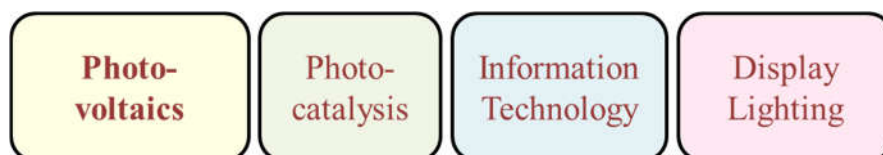


Figure 1.16: Areas where ET reaction plays vital role

The main goal of this work is to understand the electron dynamics at the interface of QDs by investigating the electronic communication between QDs and organic free radicals. The properties of QDs like band gap (size), surface ligands and quantum yield significantly affects the electron dynamics both qualitatively and quantitatively. These will be explored and discussed in details in the next chapters.

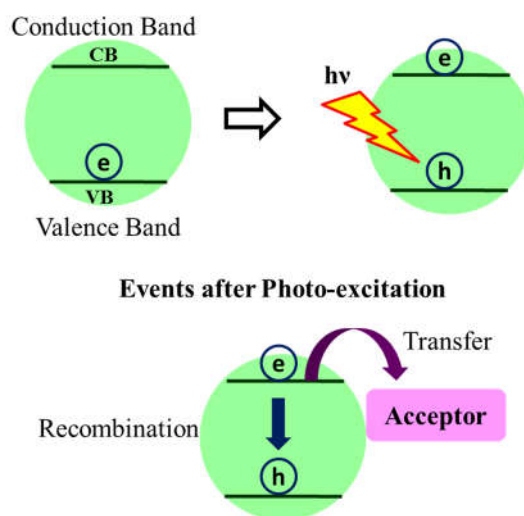


Figure 1.17: Photo-excitation of a QD and possible electron transfer (ET) process occurring in presence of a suitable acceptor

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Chapter 2: Photoluminescence Quenching of Colloidal CdSe and CdTe QDs by Nitroxide Free Radicals

Quantum dots (QDs) are emerging as a new class of light emitting, harvesting and charge-separation materials for applications such as solar energy conversion, light-emitting devices, or as labeling reagents in biotechnological applications.¹⁻⁵ The most interesting properties for a significant number of these applications are the high absorption cross-sections and size-tunable energetic levels of quantum-confined semiconductor nanocrystals (NCs).⁶⁻⁸ Furthermore, colloidal QDs are solution-processable, offering economic, versatile, and scalable approaches for commercial applications. One very important application of QDs are in the QD-sensitized solar cells which can achieve potentially higher efficiencies than dye-sensitized solar cells due to their unique capability of multiple exciton generation.⁹ More essentially, the quantitative dissociation of photo-generated excitons through interfacial charge- (electron or hole) transfer processes is a necessary step for overall optimized efficiency in many of these applications. A wide variety of organic as well as inorganic electron donor-acceptor dyads have been utilized to investigate the interfacial electron transfer (ET) reaction following photoexcitation of QDs, including QDs coupled to molecular species like organic dyes,¹⁰⁻¹⁴ transition-metal complexes,^{15,16} biomolecules^{17,18} and wide band gap semiconductors.^{4,5,19} However, in comparison only a limited number of studies have also looked at QD-free radical systems.²⁰⁻²³ Organic free radicals are interesting counterparts for studying ET to/from QDs because, unlike close-shell molecules, these generally undergo single electron transfer steps in a reversible fashion.^{24,25} Nitroxides are an interesting class of stable free organic radicals, which have recently been demonstrated in electrochemical applications such as organic batteries and photovoltaic devices (Figure 2.1).²⁶⁻³³

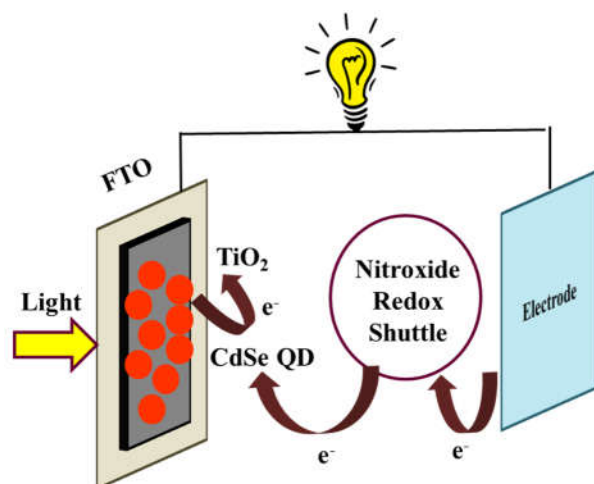


Figure 2.1: A schematic representation of the QD-sensitized solar cell utilizing Nitroxide radicals as redox-shuttle

Our goal is to investigate the ET between II-VI semiconductor QDs (CdSe and CdTe) coupled with nitroxide radicals TEMPO and 4-amino TEMPO. The molecular structures of these radicals are depicted in Figure 2.2. These are the model nitroxide radicals, commercially available, stable in air and are bright-colored species that are easily monitored via UV-vis spectroscopy and electron paramagnetic resonance (EPR), and have been the focus of a few previous studies.²⁰⁻²³ Using a combination of steady-state and time-dependent PL quenching measurements, we find that a number of conclusions previously made on this class of materials need to be revised, most importantly concerning the quantitative efficiency of the PL quenching interaction and the qualitative mechanistic aspects underlying the overall process.

2.1: Experimental Methods

2.1A: Chemicals used

Cadmium oxide (CdO, 99%), oleylamine (OLA, 70%), hexadecylamine (HDA, 98%), 1-octadecene (ODE, 90%), selenium (Se powder, 99.5%), tellurium (Te powder, 99.8%), tri-n-octylphosphine (TOP, 90%), trioctylphosphine oxide (TOPO, 99%), TEMPO (2,2,6,6-Tetramethylpiperidine 1-oxyl, 98%) and 4-amino-TEMPO (4-amino-2,2,6,6-tetramethylpiperidine-1-oxyl, 97%) were purchased from Sigma-Aldrich. Stearic acid (SA, 98%) was purchased from TCI chemicals. Tetradecylphosphonic acid (TDPA, >99%) was purchased from PCI Synthesis. Acetone (99.9+% HPLC grade), methanol (99.93%, HPLC grade), hexanes (ACS grade), toluene (ACS grade), were purchased from Macron Fine Chemicals. All chemicals were used as received without any further purification.

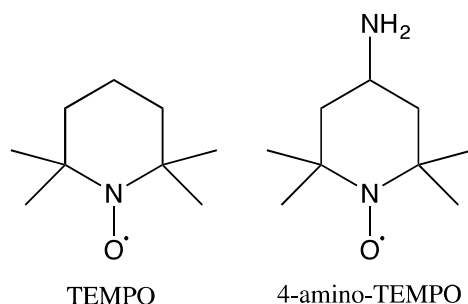


Figure 2.2: Structures of the nitroxide free radicals used in this study, (2,2,6,6-tetramethylpiperidin-1-yl)oxyl (TEMPO) and 4-amino-(2,2,6,6-tetramethylpiperidin-1-yl)oxyl (4-amino TEMPO)

2.1B: Synthesis of CdSe and CdTe Quantum Dots

The syntheses of the QDs were carried out by adapting standard literature protocols ³⁴ and modifying the methods to obtain the required QD sizes for each study. The syntheses were

conducted under N₂ atmosphere using standard Schlenk-line techniques. The details of a typical synthesis is given here. In a 25 mL round-bottom flask, 0.19 g (0.4 M) selenium (Se) was added and the flask was sealed, evacuated and then kept under N₂ atmosphere. To this, 5 mL tri-n-octylphosphine (TOP) was added. The solution was stirred at room temperature until all the Se had dissolved in TOP to give a clear solution. 0.051 g (0.4 mmol) cadmium oxide (CdO), 2.845 g (10 mmol) of stearic acid (SA), 13 mL (~42.5 mmol) oleylamine (OAm) and 9.3 mL 1-octadecene (ODE) were loaded into a 100 mL three-neck flask and then sealed. The flask was then evacuated for 15 minutes after which it was slowly heated to 250 °C under N₂ flow. After CdO was completely dissolved (an optically clear solution being obtained), the TOP-Se solution was injected swiftly into the reaction flask. After the injection, the nanocrystals were allowed to grow for different time intervals ranging from 2-30 minutes depending on the desired size of NCs. After the reaction was over, the heating mantle was removed and the flask was allowed to cool down to the room temperature. The QDs were extracted by centrifuging the contents of the reaction flask after adding toluene and methanol in 1:4 ratio. The clear supernatant solution was removed as the QDs decanted to the bottom of the flask. The QDs were then suspended into a small volume of hexane and annealed in order to obtain better surface passivation (*vide infra*). Cadmium telluride QDs were synthesized similarly³⁵ using CdO and tetradecylphosphonic acid (TDPA) instead of SA and TOP-Te (tellurium dissolved in TOP) instead of TOP-Se.

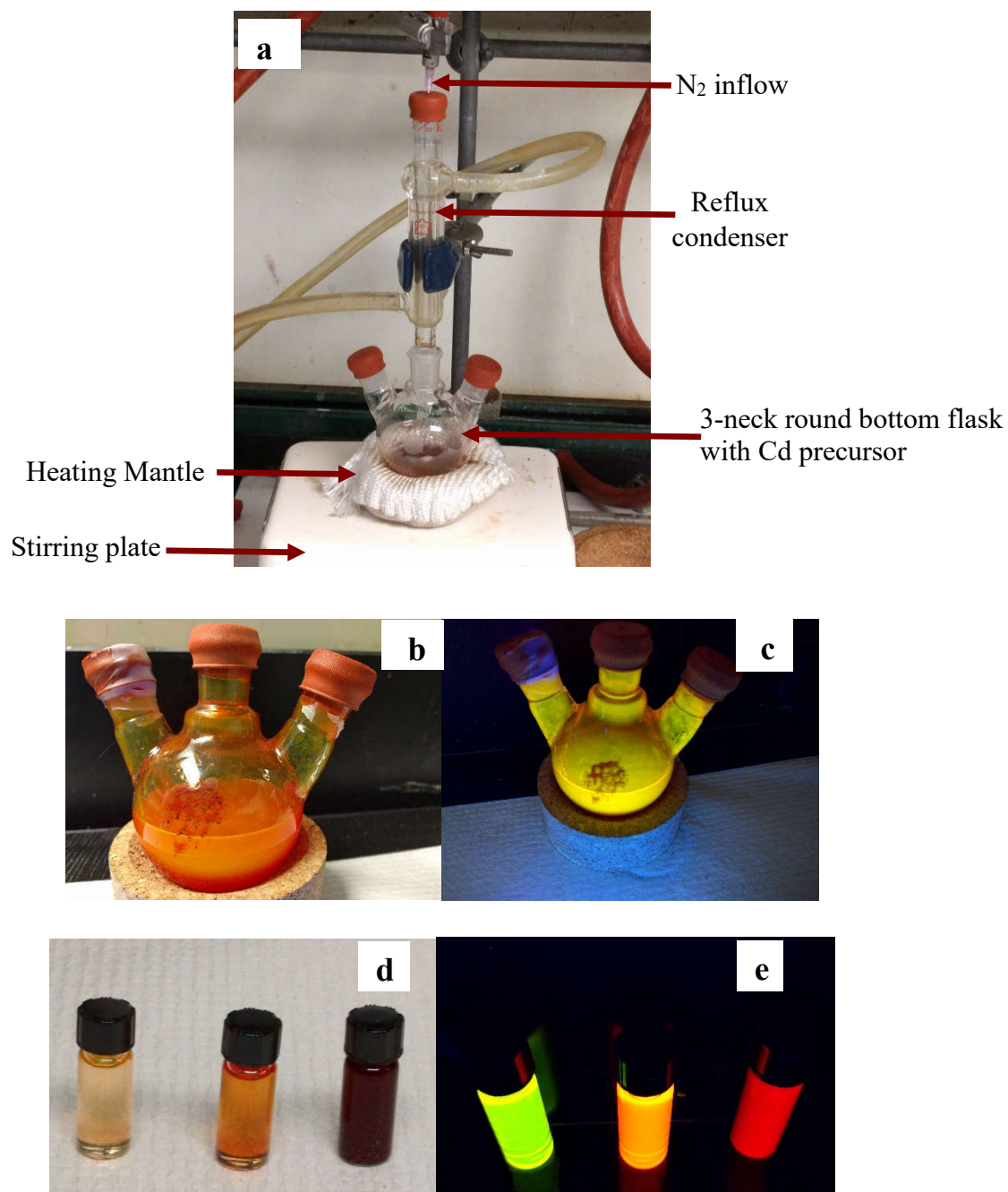


Figure 2.3: The general experimental set up for synthesis of the QDs (panel a), the QDs after the reaction is stopped on reaching desired QD size (panel b), the same dots under UV light (panel c), three different sizes of QDs obtained from the same reaction batch by withdrawing aliquots at different time (panel d) and the same dots under UV light (panel e)

2.1C: Annealing Procedure

The CdSe and CdTe QDs were annealed in order to enhance the PL QY of the samples and to ensure all QDs had similar environment. 2.2 g tri-n-octylphosphine oxide (TOPO) and 1.2 g hexadecylamine (HDA) were taken in a 50 mL 3-neck flask and heated to 130 °C under vacuum for 1 hour. The QDs suspended in hexane were then injected to the reaction mixture under nitrogen. The flask was again placed under vacuum to remove the hexane, after which 2.5 mL TOP was added. The QDs were annealed at 130 °C for two to three days. Finally, the QDs were washed with a toluene methanol mixture as described above and then suspended in toluene.

2.1D: Optical Spectroscopy

Measurements were performed on solutions of nanoparticles dispersed in toluene in 1×1 cm cuvettes. Absorption spectra were collected on an OLIS17 UV/VIS/NIR spectrophotometer with 1 nm increments and solvent background subtraction. For steady state luminescence (PL) experiments, the emission of the QDs was monitored using a Horiba-Jobin-Yvon spectrometer (IHR500, 150 grooves/mm grating blazed at 500 nm) with a CCD detector (SYMPHONY II, Liq. N₂-cooled). The PL lifetime measurements were recorded using a time-correlated single photon counting (TCSPC) set up. The data acquisition card (DAQ) is from Edinburgh Instrument (TCC900). The laser used for the experiment is a 405 nm pulsed laser from Picoquant (LDH-D-C-405M, CW-80MHz). The detector is a photomultiplier tube (PMT) from Hamamatsu (H7422-40). Absolute photoluminescence quantum yields were measured using the Hamamatsu Absolute PL Quantum Yield Spectrometer, model C11347.

2.1E: Other Spectroscopic Techniques

The Nuclear magnetic resonance (NMR) spectra were recorded on an Agilent DDR2 500 MHz NMR spectrometer equipped with 7600AS 96 sample auto-sampler running VnmrJ 3.2A. The samples were measured in deuterated benzene solvent using a relaxation delay of 25s and 16 average scans. The QDs were crashed out of the toluene solution, dried and then re-dispersed in deuterated benzene.

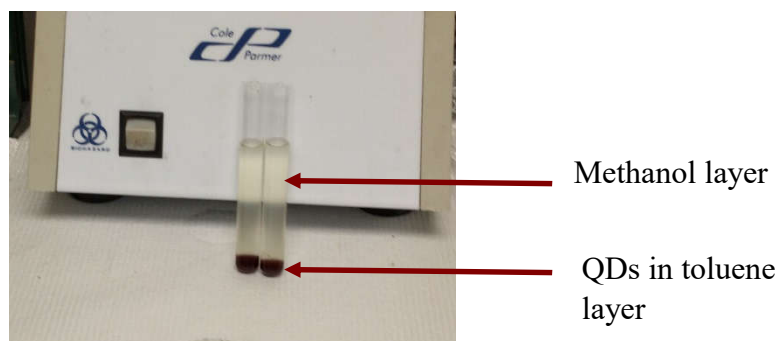


Figure 2.4: The CdSe QDs crashed out of the toluene solution using methanol

Powder X-Ray Diffraction (PXRD) was recorded on the Bruker Davinci Diffractometer ($\text{Cu K}\alpha = 0.154 \text{ nm}$). The QD solution was drop-cast on zero-background silica plates for PXRD measurements. The TEM images were recorded on a JEOL2200FS transmission electron microscope operating at 200 keV. Formvar-coated copper grids were used as NC supports for TEM. The Electron Paramagnetic Resonance (EPR) spectra were recorded on a Bruker ESP-300E X-band EPR spectrometer. The radical samples for EPR were prepared in toluene (concentration of the radicals used was $0.1 \mu\text{M}$) and each sample was degassed for an hour before measurement. Radical-QD EPR spectra were measured 15 minutes after mixing the same. The parameters used for the EPR measurements are listed here: microwave power 0.12 mW; field modulation amplitude

0.3 G; field modulation frequency 100 kHz; time constant 40 ms; receiver gain 40; 10 scans averaged for each spectra.

2.1F: Quenching Experiments

For the photoluminescence (PL) measurements, 3-5 μM QD solutions in toluene were used. Stock solutions of TEMPO and 4-amino TEMPO free radicals were prepared in toluene. Small volumes ($\sim 10\ \mu\text{L}$ - $50\ \mu\text{L}$) of the free radical solutions were added to the QD suspensions and the PL intensity and lifetime were measured. The suspensions were continuously stirred during the experiment and the data were recorded after the signal stabilized after each radical addition. The raw data obtained from the PL experiment had to be corrected for excitation light screening and re-absorption of emission by the radicals. The correction was conducted by adapting the procedure described by Credi et al.³⁶ It was also observed that the PL quenching depended somewhat on the initial quantum yield (QY) of the QDs (discussed in later section); care was taken to ensure that the initial QY of the QDs used in the study were all similar (20-25%). Time-resolved PL decays of these QD and QD-radical solutions were found to be non-single-exponential,³⁷⁻⁴¹ and the decay curves were fit using a Kohlrausch-WilliamsWatts (KWW) stretched exponential function (Eq. 2.1).⁴²

$$I(t) = I_0 \exp\left[\frac{-(t-t_0)}{t_{kww}}\right]^\beta \dots\dots\dots \text{Eq. (2.1)}$$

$$\langle \tau \rangle = \frac{1}{\beta} \cdot \Gamma\left(\frac{1}{\beta}\right) \cdot t_{kww} \dots\dots\dots \text{Eq. (2.2)}$$

Here $I(t)$ and I_0 are the PL intensities at time t and time zero, respectively. β and τ_{KWW} are the stretch factor and KWW decay time, respectively; $\Gamma(x)$ is the gamma function. The average excited-state lifetimes $\langle\tau\rangle$ are determined directly from the fit (Eq. 2.2); these parameters are taken as meaningful quantifiers for the ensemble average lifetime values without any assumptions regarding the nature of the underlying distribution of rate constants.

2.2: Results and Discussion

2.2 A: QD Photoluminescence Quenching

The UV-vis absorbance spectra of CdSe and CdTe QDs used for the experiment are shown in Figure 2.5. The lowest excitonic transition energies, derived from the maximum of the first exciton absorption peak, were used to estimate the average NC diameters (D), extinction coefficients (ϵ_{1S}), and concentration of the QD suspensions ($[QD]$) by using empirical calibration curves correlating the exciton peak energy with NC sizes.^{43,44}

For CdSe QDs:

$$D(nm) = 59.6082 - 0.5474\lambda + 1.8873 \times 10^{-3} \lambda^2 - 2.8574 \times 10^{-6} \lambda^3 + 1.6297 \times 10^{-9} \lambda^4 \dots\dots \text{Eq. (2.3)}$$

$$\epsilon_{1S}(M^{-1}cm^{-1}) = 155507 + 6.6705 \times 10^{13} \exp\left(-\frac{E_{1S}}{0.1055}\right) \dots\dots \text{Eq. (2.4)}$$

$$[QD](M) = \frac{Abs}{l(cm)\epsilon_{1S}(M^{-1}cm^{-1})} \times \frac{\Delta E_{1S,HWHM}(eV)}{0.06} \dots\dots \text{Eq. (2.5)}$$

where E_{1S} is the energy of the 1st absorption peak (eV), l is the optical pathlength and $\Delta E_{1S,HWHM}$ is the half-width-half-maximum of the first absorption peak on the low energy side.

For CdTe QDs:

$$E_{1s}(eV) = 1.51 + \frac{1}{0.048D^2 + 0.29D - 0.09} \dots\dots\dots \text{Eq. (2.6)}$$

A list of the QD samples used in this study is given in Table 2.1.

Table 2.1: QD suspensions (in toluene) used in this study

	QD	Diameter (nm)	Concentration (μM)	PL Quantum Yield, ϕ_{QD}
i	CdSe	2.5	4.9	0.24
ii	CdSe	3.4	3.5	0.28
iii	CdSe	5.3	3.7	0.22
iv	CdTe	3.9	3.3	0.19
v	CdTe	5.0	3.6	0.17

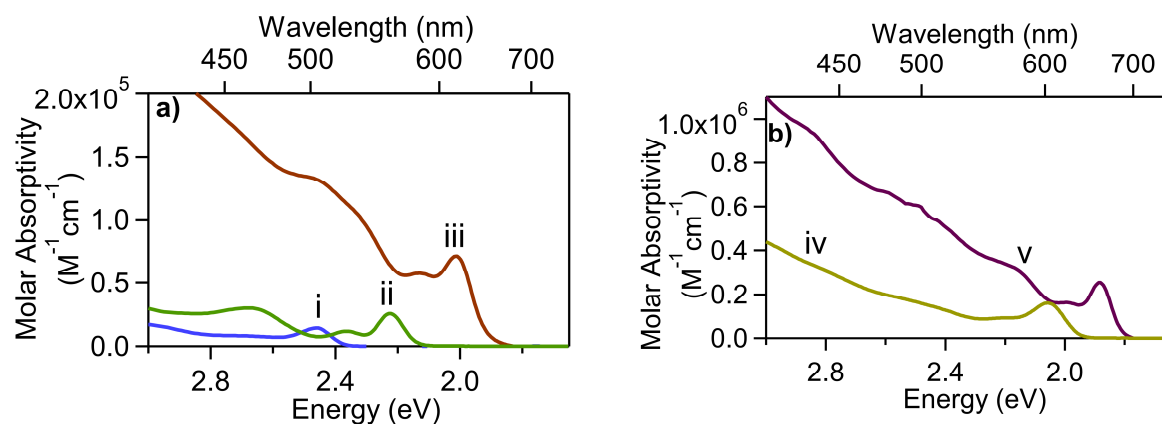


Figure 2.5: Absorption spectra of CdSe QDs (panel a) and CdTe QDs (panel b) used in the experiment (diameters are listed in Table 2.1)

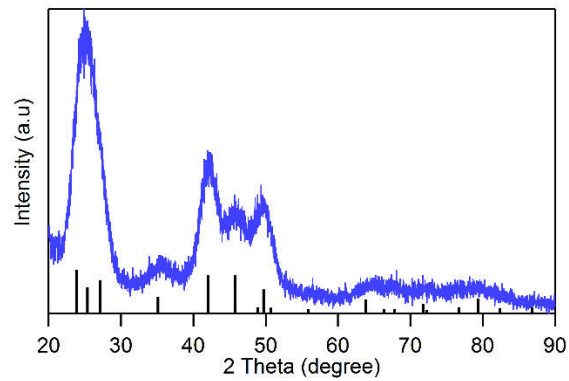


Figure 2.6: Powder X-ray diffraction (PXRD) patterns of 3.4 nm CdSe QDs. The black lines are the CdSe bulk wurtzite peak positions^{45,46}

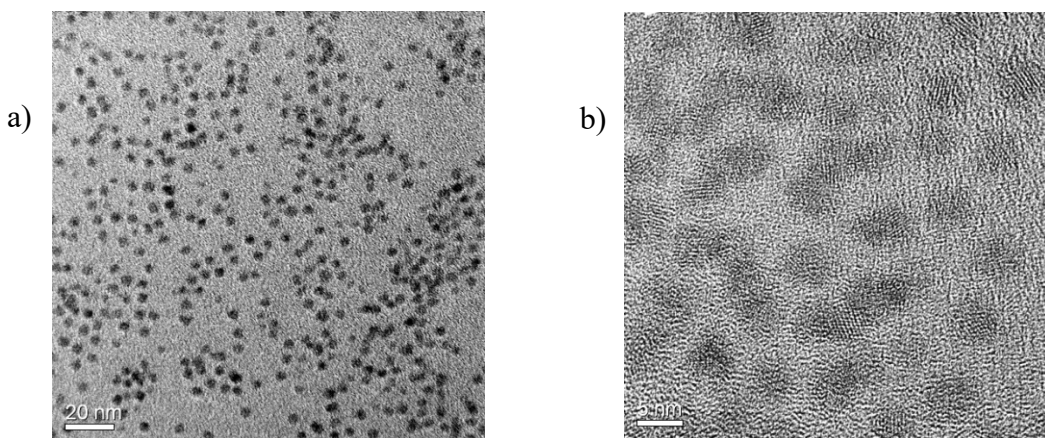


Figure 2.7: TEM image of 5.3 nm CdSe QDs (panel a), HRTEM image of the same (panel b)

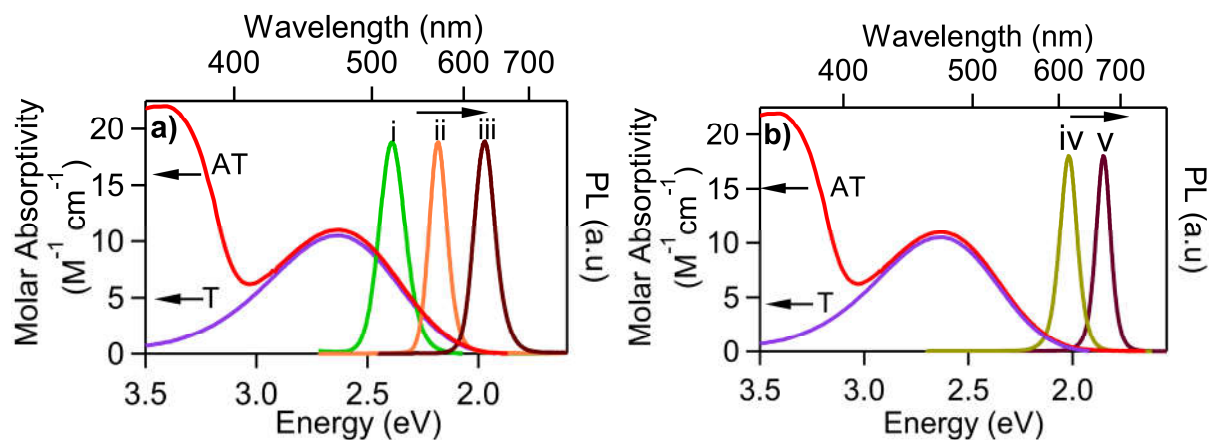


Figure 2.8: Absorption spectra of radicals TEMPO (T) and 4-amino TEMPO (AT) and photoluminescence spectra of CdSe QDs (panel a) and CdTe QDs (panel b)

As evident from the absorption spectrum (Figure 2.8) these radicals are colored species, weakly absorbing in the green part of the optical spectrum. Upon mixing of both radicals to the QD suspensions in toluene, the QD PL intensity is found to decrease (Figure 2.9), with different quenching efficiencies for each radical, consistent with previous reports. Whereas 175 mM TEMPO is required to completely quench the PL intensity of the QD, 11 mM 4-amino TEMPO is sufficient to achieve the same level of PL quenching. For comparison, the red curve in Figure 2.9a shows the extent of quenching achieved by adding ~11 mM TEMPO to a 2.5 nm CdSe QDs suspension; similar experiments conducted on the other CdSe QD sizes show that in all cases 4-amino TEMPO quenches the QD PL more efficiently than TEMPO (Figures 2.10-2.13).

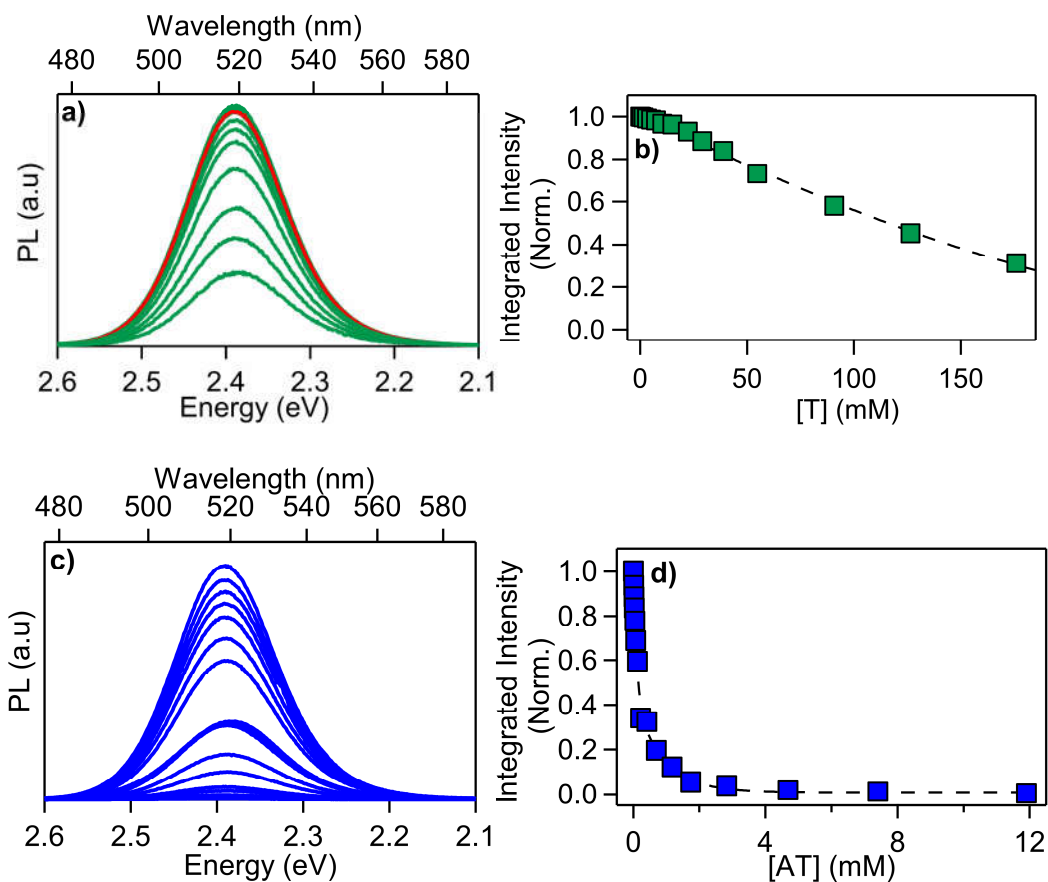


Figure 2.9: PL intensity (after correction; described in the text) of 2.5 nm CdSe with addition of TEMPO (panel a-b) or 4-amino TEMPO (panel c-d). The broken lines are guide to the eyes

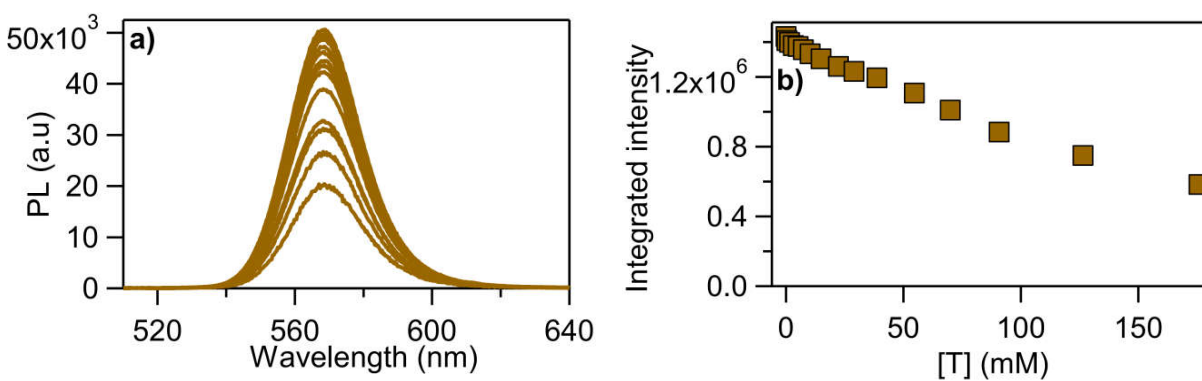


Figure 2.10: PL Intensity of 3.4 nm CdSe QD (corrected) with addition of TEMPO (panel a); the corresponding integrated intensities I^{CW} (panel b)

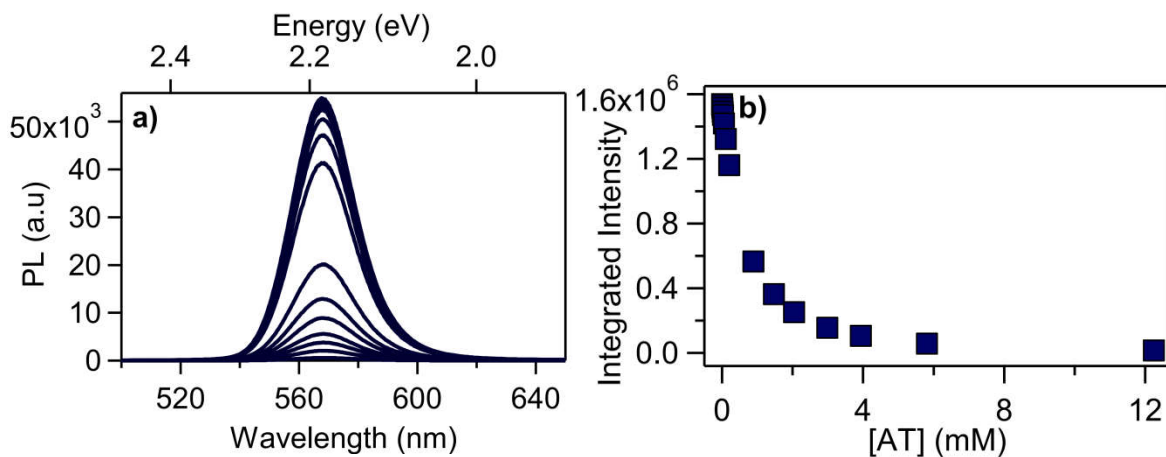


Figure 2.11: PL Intensity of 3.4 nm CdSe QD (corrected) with addition of 4-amino TEMPO (panel a); the corresponding integrated intensities I^{CW} (panel b)

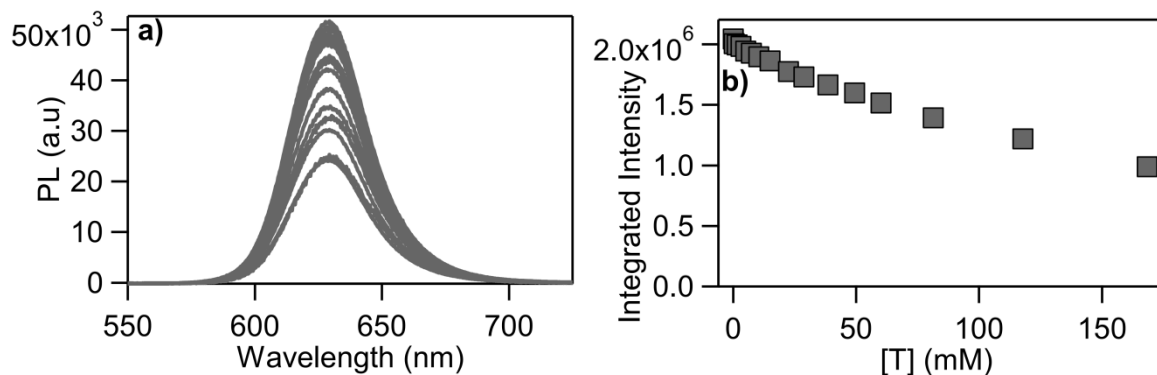


Figure 2.12: PL Intensity of 5.3 nm CdSe QD (corrected) with addition of TEMPO (panel a); the corresponding integrated intensities I^{CW} (panel b)

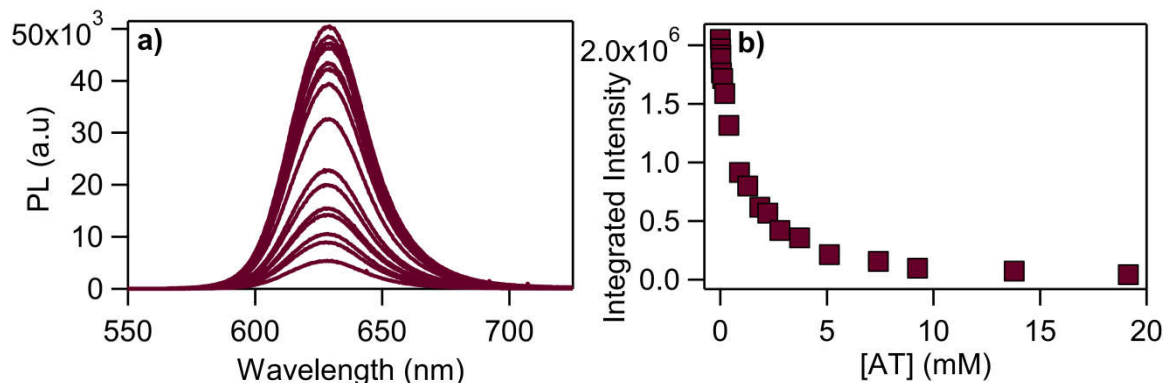


Figure 2.13: PL Intensity of 5.3 nm CdSe QD (corrected) with addition of 4-amino TEMPO (panel a); the corresponding integrated intensities I^{CW} (panel b)

The quenching efficiency of the two nitroxide radicals have been compared competitively in Figure 2.14, using Stern-Volmer plots, $(I_0/I)^{CW}$ as a function of radical concentration, where I_0 is the QD PL intensity in absence of the radical and I the PL intensity after each addition of the nitroxide radicals; the CW superscript indicates that this ratio is obtained from steady-state PL experiments (by opposition to time-dependent, TD , measurements presented later on). Obtaining reliable Stern-Volmer ratios is not a straightforward task. At the excitation wavelength used here ($\lambda_{exc} = 450$ nm), the nitroxide free radicals can absorb an appreciable amount of the excitation beam (inner-filter effect). Furthermore, the light emitted by QDs can be reabsorbed to varying extent by the radicals. Finally, because each sample is prepared by adding a precise amount of a radical solution to the QD suspension, the measured PL intensity has to be corrected by a proper the dilution factor. Each of these effects (excitation screening, emission reabsorption, and dilution factor) needs to be properly taken into account.

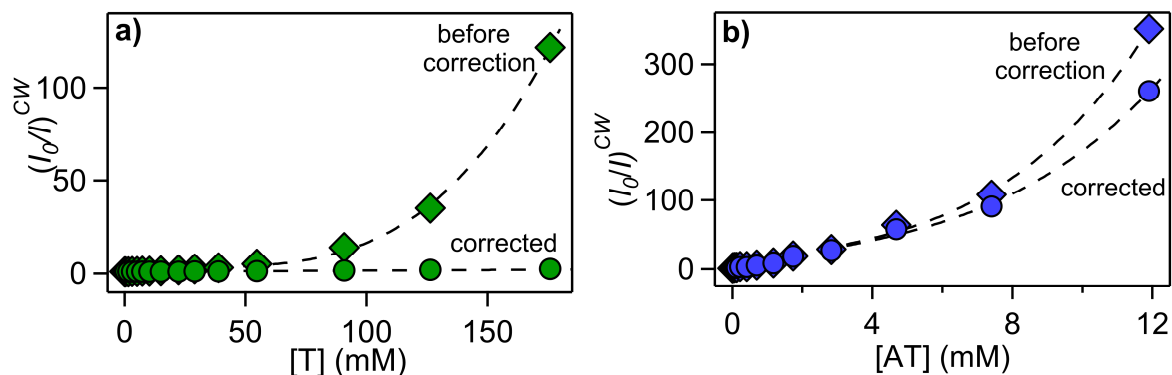


Figure 2.14: Stern-Volmer plot for quenching of 2.5 nm CdSe QDs (sample *i*) with TEMPO (panel a) and 4-amino TEMPO (panel b), before and after correcting for the inner-filter and reabsorption effects. The broken lines are guide to the eyes

It is interesting to note that the uncorrected Stern-Volmer curve shown for TEMPO in Figure 2.14 (a) is essentially identical to that reported previously, which was then described as a

non-linear quenching effect.^{20,21} It is observed that after correcting for each effects listed above, TEMPO is not an efficient PL quencher, contrary to conclusions drawn previously.²⁰⁻²² A weak linear quenching effect is still observed at very high TEMPO concentrations, but is essentially negligible ($I_0/I \sim 2$ at [TEMPO] ~ 200 mM, corresponding to a 40000:1 TEMPO:QD ratio) compared to 4-amino TEMPO, which is most likely due to small ligand displacement effects leading to the formation of surface traps rather than direct electronic quenching effects involving TEMPO itself.

Time-dependent (*TD*) PL quenching experiments for 2.5 nm CdSe QDs are shown in Figure 2.15 (other samples given in Figures 2.17-2.20); for all QD samples, we observed that the overall PL decay rate is essentially unchanged for QDs mixed with TEMPO whereas a strong reduction of the overall QD PL decay rate is seen upon addition of 4-amino TEMPO; these effects are consistent with the *CW* data presented above and will be further discussed in the next section.

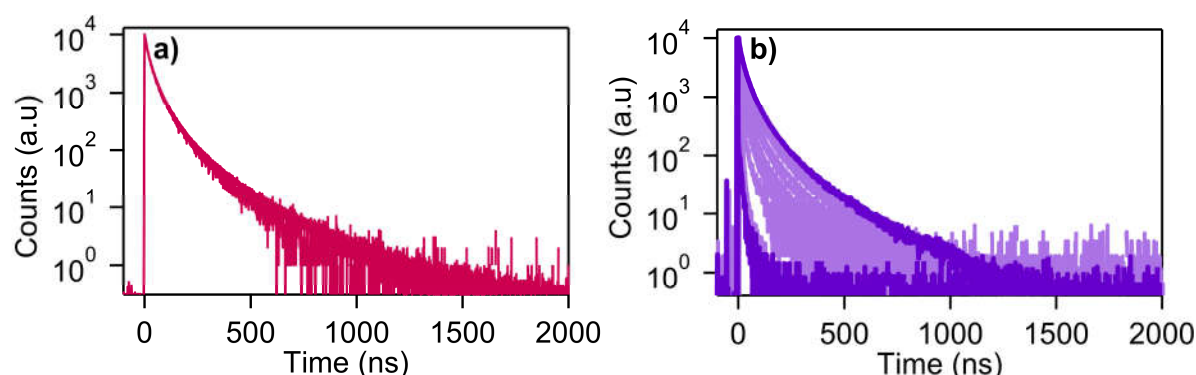


Figure 2.15: PL lifetime decay curves, normalized at $t = 0$ ns for 2.5 nm CdSe QD (sample i) with a) TEMPO (0 - 175 mM) and b) 4-amino TEMPO (0 - 12 mM)

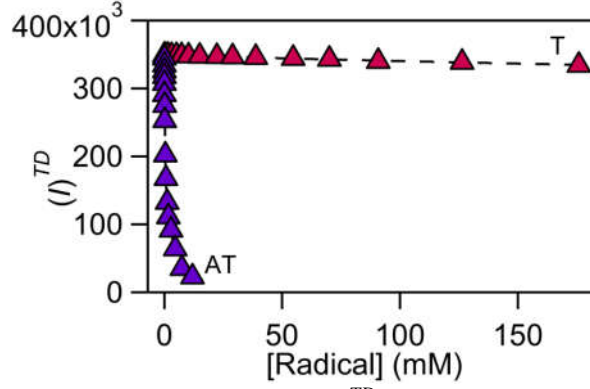


Figure 2.16: Integrated (Normalized) lifetime decay $(I)^{TD}$ for 2.5 nm CdSe QD. The broken lines are guide to the eyes

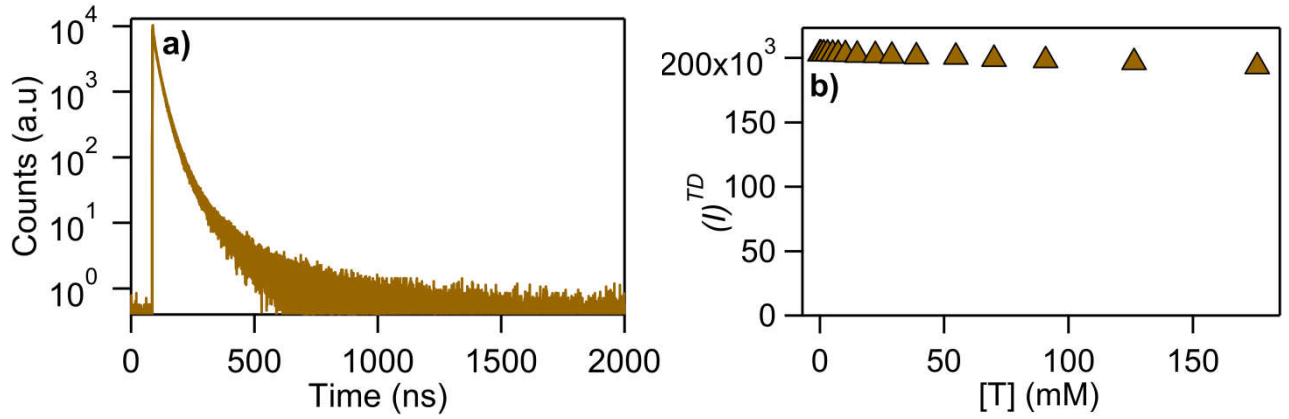


Figure 2.17: PL lifetime decay curve (Normalized) for 3.4 nm CdSe QD with T (panel a). Panel b shows the $(I)^{TD}$

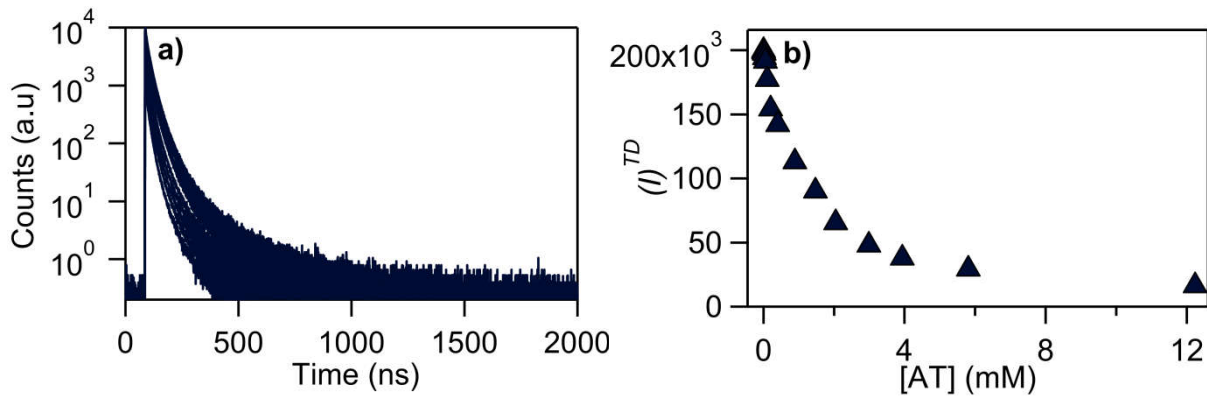


Figure 2.18: PL lifetime decay curve (Normalized) for 3.4 nm CdSe QD with AT (panel a). Panel b shows the $(I)^{TD}$

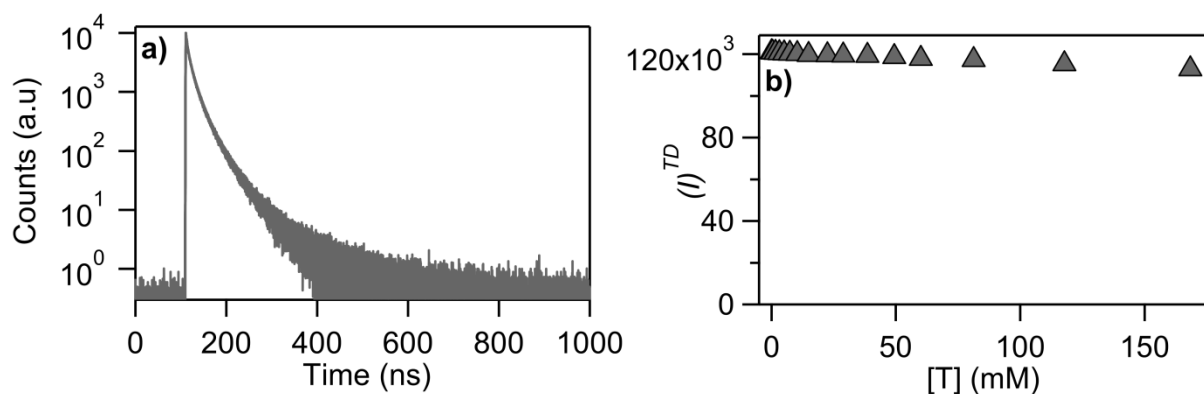


Figure 2.19: PL lifetime decay curve (Normalized) for 5.3 nm CdSe QD with T (panel a). Panel b shows the $(I)^{TD}$

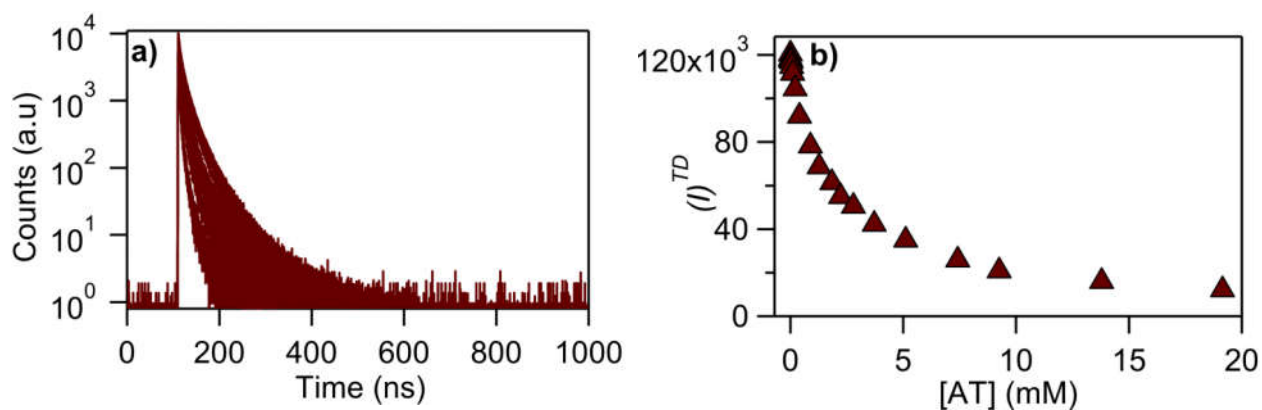


Figure 2.20: PL lifetime decay curve (Normalized) for 5.3 nm CdSe QD with AT (panel a). Panel b shows the $(I)^{TD}$

2.2 B: Mechanistic Analysis of the Quenching Process

Interestingly, the mechanism of the PL quenching of QDs by TEMPO and 4-amino TEMPO has not been determined in previous studies. PL quenching processes can arise from one of two general mechanistic pathways, either energy-transfer or electron-transfer processes. The third mechanism invoked previously, “spin-flip” quenching is not a general path, but merely a subclass of either

energy- or electron transfer processes (such as Dexter energy-transfer processes) -furthermore, the excitonic recombination in chalcogenide QDs being fully spin-allowed, it is unlikely that spin-dependent processes are required for efficient PL. The likelihood of a dipolar energy-transfer mechanism, also known as Förster Resonance Energy-Transfer (FRET)⁴⁷ has been investigated here. For each of the five QD samples listed in Table 2.1, the Förster radius was calculated from the spectral overlap of the donor (CdSe or CdTe QD) PL and acceptor (nitroxide free radical) absorption spectra (Figure 2.8):

$$R_0 = \sqrt[6]{\frac{9 \ln 10 \kappa^2 \Phi_{QD}}{128 \pi^5 N_A \eta^4} J} \dots\dots \text{Eq. (2.7)}$$

where N_A is the Avogadro constant, κ^2 is the orientation factor (taken as the isotropic limit of 2/3 here), ϕ_{QD} is the PL quantum yield of the donor, η is the solvent index of refraction ($\eta_{\text{toluene}}=1.4941$), and J is the spectral overlap between the normalized PL spectrum of the donor and the absorption spectrum (in molar absorptivity units) of the acceptor.

Table 2.2: FRET parameters for different QD - TEMPO/4-amino TEMPO dyads

QD Sample	Overlap Integral, J ($\text{M}^{-1} \cdot \text{cm}^{-1} \cdot \text{nm}^4$)	Forster Radius, R_0 (nm)
i) 2.5 nm CdSe	4.7×10^{11}	1.0 - 1.3
ii) 3.4 nm CdSe	2.1×10^{11}	0.9 - 1.2
iii) 5.3 nm CdSe	0.2×10^{11}	0.6 - 0.8
iv) 3.9 nm CdTe	0.8×10^{11}	0.8 - 1.0
v) 5.0 nm CdTe	-	-

The lower bound value is calculated using Eq. (2.7) directly, assuming that all QDs emit with the average quantum yield given in Table 2.1; the upper-bound value is calculated by assuming that all bright QDs emit with 100% quantum yield, that is, that the average quantum yield values reported in Table 2.1 correspond to the ratio of bright QDs vs. bright + dark QDs.

As listed in Table 2.2, all QD-free radical dyads present small Forster radii, smaller than the average QD radii in each case, indicating that the FRET mechanism is not likely to be responsible for the efficient PL quenching observed here. The rather inefficient FRET between QDs and the nitroxide radicals investigated here is mostly due to the very small extinction coefficient of these radicals, as well as to the small spectral overlap, especially so for larger CdSe QD sizes.

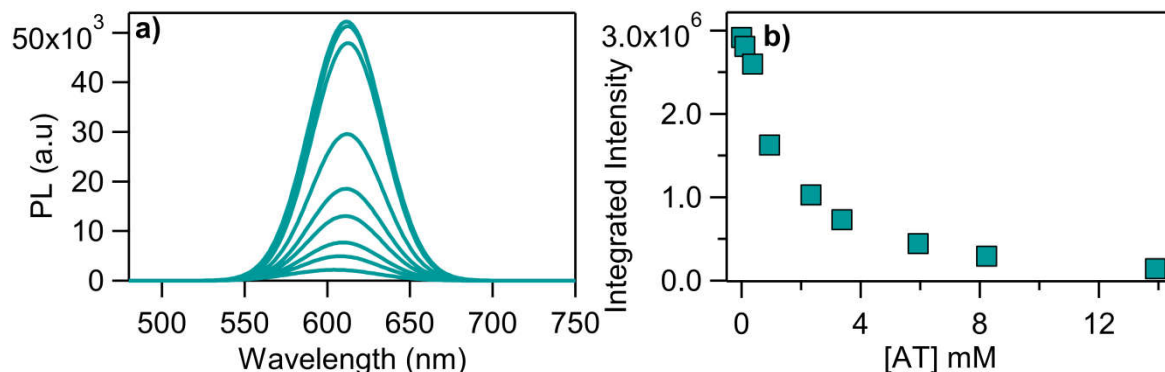


Figure 2.21: PL Intensity of 3.9 nm CdTe QD (corrected) with addition of 4-amino TEMPO (panel a); the corresponding integrated intensities I^{CW} (panel b)

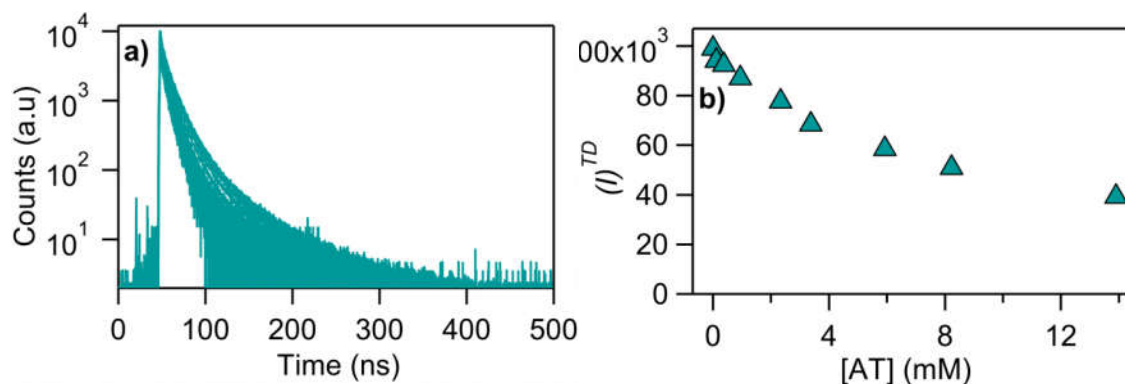


Figure 2.22: PL lifetime decay curve (Normalized) for 3.9 nm CdTe QD with AT (panel a). Panel b shows the $(I)^{TD}$

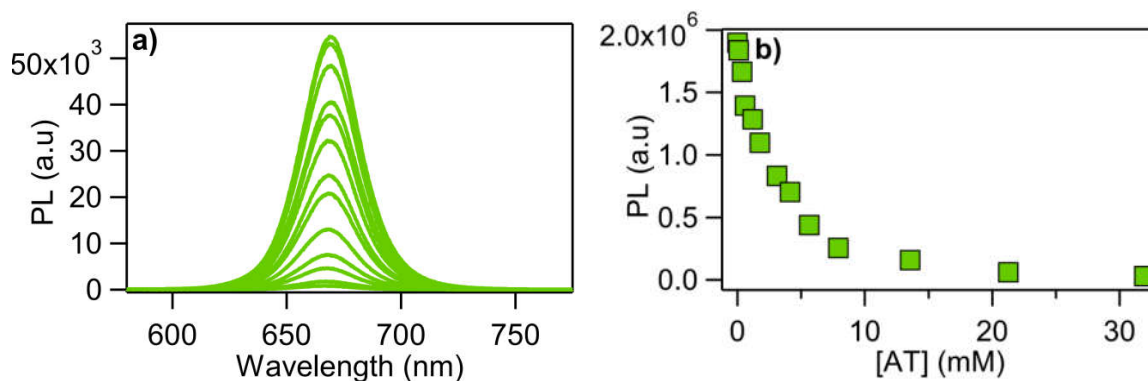


Figure 2.23: PL Intensity of 5.0 nm CdTe QD (corrected) with addition of 4-amino TEMPO (panel a); the corresponding integrated intensities (I^{CW}) (panel b)

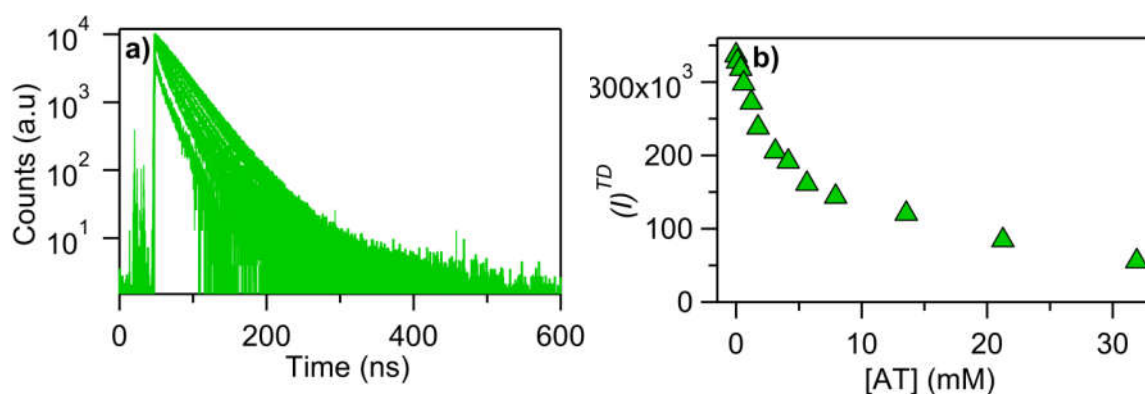


Figure 2.24: PL lifetime decay curve (Normalized) for 5.0 nm CdTe QD with AT (panel a). Panel b shows the (I^{TD})

For large CdTe QD samples, the spectral overlap between the QD PL and the nitroxide absorption spectra is almost negligible, implying that FRET cannot operate in this case. Nevertheless, substantial quenching is still observed for 5.0 nm CdTe QDs and 4-amino TEMPO, clearly demonstrating that FRET cannot be the dominant mechanism for the observed quenching. Because the transition observed around 475 nm is the lowest electronic excited state in these nitroxide radicals,^{48,49} other energy transfer mechanisms not depending on strong spectral overlap (higher multipole or exchange/Dexter energy transfer mechanisms) cannot be invoked here; furthermore,

similar ligands but without the radical functionality (*vide infra*) do not show any signs of PL quenching, leading to the conclusion that an electron-transfer process must be the acting mechanism for the PL quenching of QDs by nitroxide free radicals. The studies to elucidate the nature and direction of the charge-transfer process (oxidative or reductive quenching process) will be discussed in next chapters, however the some details of the general feature of the process can clearly be obtained from the analysis of the time-dependent quenching data.

Mechanistically, electron-transfer quenching processes can be classified according to two limiting scenarios, typically designated as the static and dynamic regimes.⁵⁰ Static quenching processes imply overall quenching rate constants which are several orders of magnitude larger than the intrinsic rate constant for the excited-state decay of the emitter, as well as a pre-association of the quencher to the emitter: in this case, quenching occurs with unity quantum yield, and the CW Stern-Volmer ratio reports on the fraction of the ensemble of emitters which is associated with the quencher. Importantly, the intrinsic rate constant of static quenching processes cannot be extrapolated from PL quenching experiments, as every emitter associated with a quencher becomes experimentally silent (dark). In the dynamic regime, the overall quenching rate constant is of a similar order of magnitude as the intrinsic excited-state lifetime of the emitter; dynamical quenching processes are often associated with diffusion-limited quenching mechanisms, but it is important to note that uncompetitive quenching processes relative to intrinsic recombination (such as would occur for slow interfacial electron-transfer between pre-associated donor and acceptor species) would also lead to a dynamical quenching signature in the absence of diffusion-limited dynamics, which is the only scenario under which intrinsic quenching rate constants could be extracted from Stern-Volmer analyses. The two limiting scenarios are straightforwardly differentiated by time-dependent PL measurements: static quenching processes do not lead to

changes of the ensemble PL decay dynamics (as the fraction of unquenched emitters decays with the same overall rate constant) whereas dynamic quenching processes are characterized by strong variations of the ensemble PL decay dynamics as the concentration of the quencher ($[R]$) is varied. The time-resolved PL decay kinetics of the QD and QD + radicals were analyzed using the kinetic model developed by Tachiya⁵¹⁻⁵³ and co-workers which provides similar results for association constants as the analysis method described below, however the results deviate significantly at higher radical concentrations.

In instances where both static and dynamic are simultaneously acting, both contributions (static and dynamic) to the overall quenching observed in the *CW* experiments can be from the *CW* and *TD* PL measurements:

$$\left(\frac{I_0}{I}\right)^{CW} = \left(\frac{I_0}{I}\right)^{t=0} \times \left(\frac{I_0}{I}\right)^{TD} \dots\dots \text{Eq. (2.8)}$$

Where $(I_0/I)^{TD}$ is obtained by first normalizing the PL decay curves at time zero and then time-integrating the PL decay curves; the static contribution is extracted from the ratio of the *CW* and *TD* Stern-Volmer ratios

$$\left(\frac{I_0}{I}\right)^{dynamic} = \left(\frac{I_0}{I}\right)^{TD} \dots\dots \text{Eq. (2.9)}$$

$$\left(\frac{I_0}{I}\right)^{static} = \left(\frac{I_0}{I}\right)^{CW} / \left(\frac{I_0}{I}\right)^{TD} \dots\dots \text{Eq. (2.10)}$$

The total quenching $(I_0/I)^{CW}$ obtained from CW PL data is generally a product of the static and dynamic components

$$\left(\frac{I_0}{I}\right)^{CW} = (1 + k_q \tau_0 [R])(1 + K_a [R]) \dots\dots \text{Eq. (2.11)}$$

$$K_a = \frac{[QD-R]}{[QD][R]} \dots\dots \text{Eq. (2.12)}$$

where the first term $(1 + k_q \tau_0 [R])$ involves the dynamic quenching and is equal to the slope obtained from the linear plot of $(I_0/I)^{TD}$ vs. quencher concentration since

$$\left(\frac{I_0}{I} \right)^{TD} = (1 + k_q \tau_0 [R]) \dots\dots \text{Eq. (2.13)}$$

and the second term $(1 + K_a [R])$ involves the static quenching component.

k_q is the dynamic quenching constant, and τ_0 is the intrinsic lifetime of the CdSe QD in the absence of any radical. As predicted from equation above, the *CW* quenching plot has a $[R]^2$ dependence that leads to the slight upward curvature of the plot at higher radical (quencher) concentrations (as seen in Figure 2.14 (b)). Thus, the static component can be derived from Eq. (2.14).

$$\left[\frac{\left(\frac{I_0}{I} \right)^{CW}}{\left(\frac{I_0}{I} \right)^{TD}} \right] = (1 + K_a [R]) \dots\dots \text{Eq. (2.14)}$$

The slope of such a plot yields a relative association constant (K_a) for the formation of the complex between the CdSe QDs and the radicals during static quenching. However, factors like the concentration of the native ligands (free/bound to the QD surface) in solution and the equilibrium between QD-native ligands and QD-radicals play an important role in determining the relative rates of static quenching process, and K_a is expected to depend directly on such factors.

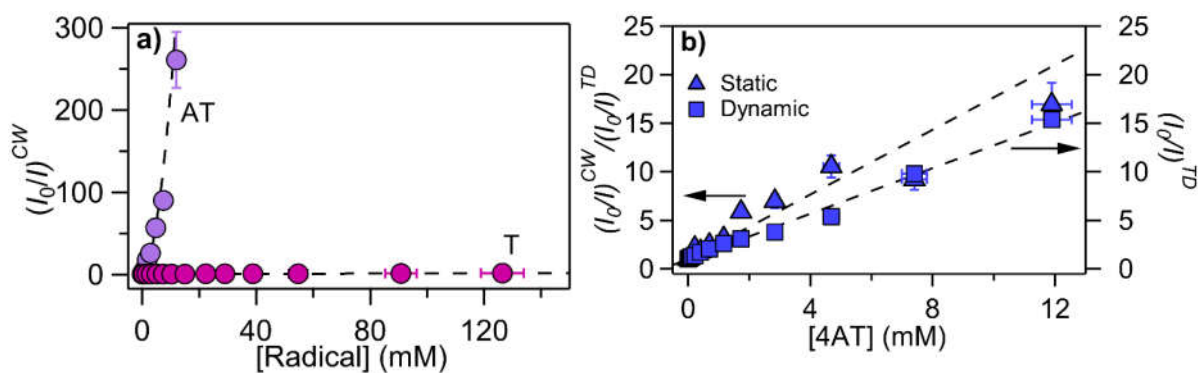


Figure 2.25: Stern-Volmer plots for the PL quenching of 2.5 nm CdSe QDs. (a) Total quenching for both TEMPO and 4-amino TEMPO. (b) Dynamic and static quenching contributions for 4-amino-TEMPO

For illustration, Stern-Volmer quenching analyses are reported in Figure 2.25 (b) for one size of CdSe QDs (2.5 nm). As concluded before, TEMPO is not an efficient quencher and will not be further discussed here. 4-amino TEMPO is seen to be a relatively better quencher, but, overall, it does not outcompete intrinsic recombination. Interestingly, the results in Figure 2.25 (b) show that for this radical both static and dynamic components contribute to the total quenching. The static quenching component observed here implies an ultrafast quenching process (in this case, given the time resolution of our PL setup, <1 ns) whenever the radicals are bound to the surface of the QDs, whereas the dynamic component is readily attributed to diffusion-limited kinetics of unbound quenchers (as listed in Tables).

Table 2.3: Calculated dynamic quenching constant and association constant for quenching of different CdSe QDs with 4-amino TEMPO

Size (nm)	τ_0 (ns)	k_0 (s^{-1})	$k_q \cdot \tau_0$ (M^{-1})	k_q ($M^{-1}s^{-1}$)	K_a (M^{-1})
2.5	28	3.6×10^7	1.2×10^3	4×10^{10}	1.68×10^3
3.4	18	5.7×10^7	1.0×10^3	5×10^{10}	0.52×10^3
5.3	10	10.3×10^7	0.6×10^3	6×10^{10}	0.22×10^3

Table 2.4: Calculated dynamic quenching constant and association constant for quenching of different CdTe QDs with 4-amino TEMPO

Size (nm)	τ_0 (ns)	k_0 (s ⁻¹)	$k_q \cdot \tau_0$ (M ⁻¹)	k_q (M ⁻¹ s ⁻¹)	K_a (M ⁻¹)
3.9	9	10.9×10^7	0.1×10^3	1×10^{10}	0.50×10^3
5.0	33	3.01×10^7	0.2×10^3	6×10^9	0.26×10^3

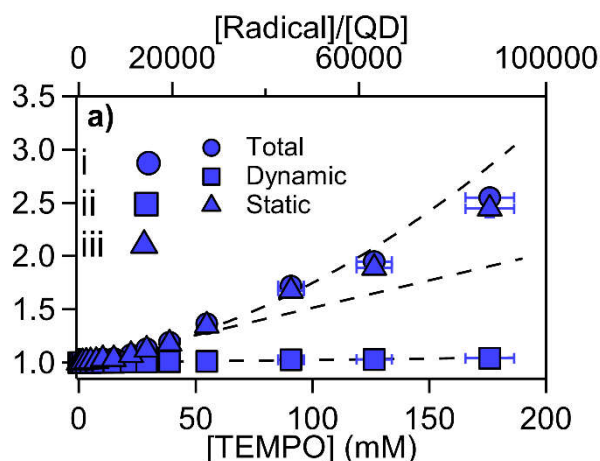


Figure 2.26: Stern-Volmer plots for a) 2.5 nm CdSe QDs and TEMPO

Table 2.5: Calculated dynamic quenching constant and association constant for quenching of different CdSe QDs with TEMPO

Size (nm)	τ_0 (ns)	k_0 (s ⁻¹)	$k_q \cdot \tau_0$ (M ⁻¹)	k_q (M ⁻¹ s ⁻¹)	K_a (M ⁻¹)
2.5	28	3.6×10^7	0.2	9×10^6	8
3.4	18	5.7×10^7	0.3	17×10^6	7
5.3	10	10.3×10^7	0.4	42×10^6	5

[The values for the dynamic quenching constants (for TEMPO) listed in this table should not be given too much meaning because the *TD* PL measurements and the Stern-Volmer plots derived from these measurements are not very reliable given for the very low quenching observed at very high TEMPO concentrations.]

The association constants derived from the static quenching plots are found to be relatively small (Tables 2.3 and 2.4), which is another result seemingly at odds with previous studies on these radicals, where values of $\sim 10^6 \text{ M}^{-1}$ were reported.²¹⁻²³ The values found here are nevertheless consistent with those reported for many other amine-CdSe QDs systems and are in line with the dynamical ligand exchange that is known to occur at the surface of II–VI QDs.⁵⁴⁻⁵⁸ Control experiments were also conducted to compare the quenching efficiency of 4-amino TEMPO against cyclohexylamine (structurally similar to 4-amino TEMPO but without the $\text{NO}\cdot$ free radical) and aniline (Figure 2.27), which shows that the free radical in 4-amino TEMPO is responsible for the quenching process and it also supports the values of K_a reported here for 4-amino TEMPO.



Figure 2.27: Structure of Cyclohexyl amine and Aniline

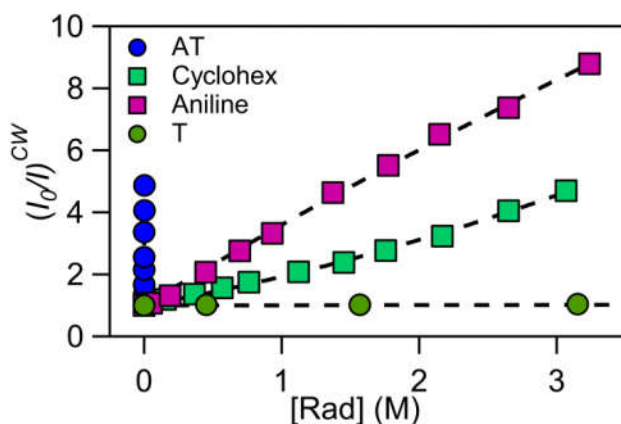


Figure 2.28: Comparison of the Stern-Volmer Plots for steady state PL quenching of 3.4 nm CdSe QDs with 4-amino TEMPO, Cyclohexylamine, Aniline and TEMPO

Finally, the association constants found here are also fully consistent with electron paramagnetic resonance (EPR) data collected on the same samples used for quenching experiments (Figure 2.29), which do not demonstrate the presence of any broadening in the radical spectra, no matter the ratio of [radical]/[QD] used. However, it is observed that in experiments where traces of phosphonic acid was present/introduced in the samples, broadening of the EPR spectra of 4-amino TEMPO was seen to occur, which could perhaps explain the difference between our results and earlier studies^{20,23} where significant EPR broadening was observed and attributed to strong radical-QD binding (the details of the EPR study is provided in the next section).

2.2 C.1: EPR studies of the QD-radical

EPR experiments can be very helpful in determining binding interactions between a paramagnetic species and another molecule because the interaction decreases the tumbling rate and shortens the relaxation time of the radical leading to line broadening in the EPR spectra. Several EPR experiments were conducted on the QD-radical mixtures. Figure 2.29 (panel a) demonstrates that there is no peak broadening of T in presence of QDs (which is expected because T lacks any anchoring group unlike -NH₂ group in AT). Surprisingly, AT-QD mixtures showed no peak broadening as well (even with appreciably high QD concentration; AT:QD = 1:6) in contrast to previously published reports.^{20,23} A number of different QDs (different sizes, QDs with different surface ligand coverage), however none of them induced EPR peak broadening of AT. A tiny broadening was observed for very high QD concentration (Figure 2.29 panel b; AT:QD = 1:250). Since, QD concentration here is exceptionally high and observed broadening is considerably minute, we can safely conclude that EPR measurements predict no strong binding between the CdSe QDs and AT radicals.

In order to investigate the discrepancy with the earlier reports where line broadening was observed for QD-AT mixtures,^{20,23} QDs were synthesized as in these references using tetradecylphosphonic acid (TDPA) ligand. Figure 2.29 (panel c) demonstrates appreciable broadening of AT-QD mixture whenever TDPA is present (whether during synthesis i.e. CdSe synthesized using reference^{20,23} and CdTe used here; or added separately during EPR measurement).

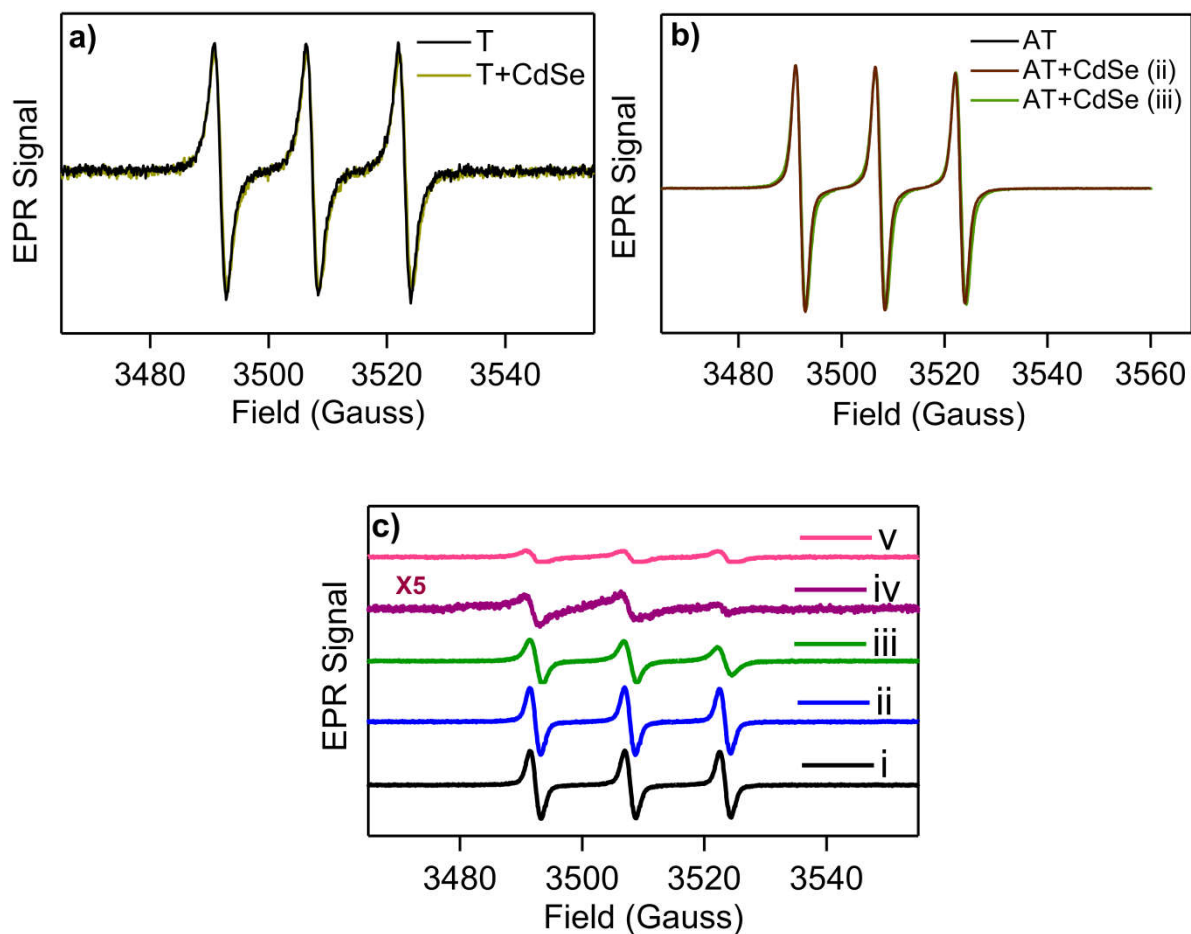


Figure 2.29: Panel a : (i) EPR spectra of T, (ii) T + 3.4 nm CdSe QD in 1:6 ratio. Panel b : (i) EPR spectra of AT, (ii) AT + 3.4 nm CdSe QD in 1:6 ratio, (iii) AT + 3.4 nm CdSe QD (1:250). Panel c : EPR spectra of (i) AT, (ii) AT + 3.4 nm CdSe (used in this experiment; 1:7 ratio), (iii) AT + TDPA ([TDPA] $\sim$ 0.15 M), (iv) AT + 3.2 nm CdSe QD (synthesized using TDPA; 1:5.5 ratio), (v) AT + 3.9 nm CdTe QDs (synthesized using TDPA; 1:5 ratio)

The peak broadening observed in previous reports was attributed to QD-radical binding however the above EPR experiments does not support this claim. The quenching efficiencies of the CdSe QDs prepared with the TDPA was compared to the QDs used in this study. Figure 2.30 shows that the $(I_0/I)^{CW}$ for i : 3.4 nm QDs without TDPA ligands vs. ii : 3.2 nm QDs with TDPA (QY~0.08) are pretty similar. This indicates that though the EPR spectra of AT in presence of these two QDs appear to be different, the difference is not reflected in the quenching behavior. The small difference in the $(I_0/I)^{CW}$ and K_a might be due to the difference in initial QY (discussed later in this chapter). This justifies the fact that the EPR broadening observed before is not related to binding of AT to QDs.

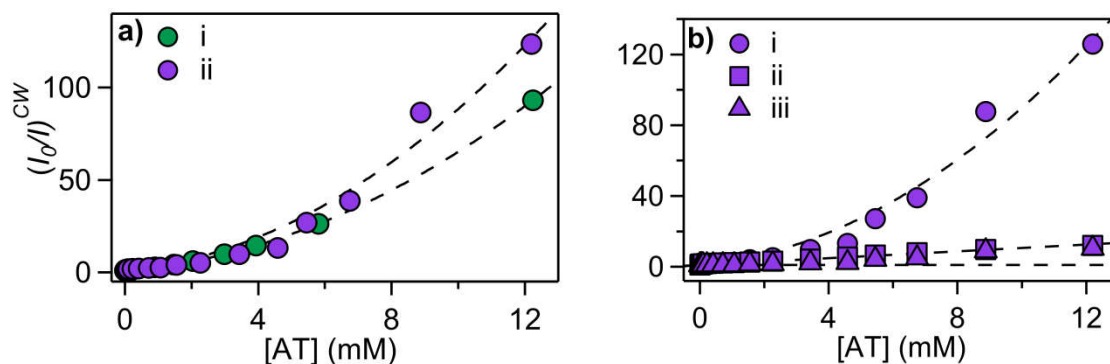


Figure 2.30: Panel a : Comparison of the Stern-Volmer plots for steady state PL quenching (total quenching $(I_0/I)^{CW}$). Panel b : (i) $(I_0/I)^{CW}$, (ii) $(I_0/I)^{TD}$ and (iii) ratio of $(I_0/I)^{CW}$ and $(I_0/I)^{TD}$ for 3.2 nm CdSe QDs + AT (synthesized using TDPA)

Table 2.6: Calculated dynamic quenching constant and association constant for quenching of CdSe QDs (i : without TDPA and ii : with TDPA) with 4-amino TEMPO

Size (nm)	τ_0 (ns)	k_0 (s ⁻¹)	$k_q \cdot \tau_0$ (M ⁻¹)	k_q (M ⁻¹ s ⁻¹)	K_a (M ⁻¹)
i	18	5.6×10^7	0.9×10^3	5×10^{10}	0.52×10^3
ii	15	6.5×10^7	1.0×10^3	6×10^9	0.73×10^3

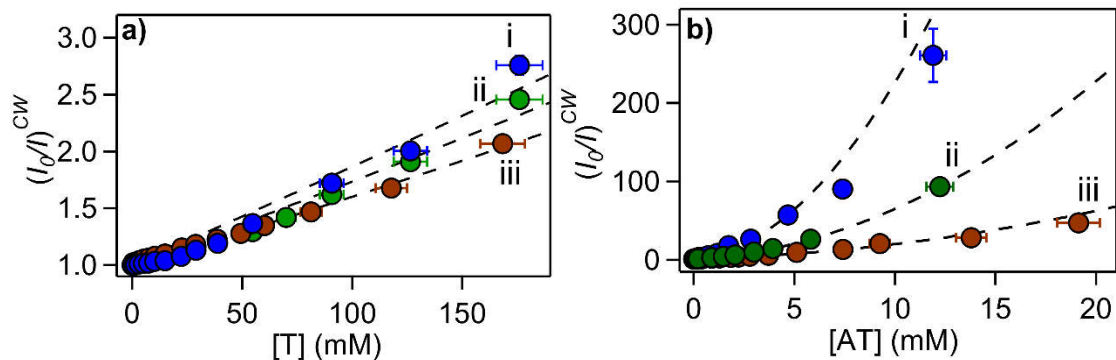


Figure 2.31: Stern-Volmer plots for (a) CdSe QD-TEMPO and (b) CdSe QD-4-amino TEMPO, measured for different QD sizes: i, 2.5 nm; ii, 3.4 nm; and iii, 5.3 nm

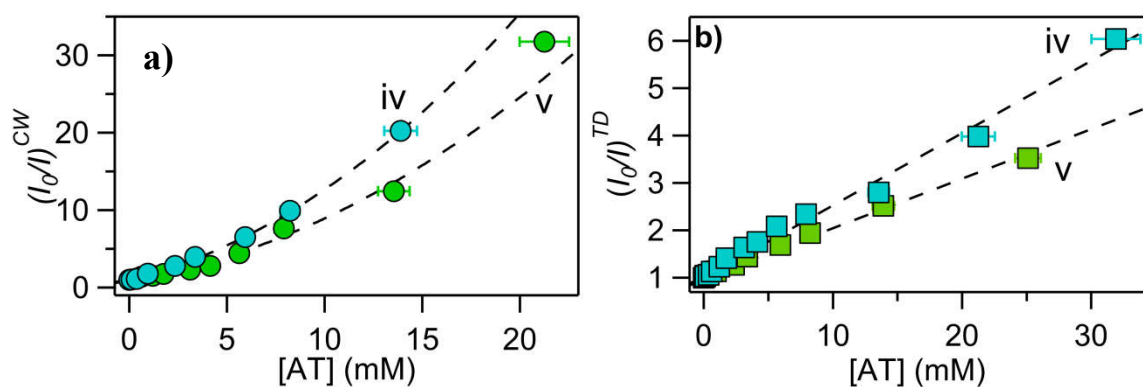


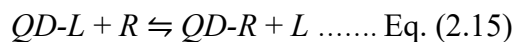
Figure 2.32: Stern-Volmer plots for a) Total quenching $((I_0/I)^{CW})$ and b) dynamic contribution $((I_0/I)^{TD})$ for CdTe QDs and AT (iv : 3.9 nm, v : 5.0 nm)

Finally, a clear size-dependence of the quenching of CdSe and CdTe QDs is observed for 4-amino TEMPO, as shown in Figures 2.31 and 2.32, where smaller QDs are quenched more efficiently by radicals. From Tables 2.3 and 2.4, a large part of this size effect is seen to arise from the static component, where K_a changes by an order of magnitude overall. This observation however cannot directly support or disprove the proposal that quantum-confinement effects play

a role in the interaction between nitroxide radicals and QDs.²⁰⁻²² The size-dependent quenching observed here most likely arises from slight changes in effective surface coverage. The role played by native ligands in the overall quenching efficiency is discussed next.

2.2 C.2: Effect of the Native Ligands

The quenching efficiency of the radical depends on the ease of the radicals reaching the QD surface, which, for ideally passivated QDs, leads to a competition for surface binding with native ligands. As such, a dynamic equilibrium between the native ligands and the radicals must be established



$$K_{eq} = \frac{[QD-R][L]}{[QD-L][R]} = K_a[L] \dots\dots \text{Eq. (2.16)}$$

where L and R denote the native ligands on the QD surface and radicals approaching the QD surface respectively, and $QD-R$ and $QD-L$ denote QDs bound with either type of molecule.

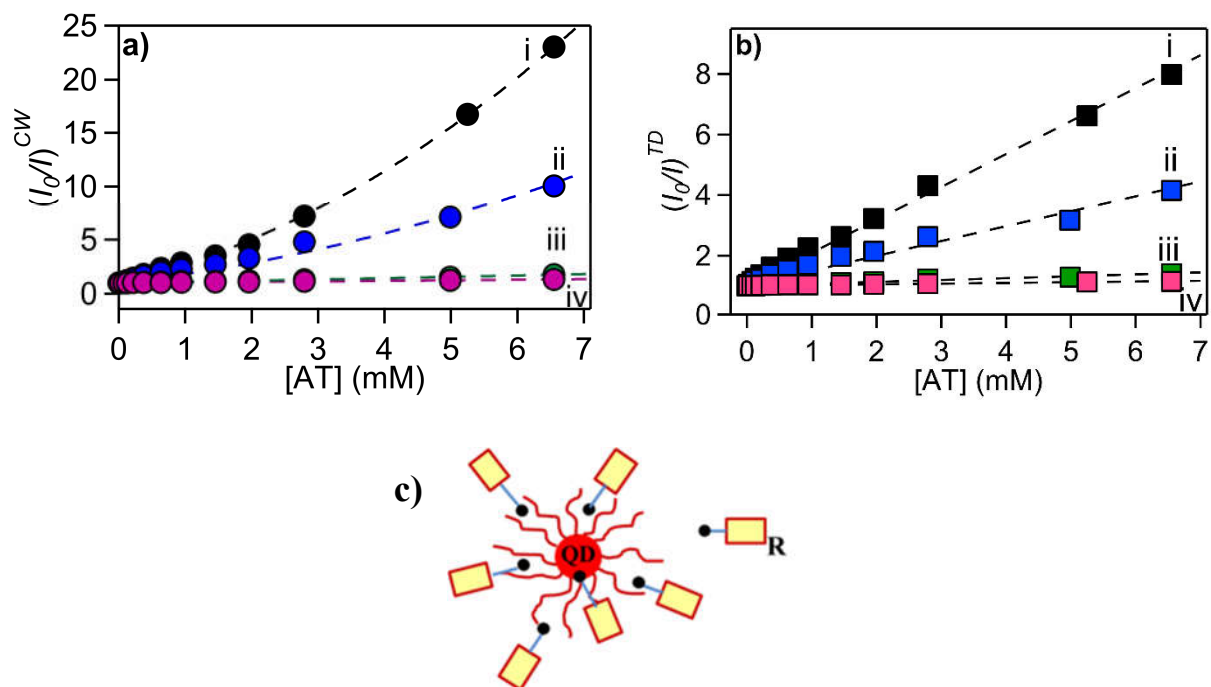


Figure 2.33: Stern-Volmer plots for (a) total PL quenching and (b) dynamic quenching for 4.0 nm CdSe QDs + 4-amino TEMPO with different amounts of native ligands added to the suspension: i, no excess HDA added; ii, 2 mM HDA added; iii, 20 mM HDA added; and iv, 200 mM HDA added. Panel (c): a simple scheme depicting the competition (as evident from Eq. 2.15) between the native ligands on the QD surface and the radicals approaching the QD-surface during the quenching event

Table 2.7: Calculated dynamic quenching constant and association constant for quenching of different CdSe QDs with 4-amino TEMPO in presence of excess HDA

[HDA] (mM)	QY	τ_0 (ns)	k_0 (s ⁻¹)	$k_q \cdot \tau_0$ (M ⁻¹)	k_q (M ⁻¹ s ⁻¹)	K_a (M ⁻¹)
0	0.21	21	4.9×10^7	1.2×10^3	6×10^{10}	0.25×10^3
2	0.23	22	4.6×10^7	0.5×10^3	2×10^{10}	0.23×10^3
20	0.24	22	4.6×10^7	0.6×10^2	3×10^9	0.04×10^3
200	0.24	22	4.6×10^7	0.3×10^2	1×10^9	0.02×10^3

In order to study the effect of this equilibrium, an experiment was designed where the quenching behavior of 4-amino TEMPO radical was investigated after addition of excess HDA (native ligands for the CdSe QDs used in this work) to the QD solution.

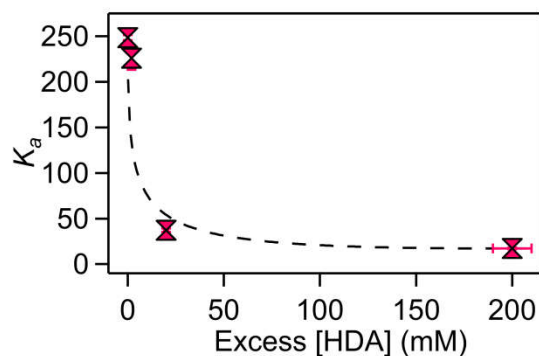


Figure 2.34: Association constant vs. excess ligand (HDA) concentration

Figure 2.33 shows that the quenching becomes less and less efficient as the concentration of free native ligands increases, pushing the equilibrium shown in Eq. (2.15) to the left; the effects of the free ligands on the static and dynamic parameters are given in Table 2.7 which simply shows, as expected, that the binding constant can indeed be modulated by over an order of magnitude by changing the free ligand concentration. Lesser effects are also seen in the dynamic components, which are very likely arising from changes to the viscosity of the medium at high aliphatic amine concentrations (>100 mM). Importantly, we note that the addition of excess HDA does not affect the intrinsic QD PL lifetime or the absolute quantum yields (Table 2.7) significantly, showing that the addition of excess native ligands does not perturb the nature of the QD surface.

The QY of QDs were also found to affect their quenching behavior. Figure 2.35 compares the quenching behavior of AT on CdSe QDs (4.0 nm) with widely different QY. The QD with higher QY (0.7) has comparatively lower binding constant. This could be result of higher ligand concentration (bound to surface and free ligands in solution) in a higher QY sample (better ligand passivation of QD surface; also evident from the significantly longer lifetime of the particular sample). Again, the difference in dynamic component could be due to the higher viscosity of a QD sample with greater ligand concentration.

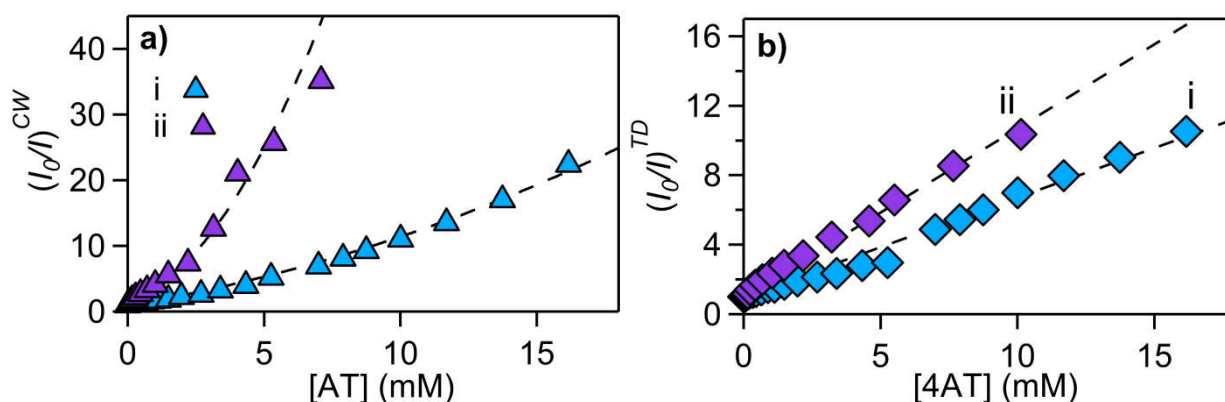


Figure 2.35: Stern-Volmer plots for total PL quenching ($(I_0/I)^{CW}$, panel a) and dynamic quenching ($(I_0/I)^{TD}$, panel b) for 4.0 nm CdSe QDs + AT, i : absolute QY= 0.7, ii : absolute QY = 0.2

Table 2.8: Calculated dynamic quenching constant and association constant for quenching of 4.0 nm CdSe QDs with 4-amino TEMPO

QY	τ_0 (ns)	k_0 (s ⁻¹)	$k_q \cdot \tau_0$ (M ⁻¹)	k_q (M ⁻¹ s ⁻¹)	K_a (M ⁻¹)
0.2	19	5.3×10^7	1.0×10^3	5×10^{10}	0.55×10^3
0.7	29	3.4×10^7	0.6×10^3	2×10^{10}	0.03×10^3

Importantly, at very high HDA concentrations (>100 mM), the static component can be practically eliminated, as evident from Fig. 2.36 (300 mM excess HDA), where the Y axis reports the efficiency of the static quenching and the X axis is now reported in $[R]/[QD]$ ratio units. Interestingly, under this regime, the Stern-Volmer static quenching rate is clearly independent of the QD size, which further supports the claim that quantum-confinement effects are marginally involved, if at all, in the overall quenching process.

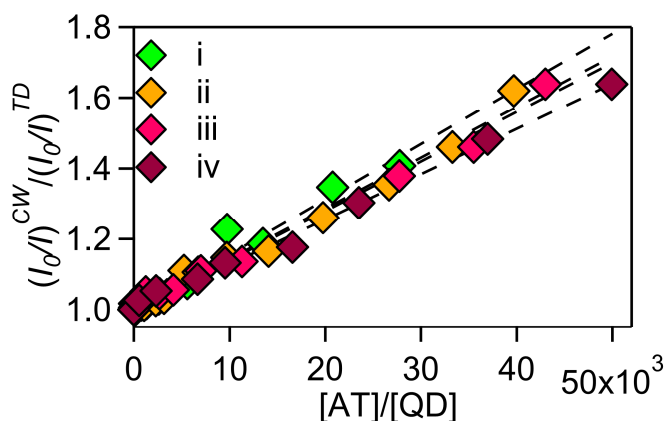


Figure 2.36: Static Stern-Volmer analysis for CdSe QDs + 4-amino TEMPO with 300 mM excess HDA, for different QD diameters: i, 2.8 nm; ii, 3.6 nm; iii, 4.3 nm; and iv, 7.2 nm

From this observation and using NMR spectroscopy (discussed in the next section) to directly quantitate the concentrations of the free (i.e., unbound) ligands in solution, the effective equilibrium constants (K_a) obtained from the Stern-Volmer analysis in Table 2.3 can be further converted into the overall equilibrium constants given by Eq. 2.24 (K).

2.2 D: Analysis of the Equilibrium Constant

As discussed earlier, the quenching efficiency of the radical depends on how easily the radicals can reach the QD surface, which results in a competition for surface binding with native ligands. The dynamic equilibrium that must be established between the native ligands and the radicals is given in Eq. (2.15).

The equilibrium constant for this dynamic equilibrium would be:

$$K = \frac{[QD-R][L]}{[QD-L][R]} \quad \text{..... Eq. (2.17)}$$

This can be correlated with the PL intensity,

$$[F]_0 = \text{tot. fluorophore concentration} = [QD-R] + [QD-L] \quad \text{..... Eq. (2.18)}$$

$$\text{Fraction of remaining fluorescence} = \text{fraction of un-complexed fluorophore} = [F]/[F]_0 \quad \text{.....Eq. (2.19)}$$

$$K = \frac{([F] - [F]_0)[L]}{[F][R]} \quad \text{..... Eq. (2.20)}$$

Rearranging,

$$\frac{I_0}{I} = \frac{[F]_0}{[F]} = 1 + K \frac{[R]}{[L]} = 1 + K_a [R] \quad \text{..... Eq. (2.21)}$$

The relative association constant K_a obtained from the Stern Volmer plot (static quenching) has the free ligand concentration in QD solution ($[L]$) embedded in it.

$$K_a = \frac{K}{[L]} \quad \text{..... Eq. (2.22)}$$

The equilibrium constant K can be determined from the experiment where excess HDA is added to the QD solution before conducting the quenching experiment. This experiment was carried out for the QD sizes (2.4 nm, 3.5 nm and 5.0 nm) where the PL quenching was measured in presence of 0 mM (no excess ligands were added), 2.5 mM, 5 mM, 10 mM and 20 mM HDA.

$$\frac{1}{K_a} = \frac{[L]}{K} \quad \text{..... Eq. (2.23)}$$

$$\frac{1}{K_a} = \frac{a + x}{K} \quad \text{..... Eq. (2.24)}$$

(a = free ligand concentration in the QD solution and x = added excess free ligands during the experiment). Thus, by plotting the measured $1/K_a$ (K_a obtained from the Stern-Volmer plots of the total quenching and dynamic quenching as explained earlier) vs. x for three different QD sizes, the equilibrium constant (K) can be obtained (Table 2.9). The free ligand concentration in solution (a) has been determined using NMR spectroscopy of the individual QD solutions.

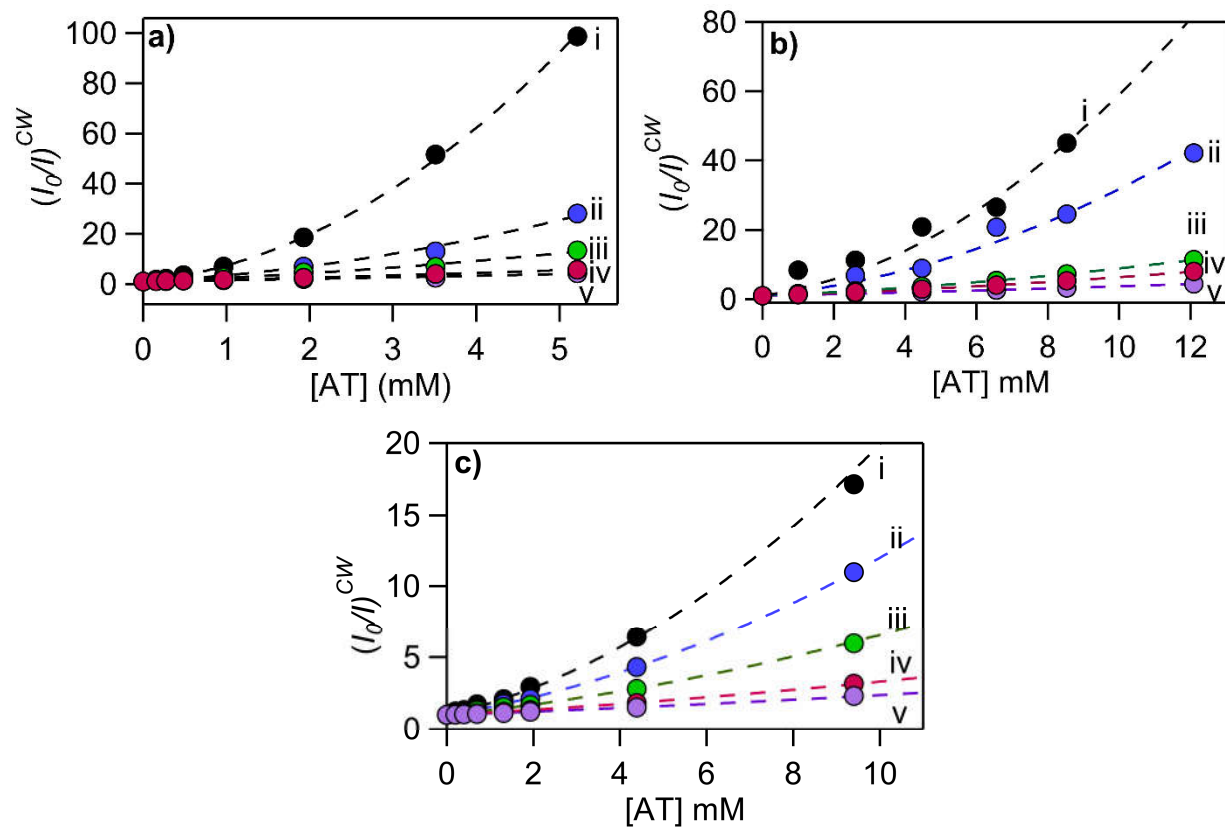


Figure 2.37: Stern-Volmer (total PL quenching) plots for CdSe QDs + 4-amino TEMPO
a) 2.4 nm, b) 3.5 nm and c) 5.0 nm with different amounts of native ligands added to the QD suspension. i : no excess HDA added, ii : 2.5 mM HDA added, iii : 5 mM HDA added, iv : 10 mM HDA added and v: 20 mM HDA added

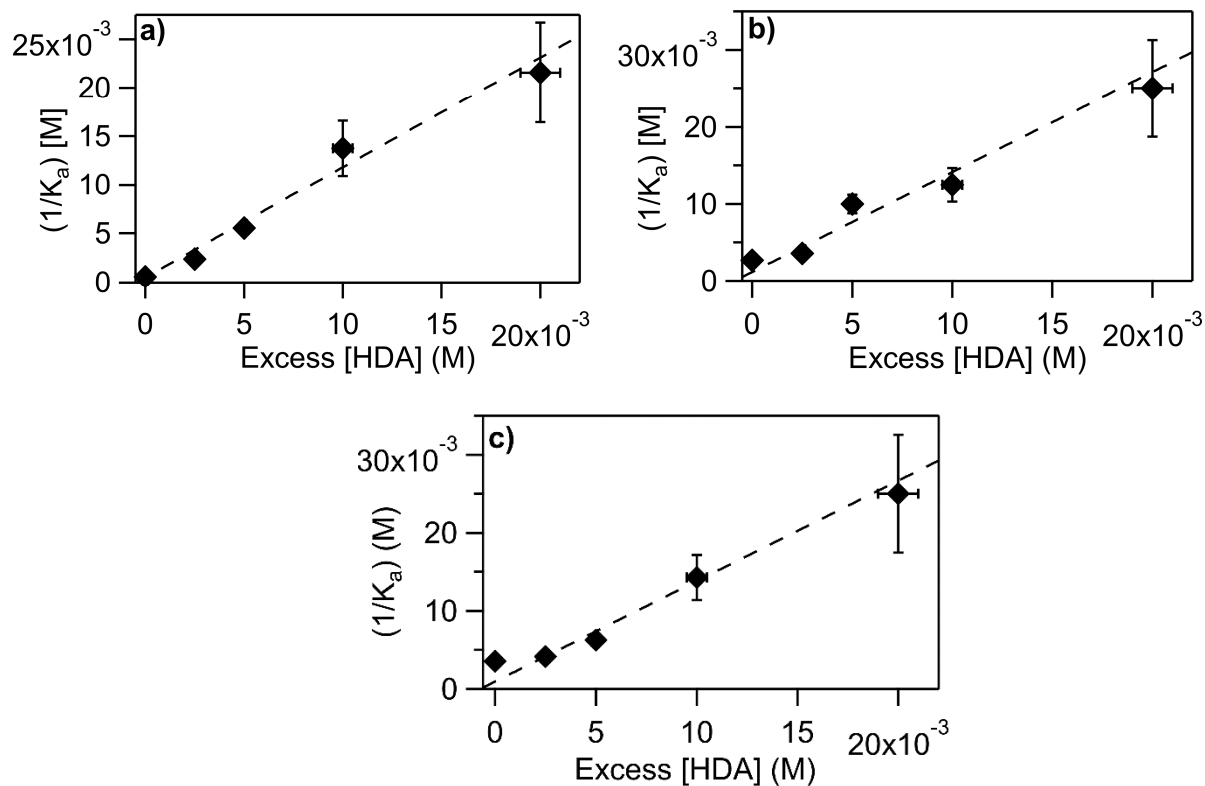


Figure 2.38: Plot of $1/K_a$ vs. excess [HDA] added for CdSe QDs + 4-amino TEMPO a) 2.4 nm, b) 3.5 nm and c) 5.0 nm

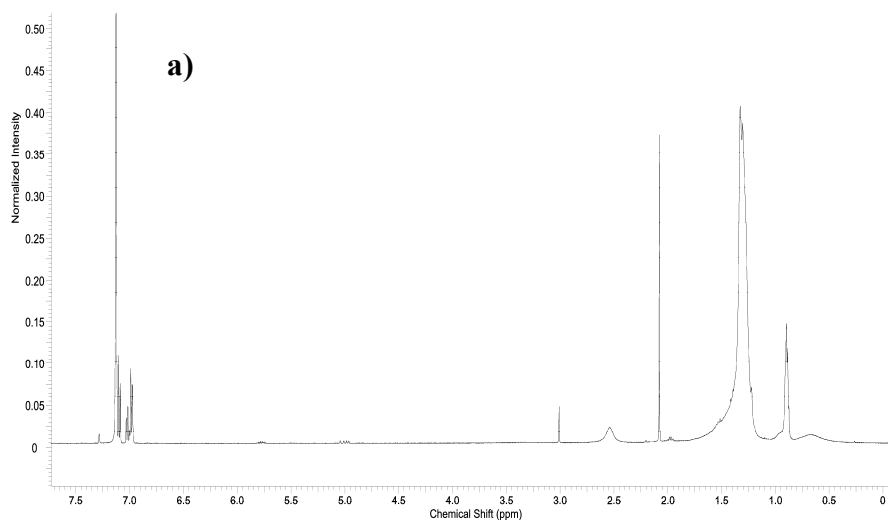


Figure 2.39: NMR spectra of the CdSe QDs in C_6D_6 : a) 70 μM 2.4 nm, b) 40 μM 3.5 nm, c) 45 μM 5.3 nm

Figure 2.39 (Cont'd)

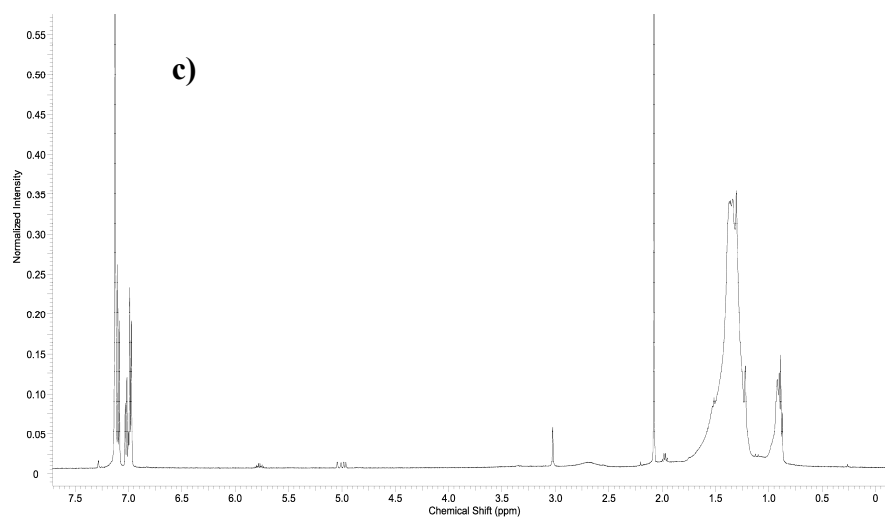
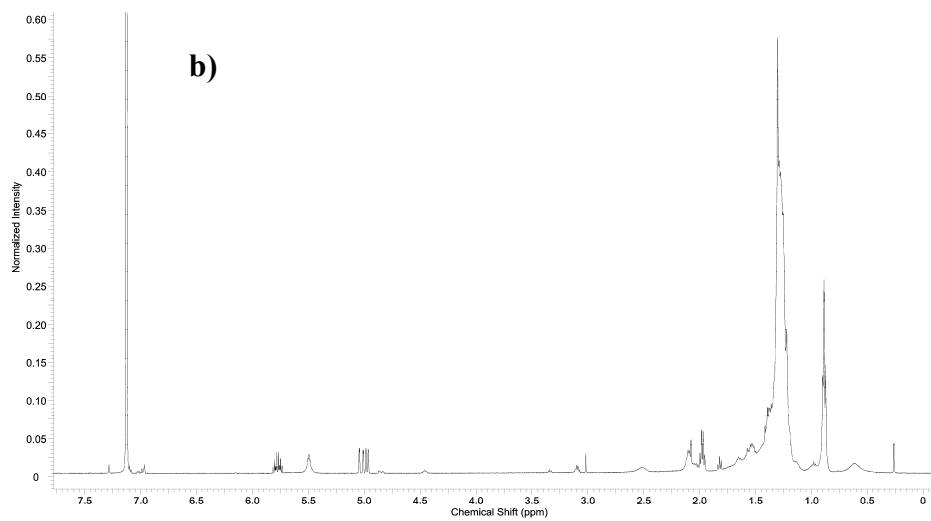




Figure 2.40: NMR tubes containing the different QD solutions in deuterated benzene

The peak ~ 7.2 ppm is due to the solvent, the peak at 2.09 ppm and 7 ppm is from the residual toluene. The ligand peaks are at 2.5 ppm (HDA), 5.0 and 5.8 ppm (ODE) and 5.5 ppm (OAm). The peak at ~ 0.9 ppm is due to the terminal -Me groups and the one ~ 1.2 ppm is from the -CH₂ group from all the free ligands in QD solution. The peak at 0.9 ppm was integrated and the concentration was determined from the instrumental standard calibration. The ligand concentrations were calculated to be 15 mM, 18 mM and 22 mM for the 70 μ M 2.4 nm, 40 μ M 3.5 nm and 45 μ M 5.0 nm CdSe QD solutions used for the measurement. The free ligand concentration in the QD solutions for the quenching experiment was calculated (Table 2.9). The CdSe concentrations used for the quenching experiment was 2.1 μ M, 2 μ M and 1.5 μ M for 2.4 nm, 3.5 nm and 5.0 nm respectively.

Table 2.9: Calculated equilibrium constant for quenching of CdSe QDs with 4-amino TEMPO

Size (nm)	a (mM)	K
	[from NMR]	
2.4	0.45	0.88 (± 0.03)
3.5	0.90	0.77 (± 0.05)
5.0	0.74	0.78 (± 0.01)

From the free ligand concentration present in the QD solutions and the relative association constant (K_a) obtained from the Stern-Volmer analysis of the PL quenching measurements, the overall equilibrium constants K can be calculated using Eq. 2.24. As reported in Table 2.9, for all QD sizes $K \sim 0.8$. This illustrates that amino-functionalized nitroxide radicals have very similar binding affinities as those of the HDA ligands used to cap the quantum dots in this study and that NC size impacts very little, if at all, the equilibrium dynamics studied here.

2.3: Conclusion

In this chapter, the details of the PL quenching of CdSe and CdTe QDs with two nitroxide free radicals, TEMPO and 4-amino TEMPO have been investigated. It has been demonstrated that 4-amino TEMPO is indeed an efficient PL quencher, but it is simultaneously limited by slow diffusion kinetics and low surface binding affinities whereas TEMPO does not quench the QDs appreciably. The key feature of this work was the use of the TD PL studies to investigate the details of this quenching process. The results also highlight that the nature of ligand passivation of the QD surface is a very important factor in controlling the interaction of nitroxide radicals with QDs, a key aspect to consider in future applications involving such dyads.

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Chapter 3: Temperature dependence of Photoluminescence

Quenching of Colloidal CdSe by Nitroxide Free Radicals

3.1A: Motivation behind this work

Probing the temperature dependence of the PL quenching of QD-Radical mixtures can provide additional information regarding their mechanism. Temperature-dependent photoluminescence (TDPL) is one of the most fundamental and technologically important tools for characterizing NCs.¹⁻⁹ Based on PL spectra measured at different temperatures, an understanding of the carrier dynamics and surface defects giving rise to non radiative processes can be achieved. However, before understanding the temperature effect on the QD-Radical PL, it is important to investigate the temperature dependent PL dynamics of the QD itself. Hence, the effect of lowering temperature on the CdSe QD itself, is first discussed in details in this chapter.

3.1B: PL dynamics of CdSe QDs

For the QD-Radical interaction, the photo-generated excitons in the QDs need to dissociate and transfer charge carriers to the radicals in a controlled manner; however, this process can be perturbed by the influence of surface-localized states that trap carriers. In QDs, perturbations due to traps are substantial because of the significant surface-to-volume ratios typical of small colloids.^{10,11} Surface sites can act as charge acceptors that dissociate excitons and therefore reduce the PL QY. Additionally, changes in the solvent or surface ligands used to passivate the NC surface have been found to affect these surface traps and thereby influence steady-state^{12,13} and time-resolved^{14,15} NC PL. Properties intrinsic to NC excitons have been examined in detail¹⁶⁻¹⁸ but comparatively a lot is unclear about the interplay between intrinsic excitons and surface states. The

precise number of trap sites in a NC is highly inhomogeneous and sample dependent; however an approximate upper limit to this number can be obtained by calculating the number of atoms near the surface in a wurtzite NC.¹⁹

NC trap states are generally dark, so their presence can only be probed indirectly from PL signals.²⁰ Typically, the time-resolved NC PL is multi-exponential and often sustains for ten to hundred times longer than the 20-ns lifetime of the optically active exciton states from which PL arises.^{14,15,21} As discussed in Chapter 1 (Section 1.7 B), a “dark” exciton state with a PL lifetime of $\sim 1 \mu\text{s}$ ²² is present $\sim 20 \text{ meV}$ below the bright exciton in wurtzite CdSe NCs, however this state does not account for the long PL decay tail observed for QD at room temperature, due to Boltzmann statistics. Instead, the non-exponential PL decays indicate contribution of surface-related trap states in the relaxation process.

3.2: Experimental Methods

3.2 A: Low Temperature PL measurements

The low temperature PL measurements were conducted on 2-4 μM CdSe QD suspension in toluene. The suspensions was placed inside a EPR tube and the tube was mounted on to the probe using a cryogenic laboratory tape and introduced into a nitrogen/ helium gas continuous-flow cryostat (Janis Research Company). The temperature was varied from 78 K to 300 K (for N_2 cooling) and 5K to 300K (for Helium cooling) and was controlled using a temperature controller (Lake Shore 335). As the desired temperature was reached, the QD solution was left at that particular temperature for 15 minutes before measuring the PL intensity and decay.

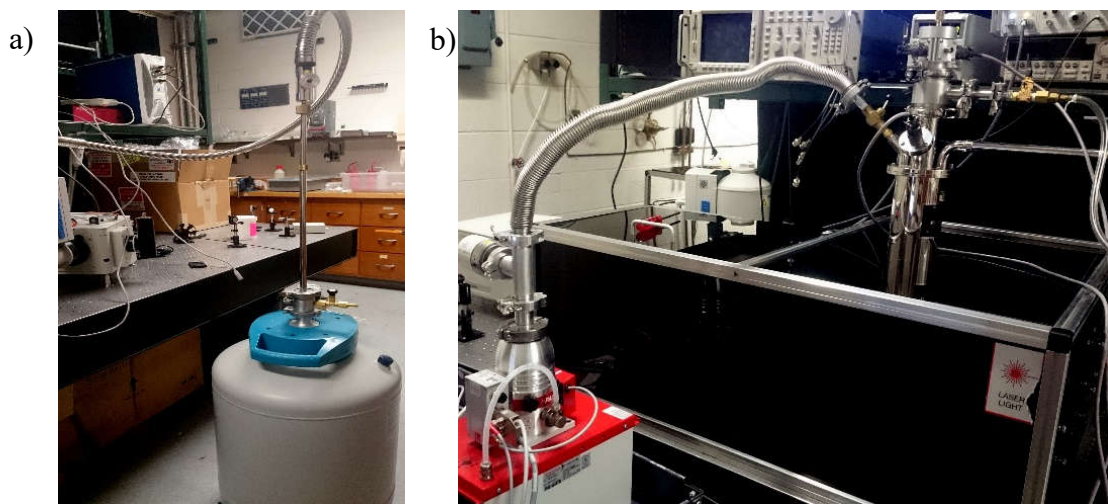


Figure 3.1: The liq. N₂ dewar connected to the cryostat (panel a), the QD solution inserted in the cryostat and connected to a vacuum pump (panel b)

3.2 B: Transient Absorption measurements

Transient Absorbance (TA) measurements were performed on the CdSe solutions in a 1 cm cuvette and the solutions were typically prepared such that the optical densities were ~ 0.2 at 3.1 eV. The CdSe samples in toluene were excited with near-band-edge photons generated by doubling the signal pulses of a homemade, β -BaB₂O₃ (BBO-) based optical parametric amplifier pumped by the 800 nm output of a 1-kHz Ti:Sapphire laser amplifier (Spectra Physics Spitfire PRO-XP). The probe pulses consisted of a super-continuum generated by focusing ~ 1 μ J of the laser output in a 1-mm-long c-cut sapphire crystal. The continuum was compressed for minimum dispersion in the vicinity of 2.14 eV with a pair of Brewster-angle fused silica prisms. Broadband detection was performed with a CCD spectrometer (Ocean Optics USB2000+, 600 lines/mm grating, 50 μ m entrance slit, 2 nm resolution) synchronized to an optical chopper that modulated the pump pulses

on and off with a 12 ms period. The TA instrument response is ~ 130 fs. Residual dispersion across the probe spectrum was determined by acquiring TA spectra in a BBO crystal placed at the sample position. In all TA measurements, the pump fluence was kept low, in order to ensure the measurements were conducted in the single-exciton region.

3.2 C: Up-conversion PL measurements

In up-conversion photoluminescence (uPL) measurements, CdSe QD samples were excited with 400 nm photons generated by doubling the 800 nm, 100-fs output from a 1-kHz Ti:sapphire laser amplifier (Spectra Physics Spitfire PRO-XP) with a β -BaB₂O₃ (BBO) crystal. Another delay-variable 800 nm output from the Ti:sapphire laser was mixed in another BBO crystal with the PL from samples to generate a sum-frequency signal in the UV region. The sum-frequency signal was filtered by two UV short pass filters (Thorlabs FGUV11), and detected by a liquid N₂ cooled CCD mounted on a monochromator (Acton SP-300i) with a grating of the groove = 1200/mm. The time resolution of the whole setup was less than 1 ps. In all uPL measurements, the pump fluence was kept in the single-exciton region, which avoid the effects of fast Auger recombination.

3.2 D: Chemicals and Methods used

The CdSe QDs used in these experiments have been synthesized and annealed with TOP, TOPO and HDA as described in Chapter 2. The average PL lifetime was calculated using the stretched exponential function (Eqs. 2.1 and 2.2)

3.3: Experimental Results

3.3 A: Change in the nature of PL spectra at low temperatures

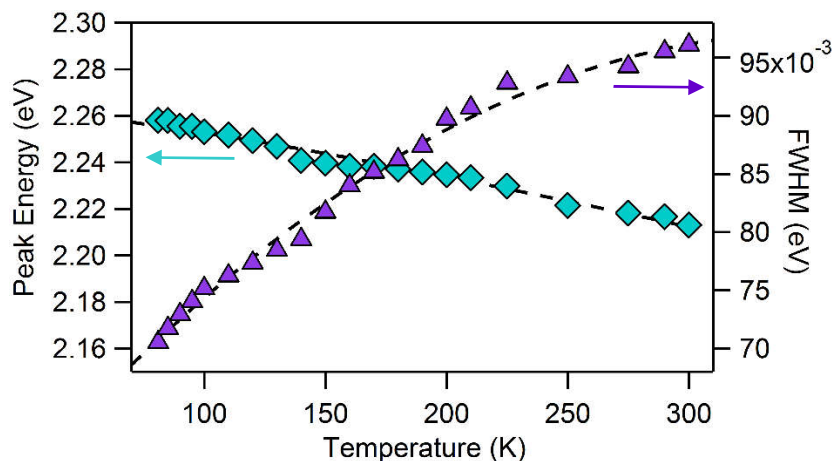


Figure 3.2: Peak energy and FWHM of the band edge PL of 3.3 nm CdSe QDs with temperature

The PL spectra at low temperatures are similar to that at room temperature, however the full width at half maximum (FWHM) of the band edge PL spectra decreases from 0.096 eV (300 K) to 0.07 eV (81 K) as depicted in Figure 3.2. The exciton peak also blue shifts from 2.22 eV (300 K) to 2.26 eV (81 K). The blue shift of the exciton peak energy is due to the temperature dependence of the band gap and is found to be similar to bulk CdSe.^{23,24} Other sizes of CdSe QDs used in this study also portray similar behavior (Figure 3.3).

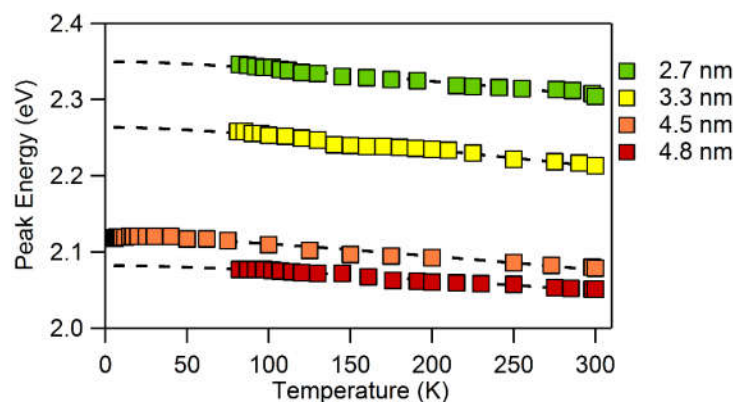


Figure 3.3: Peak energy of the band edge PL of different CdSe QDs with temperature

Here, the exciton PL linewidth is due to inhomogeneous broadening (size and shape inhomogeneities in the QD ensemble) and homogeneous broadening (due to exciton-phonon interactions) and is hence temperature dependent.²³

3.3 B: Change in the Average Lifetime of QDs with Temperature

Two regimes (A and B) are observed in the PL lifetime plot vs. temperature for all the CdSe QDs investigated here (2.7 nm, 3.3 nm and 4.5 nm, Figures. 3.4, 3.5 and 3.6 panel ii). The behavior of PL Intensity and PL lifetime is reproducible and fully reversible. The behavior has been tested for heating and cooling cycles and have been found to be identical (no hysteresis has been observed).

In Regime A, as the temperature is increased from ~100 K to ~240 K, the PL intensity decreases (Figures 3.4, 3.5 and 3.6 panel i), the PL decay becomes faster and more and more non-exponential, indicating thermally activated exciton trapping and non-radiative decay. This region is often known as the “quenching regime”.^{25,26} Regime B depicts a rather interesting observation, as the temperature is increased from ~250 K to ~300 K, the PL intensity increases and along with it the lifetime of the QDs are also found to increase.

Decrease in PL intensity (PL quenching) with increase in temperature is a common occurrence in QDs, whether in colloidal form or in solvent-free systems such as polymer matrices or solid films, and is a result of the thermally-activated carrier trapping as reported earlier in literature.^{23,27,28} However, the PL enhancement observed in Regime B with increasing temperature is unexpected. This effect was first explored in details by the Meijerink group in 2004 and was named as Low Temperature Anti-quenching (LTAQ).^{26,29} The onset of PL recovery is found to be strongly dependent on the nature of the surface ligands in the QD. LTAQ is a result of a phase transition in the capping layer allowing surface reconstruction owing to the subtle displacement of the surface Cd and Se atoms which in turn removes the surface trap sites from the band gap.³⁰ The alkylamines (HDA) used for capping the CdSe QDs used in this work has been reported to undergo a phase transition that allows more flexibility in their tilt angles.²⁶ This allows vertical displacement of the surface atoms bound to the polar head group of the ligands and hence surface repair of the CdSe QD surface, resulting in PL enhancement.

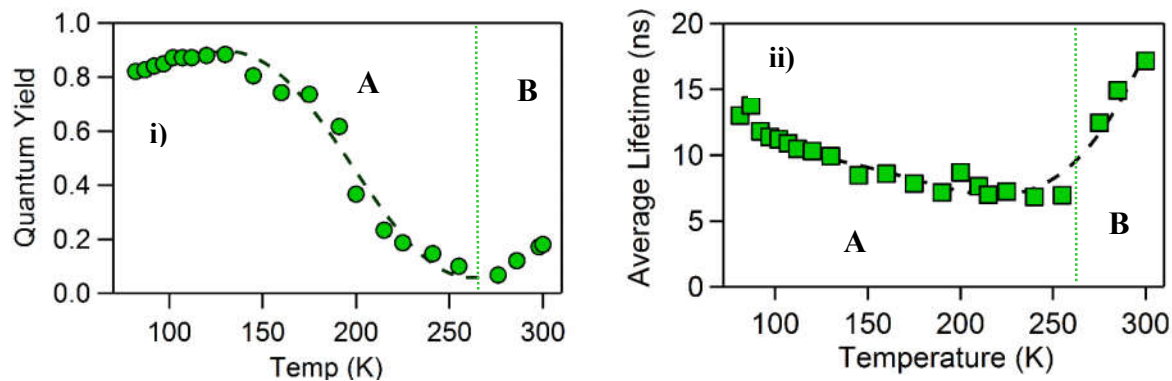


Figure 3.4: Change in PL QY of 2.7 nm CdSe QDs (panel i) and change in average PL lifetime (panel ii) with temperature. The QY at room temperature is 0.18

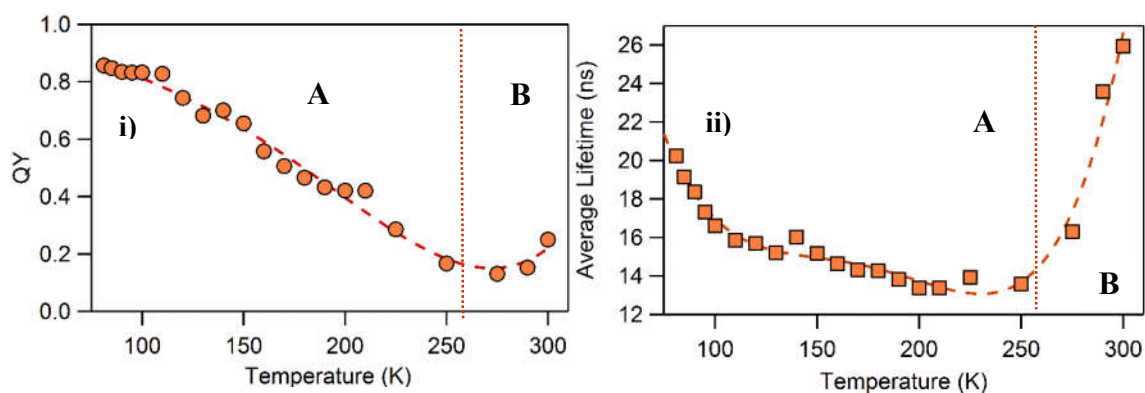


Figure 3.5: Change in PL QY of 3.3 nm CdSe QDs (panel i) and change in average PL lifetime (panel ii) with temperature (room temperature QY ~ 0.25)

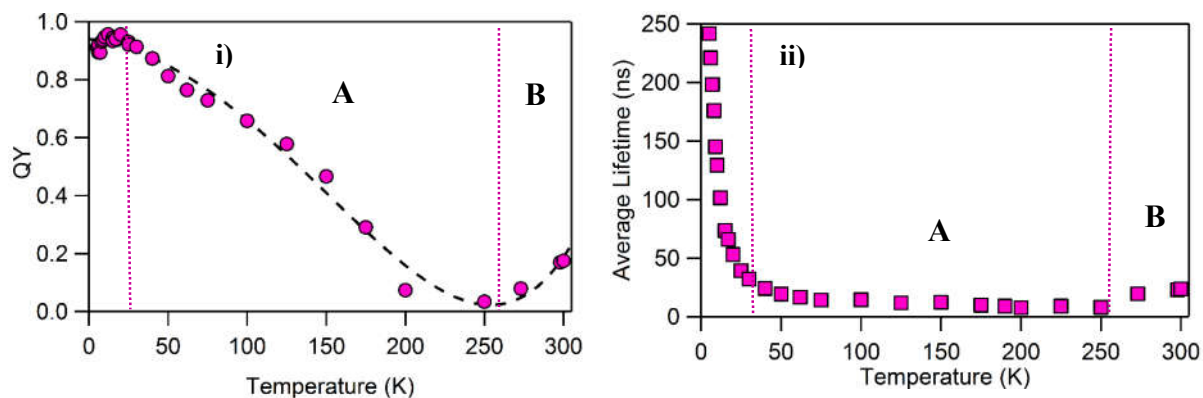


Figure 3.6: Change in PL QY of 4.5 nm CdSe QDs (panel i) and change in average PL lifetime (panel ii) with temperature (room temperature QY ~ 0.17)

The low temperature region for the 4.5 nm CdSe QD sample from ~ 5 K to ~ 50 K has nearly constant PL QY (Figure 3.6, panel i) and single exponential PL decay (Figure 3.7, decay at 12K)

due to the purely radiative excitonic decay at that temperature. This region is also referred as the radiative regime.²⁵

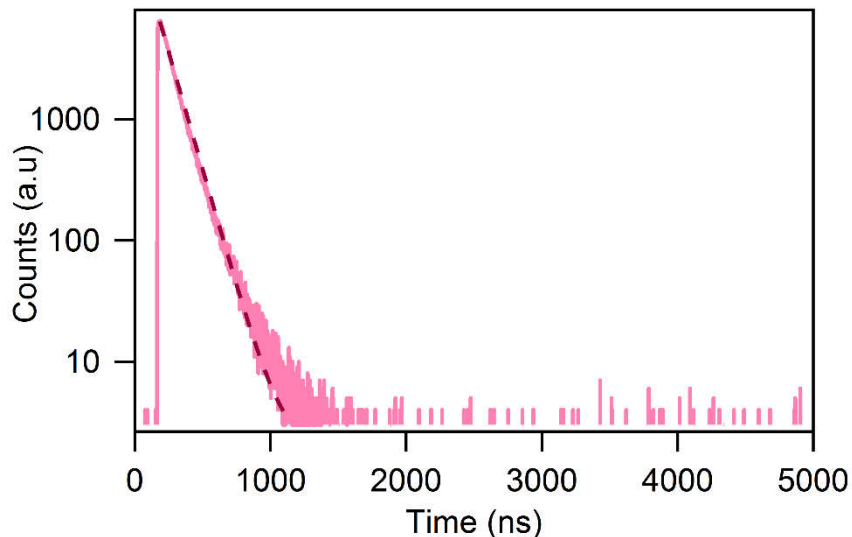


Figure 3.7: PL decay of 4.5 nm CdSe QDs at 12 K showing mono-exponential behavior

It is also interesting to note that the QY of the CdSe QDs changes from ~ 0.1 ($\sim 250\text{K}$) to ~ 0.8 (120K) in Fig. 3.4 (panel i), whereas the change observed in the average lifetime of the PL decay is comparatively less pronounced in the same temperature range (Figure 3.4 panel ii). The other CdSe QDs show similar trend as well. Klimov et al.²⁷ had reported similar observations earlier. Ultrafast studies have shown that the primary cause of reduced QY is picosecond-timescale trapping of holes on a sub-ensemble of the QDs. These dots are rapidly removed from the system and are distinct from the ensemble of radiatively decaying dots which still decay with same lifetime, hence the change in lifetime is much less significant as compared to the change in QY.³¹

To investigate the details of the increase in QY and average lifetime increase in the experimental temperature regime, Upconversion PL (uPL) and Transient Absorbance (TA) measurements were conducted.

TA spectroscopy monitors the population dynamics of excitonic states of the QDs and, in many cases, spectrally isolates the contribution of excitonic electrons to these dynamics from that of excitonic holes, with time resolution limited by the width of the laser pulse that serves as the pump (and typically the probe). PL spectroscopy is a standard photophysical technique, which in its time-resolved form-either through time-correlated single-photon counting with a typical time resolution of ~ 100 -400 ps or through PL upconversion with a time resolution limited by the width of the laser pulse-is complementary to TA spectroscopy.³² These two techniques should yield the same time constants for excitonic decay if both are performed over the entire relevant spectral range and timescale.³³ In CdSe and CdS QDs, the degeneracy of the valence band-edge state is eight (including spin), and the degeneracy of the conduction band-edge state is two, such that occupation of the valence band edge by a single hole contributes negligibly to the ground-state bleach signal, and this signal is effectively a measure of the population of the 1S_e state by the electron.³⁴

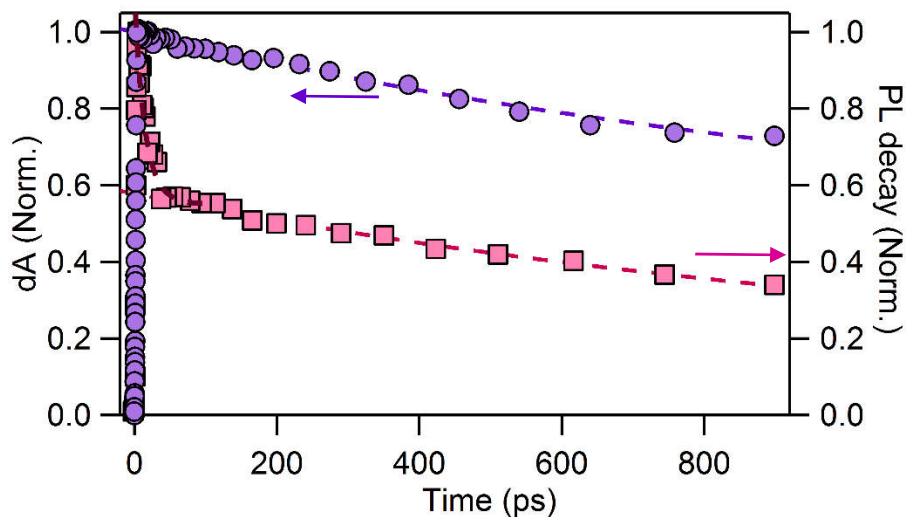


Figure 3.8: TA spectra of the CdSe QD in toluene depicting the 1st Exciton decay and the QD PL decay in the same time range (normalized at time zero). These spectra were measured at room temperature

As evident from the comparison of the ultrafast TA and Upconversion PL dynamics (Figure 3.8) on similar QDs, there is indeed an ultrafast hole trapping process (not observed in the TA) with time constant ~ 14 ps similar to that reported earlier.³¹

3.3 C: Quenching of CdSe QD + 4-amino TEMPO Temperature at low temperatures

The quenching behavior of CdSe QDs with 4-amino TEMPO was investigated for 2 different QD samples. The PL QY is obtained by integrating the PL intensity and measuring the absolute QY of the QD at room temperature and calculating the PL QY at other temperatures using the measured PL spectra. The PL spectrum were corrected for excitation screening and emission reabsorption by the procedure mentioned in Chapter 2. The PL intensity and PL decay curves for both the QD (Figure 3.9) and QD+AT (Figure 3.10) are shown next.

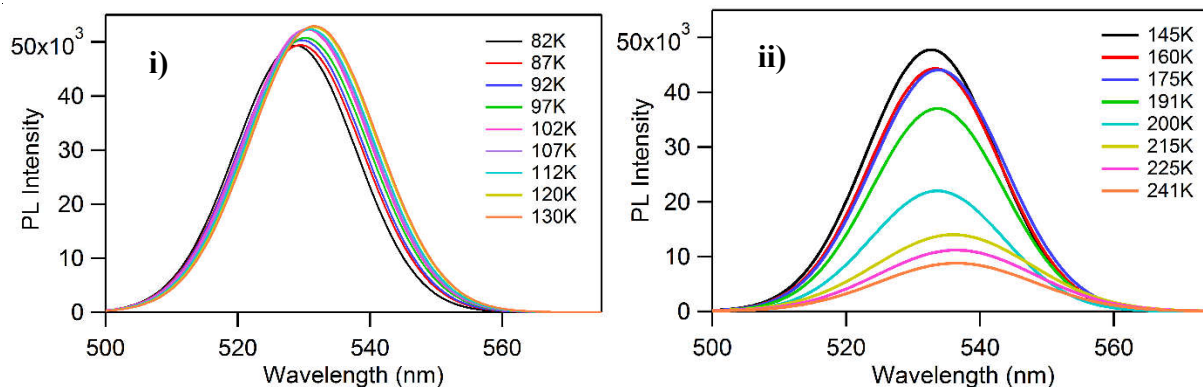
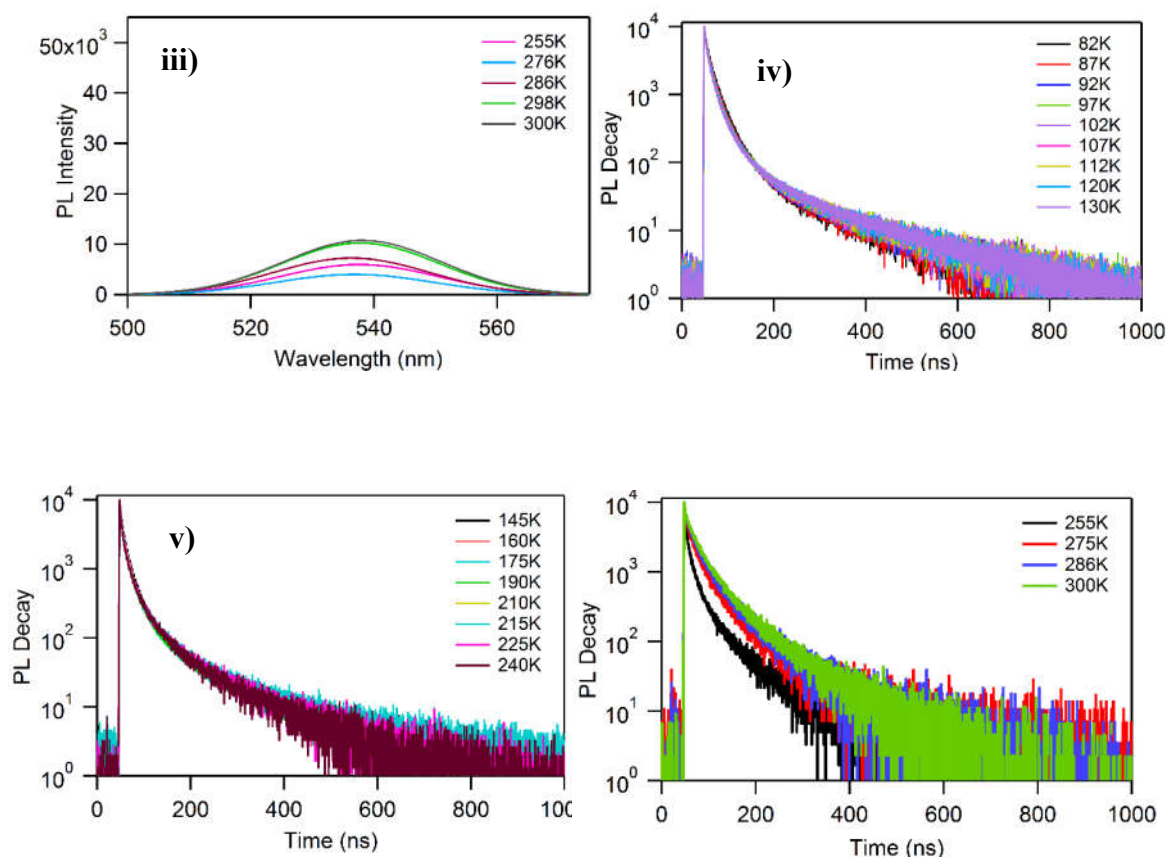


Figure 3.9: The PL spectra of the 2.7 nm CdSe QDs at different temperatures (panel i: 82 K-130 K, panel ii: 145-241 K, panel iii: 255-300K). The PL decay curves of the same (panel iv, v, vi). The y-axis is in logarithm scale

Figure 3.9 (Cont'd)



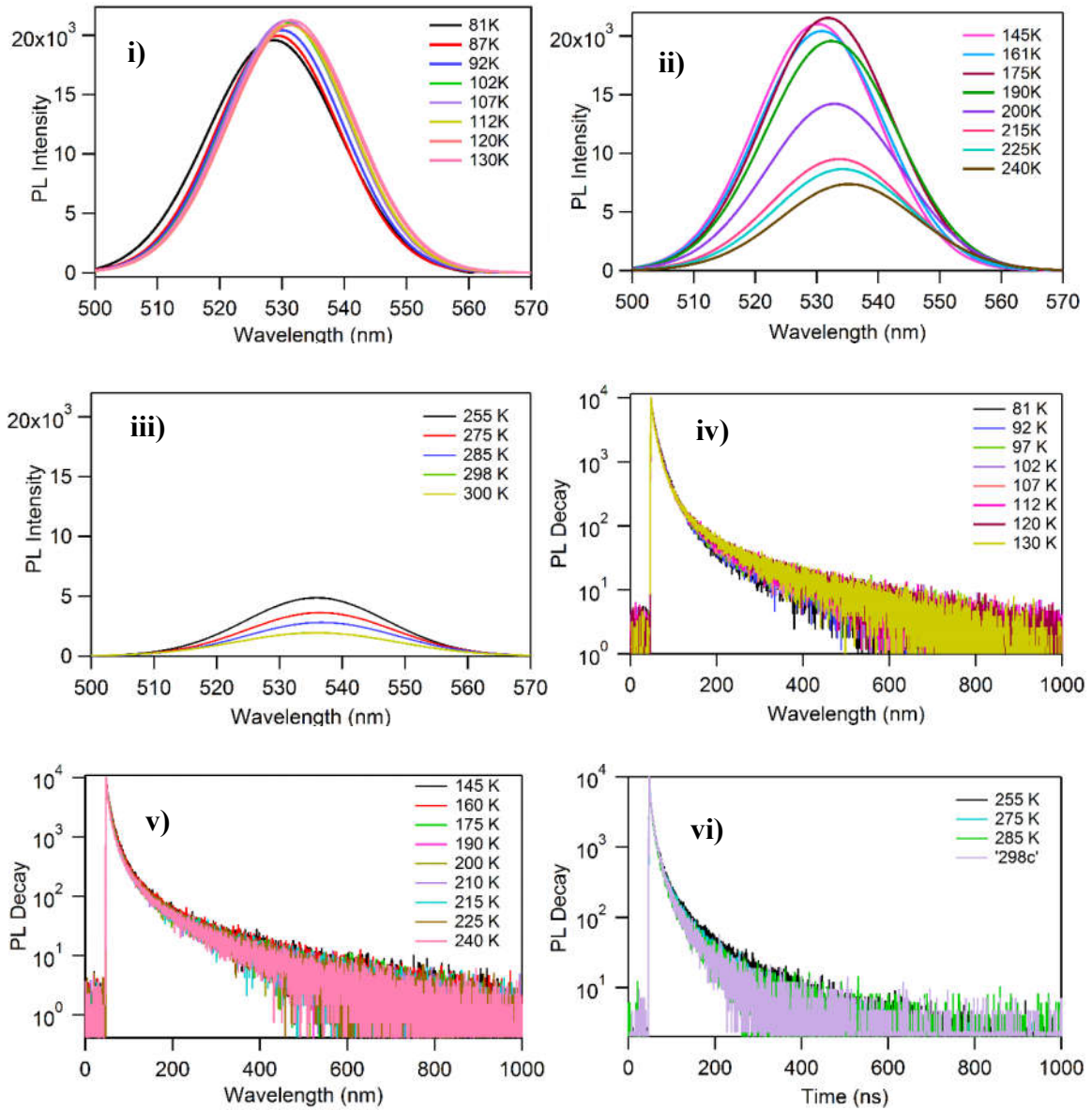


Figure 3.10: The PL spectra of the 2.7 nm CdSe QDs + 0.75 mM 4AT at different temperatures (panel i: 82 K-130 K, panel ii: 145-241 K, panel iii: 255-300K). The PL decay curves of the same (panel iv, v, vi). The y-axis is in logarithm scale

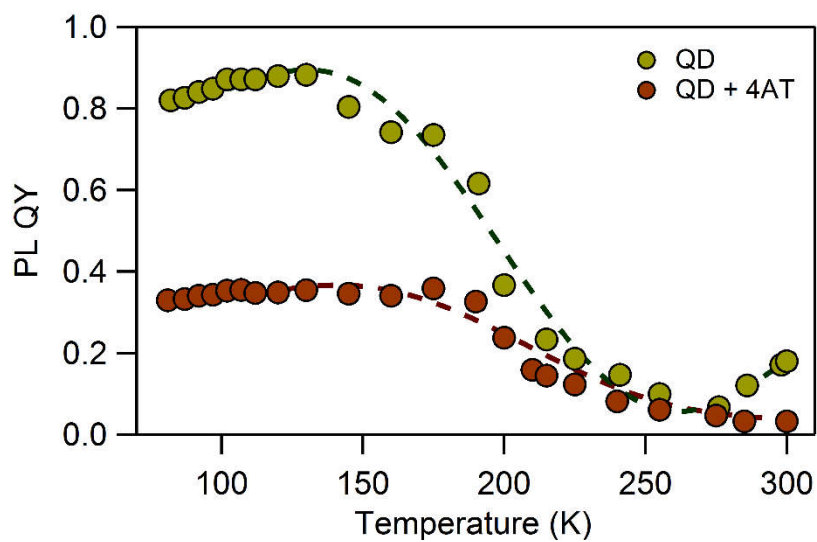


Figure 3.11: Comparison of PL QY for 4 μM 2.7 nm CdSe QD and QD + 0.75 mM AT with temperature (Individual PL data and decay curves are shown in Figures. 3.9 and 3.10). The $(I_0/I)^{CW}$ value at room temperature is 5.5

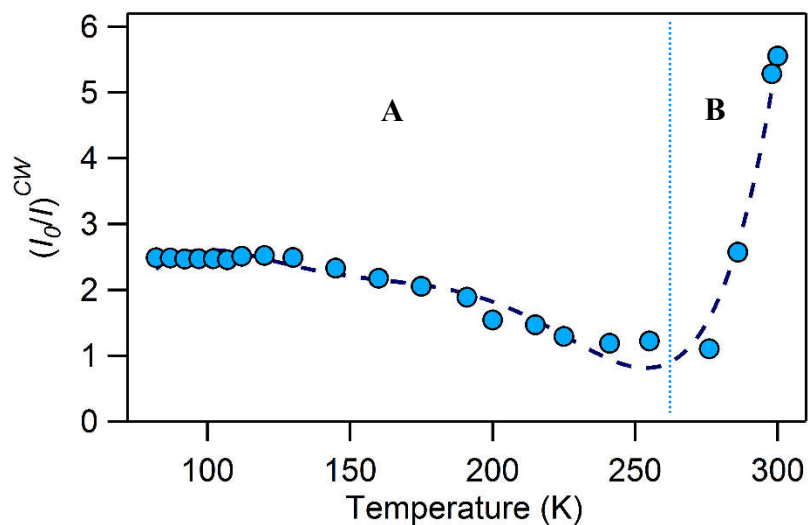


Figure 3.12: $(I_0/I)^{CW}$ of 2.7 nm CdSe QD with 0.75 mM 4-amino TEMPO with decreasing temperature

The quenching efficiency (Figure 3.12) is found to decrease as the temperature is reduced from 300 K to ~250 K (region B), whereas in the region A, it is found to increase gradually with increase in temperature. These behavior can be interpreted by understanding the competitive processes by which an exciton can recombine.

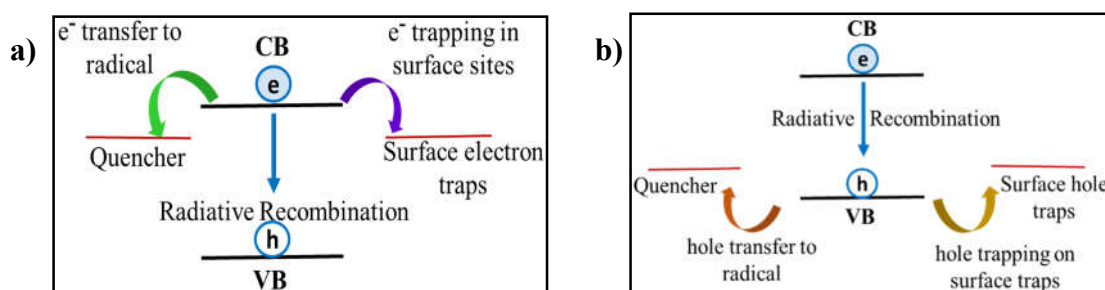


Figure 3.13: The possible pathways for the photo-excited electron in the CB (panel a) and the photo-generated hole in the VB (panel b)

Whether the quenching process is due to an electron transfer process (Figure 3.13 a) or a hole transfer process (Figure 3.13 b), the surface electron/hole traps always act as competing pathways for the photo-generated carriers. In regime B, as the temperature decreases from 300 K to 250 K, the carrier trapping process is enhanced (as discussed in section 3.3 b) due to rearrangement of the capping ligands. As more and more carriers are now trapped in the surface sites, the transfer to quencher is hampered and hence the PL quenching efficiency as depicted by the $(I_0/I)^{CW}$ values in Figure 3.12.

In regime A, as the temperature decreases from 250 K to ~80 K, non-radiative recombination and surface trapping becomes less and less significant, thus allowing more and more carriers to be

quenched by the radical. This results in a gradual enhancement in the quenching efficiency as represented by Figure 3.12.

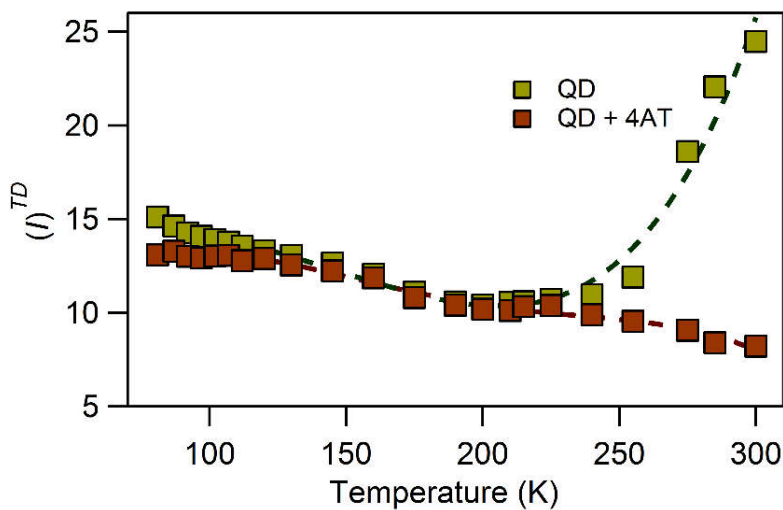


Figure 3.14: Integrated normalized PL decay of 2.7 nm CdSe QD with 0.75 mM 4-amino TEMPO with decreasing temperature

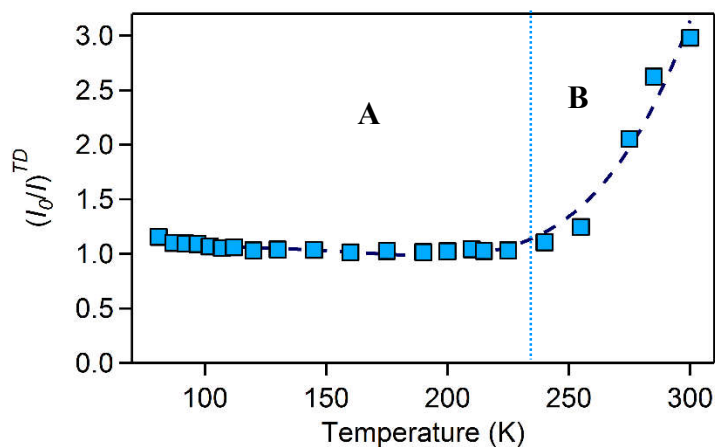


Figure 3.15: $(I_0/I)^{TD}$ plot of 2.7 nm CdSe QD with 0.75 mM 4-amino TEMPO with decreasing temperature

In the regime B, as the temperature decreases from 300 K to ~250 K, the $(I_0/I)^{TD}$ which depicts the diffusional quenching efficiency is found to decrease significantly. This is easy to comprehend because the lifetime of the CdSe QDs is found to decrease in this regime as a result of which the probability of the quencher diffusing to the QD and quenching it within its lifetime; decreases. This is reflected as the decrease in the $(I_0/I)^{TD}$ value in Figure 3.15.

In region A, the $(I_0/I)^{TD}$ is found to be almost independent to changes in temperature and is also close to unity. This shows that the diffusional quenching is completely shut down at these temperatures (where the system is frozen) and hence the total quenching is only due to a fast/instantaneous static mechanism.

Similar trends are observed for 3.3 nm CdSe QD sample where two different AT concentrations were used to monitor the quenching pattern at lower temperatures. It is interesting to note that the quenching is never completely shut down at cryogenic temperatures which is generally expected for charge transfer processes.

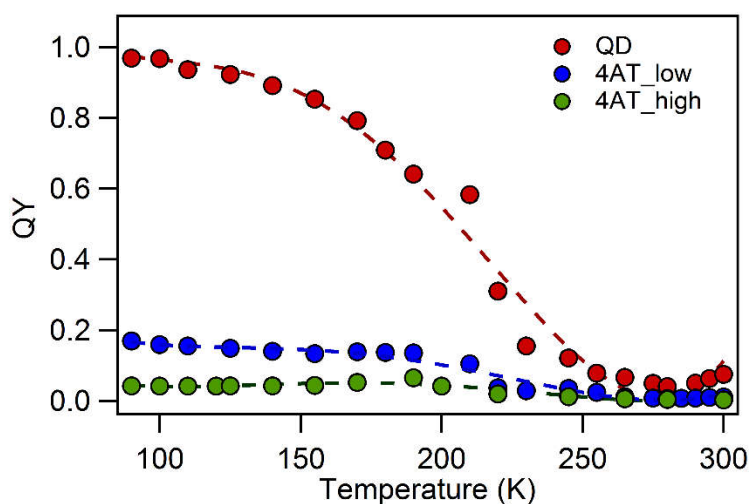


Figure 3.16: PL QY of 3.2 nm CdSe QD and QD + 4AT for two different concentrations. The concentration of 4-amino TEMPO used were 1.8 mM (low) and 4.7 mM (high)

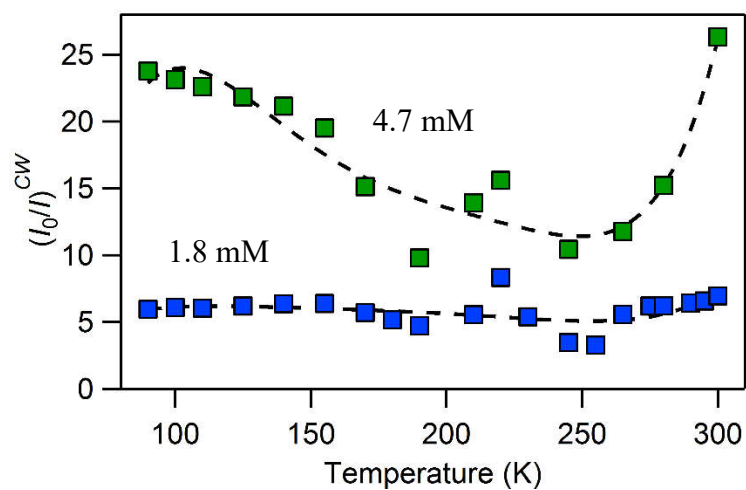


Figure 3.17: Comparison of $(I_0/I)^{CW}$ for the two different concentrations of 4AT. 1.8 mM (low) and 4.7 mM (high)

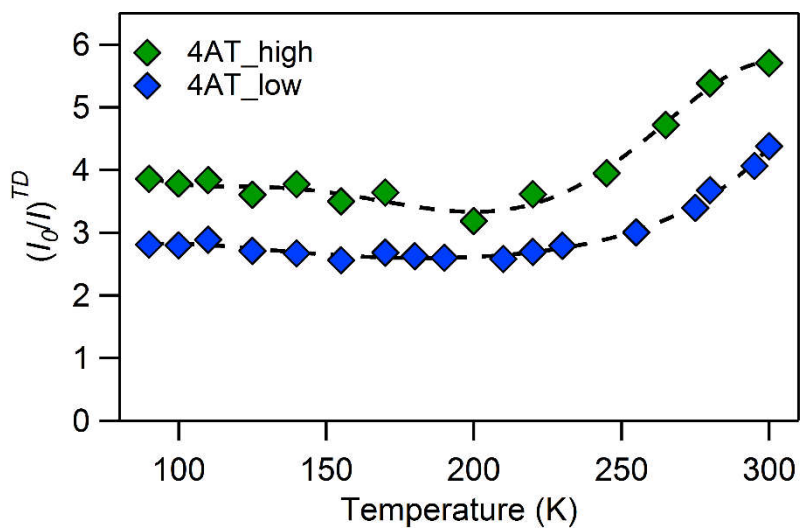


Figure 3.18: Comparison of $(I_0/I)^{TD}$ for the two different concentrations of 4AT. 1.8 mM (low) and 4.7 mM (high)

3.4: Conclusion

The quenching of the CdSe QD by 4-amino TEMPO decreases as the temperature is first decreased to ~ 250 K, below which the total quenching gradually increases. The diffusional quenching also decreases up to ~ 250 K however, below 250 K the diffusional quenching remains almost constant. The interesting observation is that even at ~ 80 K, the quenching is not shut down completely.

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REFERENCES

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Chapter 4: PL quenching of CdSe and CdTe QDs by 4-amino TEMPO, Hole Transfer vs. Electron Transfer

4.1: Motivation behind this work

Understanding the dynamics of charge carriers in photo-excited QDs is an essential part of designing new QD-based technologies as well as modifying the existing ones for higher efficiencies. These applications almost exclusively depend on efficiently harnessing the energy stored in an excited electron-hole pair either through radiative recombination or through charge separation to produce chemical or electrical work. To this day, the majority of commercially viable applications of QDs rely on the former process, however both fluorescence and charge transfer processes, must compete with recombination pathways such as charge trapping to localized interfacial and surface states. A mechanistic understanding of many of these competing de-excitation pathways is however still lacking; owing to the difficulty in characterizing the spatial separation and energetic distribution of these contributing states. A deeper understanding of interfacial charge transfer could greatly improve the design of QD-based devices since charge transfer has been shown to be a major factor limiting efficiencies in colloidal hydrogen generation schemes¹ as well as QD-sensitized solar cells.^{2,3}

Using a suitable adsorbate molecule (electron or hole acceptors) on photo-excited QD materials, ultrafast exciton dissociation can be a reality. Exciton dissociation in the ultrafast time scale through electron transfer (ET) in QD/molecular adsorbate and QD/semiconductor nanoparticle (TiO₂, ZnO etc.) systems has been widely investigated.⁴⁻¹¹ Electron transfer time constants are reported to be tens of picosecond to tens of femtosecond. However, in comparison, fewer reports are available on hole transfer (HT) dynamics from the photo-excited QD to a molecule.¹²⁻¹⁴ One

of the main reasons is that holes are not characterized properly due to featureless weak absorption in the near IR region, and also the nature of the transition in transient absorption is not well understood.¹⁵⁻¹⁷ Hole transfer time constants are reported to be in hundreds of picoseconds to nanosecond time scale.^{7,18-20}

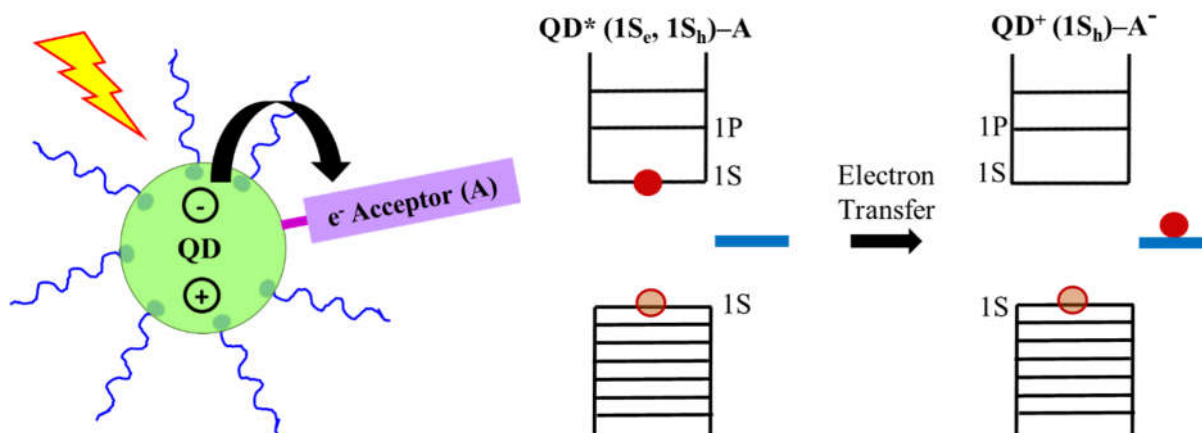


Figure 4.1: Scheme of light-driven charge separation by electron transfer (ET) in QD-electron acceptor complexes

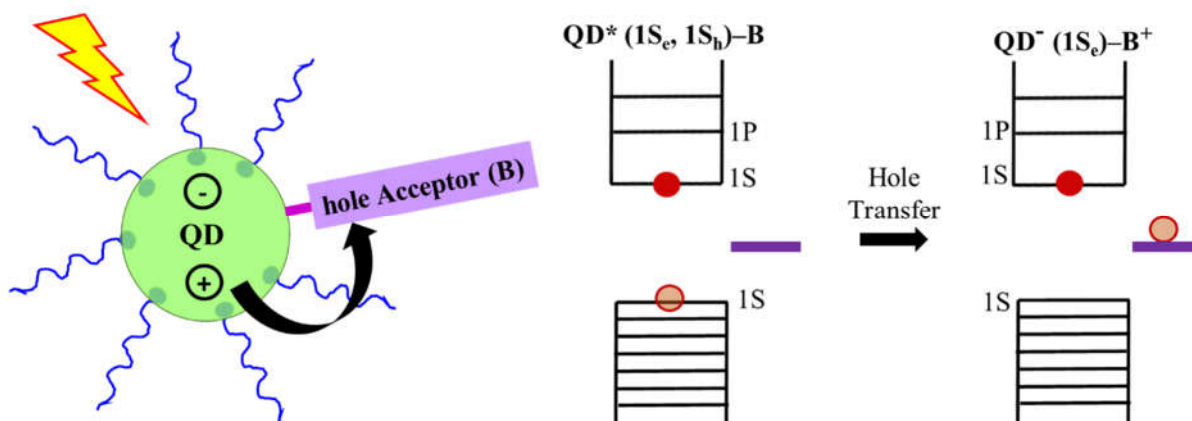


Figure 4.2: Scheme of light-driven charge separation by hole transfer (HT) in QD-hole acceptor complexes

In the previous chapters, it has been demonstrated that 4-amino TEMPO is an efficient quencher of the PL of II-VI QDs. In this study, we aim to investigate the nature and mechanistic details of the pathway leading to such an interaction.

4.2: Determining the Charge Transfer Rates

In QD-electron acceptor complexes, exciting with energy greater than the band gap energy of QDs, initiates the transfer of a 1S CB electron to the acceptor, generating a charge-separated state with a hole in the QD and a reduced acceptor (Figure 4.1). In the absence of further redox active species (such as catalysts or sacrificial electron donors), the charge-separated state eventually undergoes interfacial charge recombination, or back ET, to regenerate the complex in the ground state. The back ET process can also be formally viewed as a HT from the QD. The HT from QD to the hole acceptor is depicted in Figure 4.2.

The dynamics of ET and HT processes can be acquired by measuring the population evolution of QDs in the 1S excited state ($\text{QD}^*[\text{1S}_e, \text{1S}_h]$), of oxidized QDs (QD^+), or of reduced acceptors (A^-) as functions of time by time-resolved (TR) spectroscopy.

Various TR spectroscopy techniques have been utilized to study the dynamics of charge transfer (CT) from QDs, including PL decay^{12,21}, transient absorption (TA) in the visible and IR²²⁻²⁵ ranges, TR-terahertz (THz),²⁶⁻²⁸ TR-second harmonic generation,⁸ and TR-two photon photoemission.²⁹

PL decay can be used to monitor the quenching effect of CT on photon emission from excited QDs. By comparing the PL decay with and without a charge acceptor and assuming that CT is the only additional non-radiative channel in QD-acceptor complexes, CT rates can be extracted, even on the single-QD level.^{12,21,30} However, QD PL decay alone cannot differentiate ET, HT, and non-

CT pathways, so these measurements have to be supplemented with more direct spectroscopic techniques. TA spectroscopy provides the most powerful way to follow CT processes from QDs. Not only does it have the capacity to probe both the reactant decays and product formations, it also has a broad spectral range (from UV to IR to THz) and temporal range (from a few femtoseconds to as long as needed). In the ultrafast version of this technique, the absorption change ($\Delta\alpha$ or dA) induced by a short pump pulse is measured using a second, low-intensity, short probe pulse. By monitoring α in both the time and spectral domains, one can obtain information on electronic energies, the spectral distribution of photoexcited carriers, and carrier energy-relaxation and recombination dynamics.

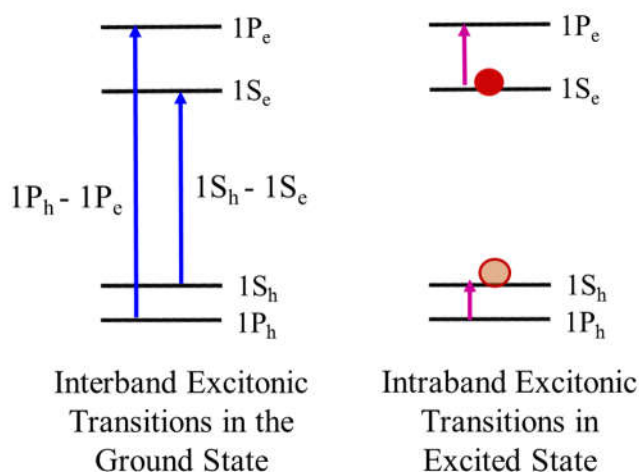


Figure 4.3: The interband exciton transitions ($1S_e-1S_h$, $1P_e-1P_h$) in the ground state and the excited-state intraband ($1S$, $1P$) transitions of electrons and holes in QDs

The presence of a $1S$ CB electron produces an electron state filling induced $1S$ exciton bleach and $1S-1P$ intra band absorption in TA spectra, as shown in Figure 4.3. The exciton bleach falls in the visible range for CdX QDs and in the near-IR range for PbX QDs ($X=S, Se, Te$).³¹ The

1S-1P electron and hole intraband transitions are often in the mid-IR range.^{4,23,32-34} The state filling induced bleach of VB holes has not been observed in CdX QDs. Though the reason is not very clearly understood, this is often attributed to the greater degeneracy of VB edge hole states.³¹ This hypothesis has been justified by selectively removing the CB electrons/VB holes using molecular electron acceptors^{4,33} or hole acceptors.^{6,19}

The 1S exciton bleach in excited CdX QDs thus selectively measures the CB 1S electron population and can be used to follow ET processes.^{4,5,31,33,35} Unlike CdX QDs, PbX QDs have similar CB and VB electronic structures^{36,37} as a result of which the 1S electrons and 1S holes have nearly equal contributions to the 1S exciton bleach in PbX QDs.^{38,39} In addition to these QD TA features, a complementary and unambiguous way to probe the CT process is the direct measurement of the TA features of CT products, i.e., the electronic and/or vibration spectra of reduced/oxidized molecular acceptors.^{5,33}

In this work, investigation of ultrafast charge carrier dynamics have been carried out using ps transient absorption (TA), time-resolved PL upconversion (uPL) and TCSPC (ns and ps regimes) experiments. As discussed above, in TA, the dynamics of the pump-induced absorption changes (at the lowest energy, 1S transition) reports directly the depopulation rate of the electron 1S state.⁴⁰ In contrast, PL is proportional to rate of change of excitonic (electron and hole) population; therefore PL dynamics are dominated by the carriers with the shortest relaxation time. Thus, PL relaxation is dominated by hole dynamics if they are significantly faster than electron dynamics.⁴¹ A combination of these two techniques provide us with valuable information about the nature of the CT in the CdSe/CdTe QD-nitroxide radical dyads.

4.3: Experimental Results

4.3 A: Comparison of TA and uPL measurements

The first step towards understanding the nature of the charge transfer occurring in the QD-radical system was investigating the electron dynamics through transient absorbance spectroscopy and comparing it with the exciton dynamics from the uPL decay measurement conducted in the same time range.

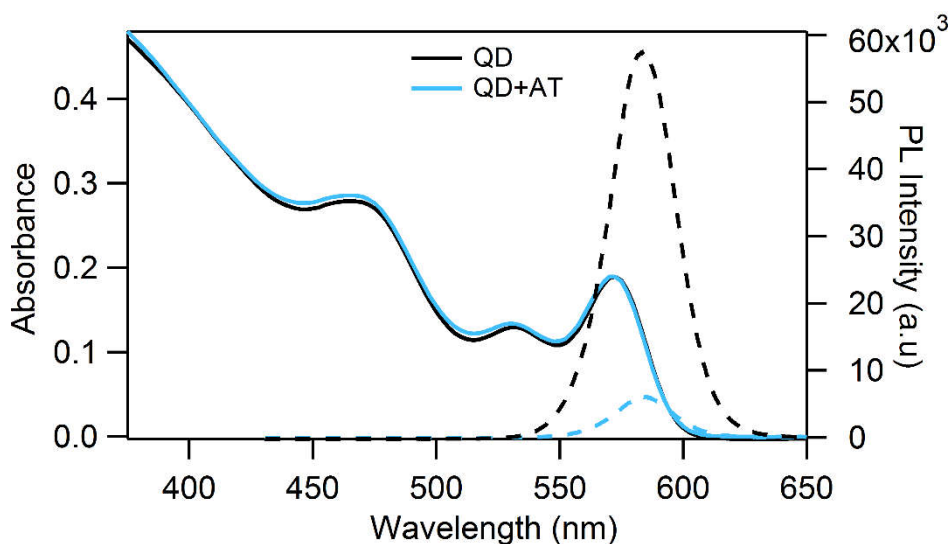


Figure 4.4: Absorbance spectra and PL spectra of 2 μM 3.6 nm CdSe QDs in absence and in presence of 5 mM 4-amino TEMPO

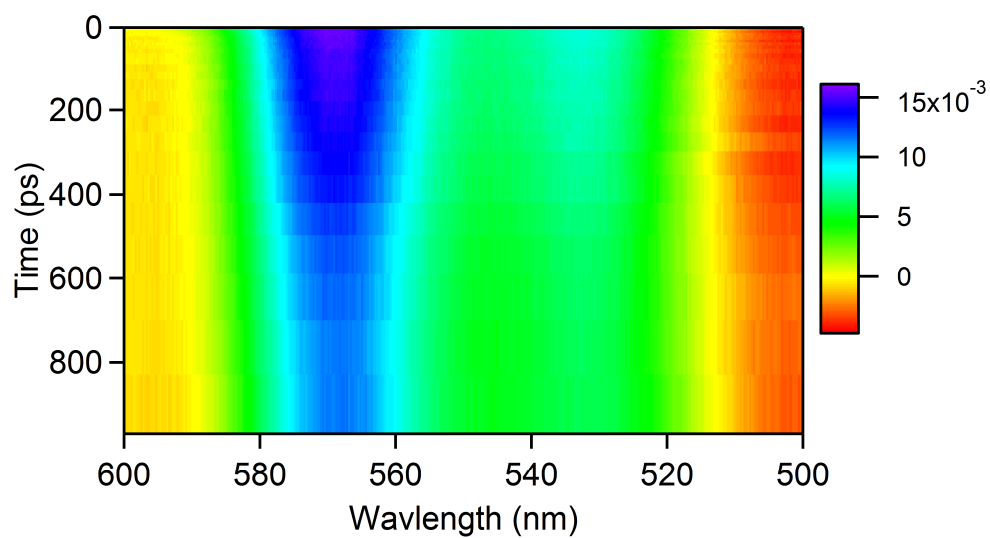


Figure 4.5: Contour plot of the time resolved transient absorption spectra of 2 μM 3.6 nm CdSe QDs

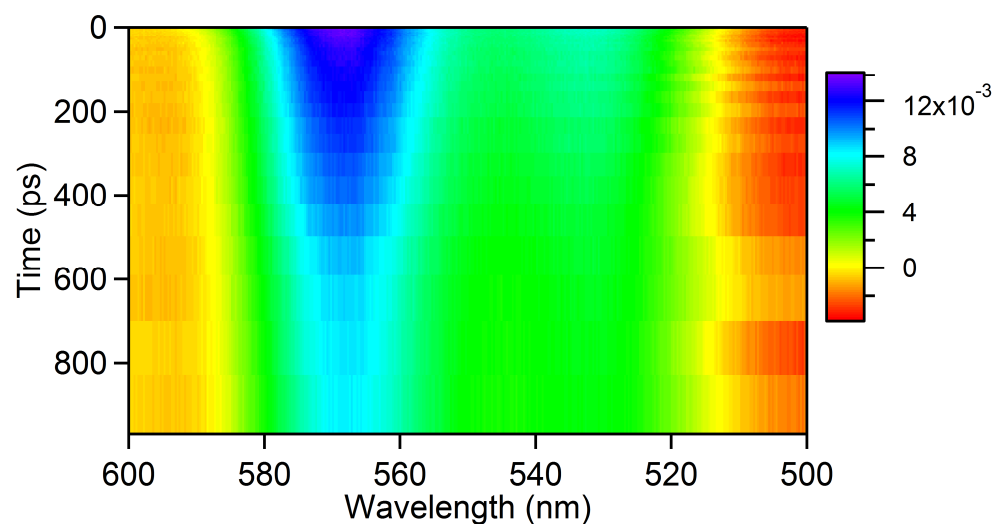


Figure 4.6: Contour plot of the time resolved transient absorption spectra of 2 μM 3.6 nm CdSe QDs + 5 mM 4-Amino TEMPO

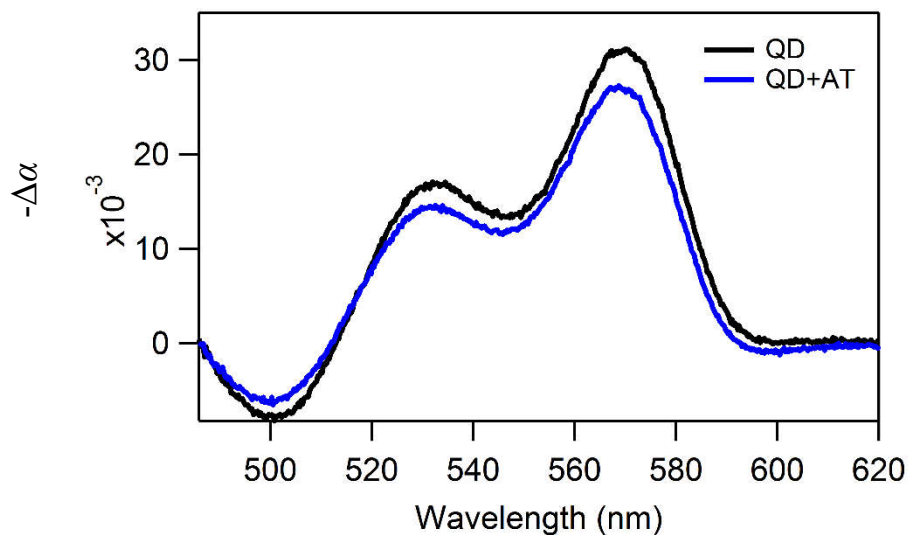


Figure 4.7: Transient absorption spectra of CdSe QDs in the absence and in the presence of 4-amino TEMPO at 5 ps delay time. The peak at 570 nm denotes the 1st exciton and is used to look at the electron dynamics

The TA spectra of the system (Figure 4.7) is characterized by an excitonic bleach centered around 570 nm which closely corresponds to the first exciton band maximum of the QDs in the ground state absorbance spectrum (Figure 4.7). As 400 nm excitation populates the states well above the conduction band edge, the intraband relaxation of non-thermalized electrons to the conduction band edge 1S state (thus producing the cold electrons)^{15,22} is mainly expected.

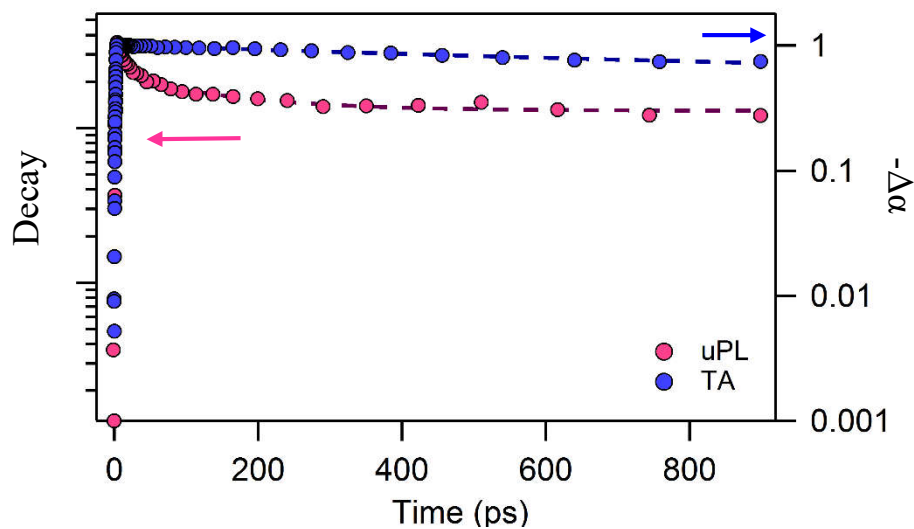


Figure 4.8: Comparison of the TA (normalized at $t=0$) and uPL dynamics measured for 3.6 nm CdSe QDs. The dashed lines are guide to the eyes, the y-axes in logarithmic scale. The arrows indicate the respective axes

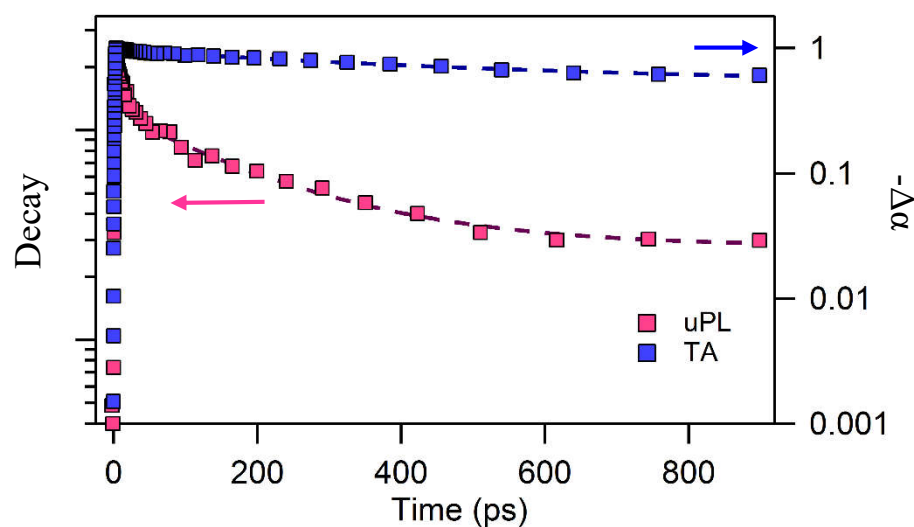


Figure 4.9: Comparison of the TA (normalized at $t=0$) and uPL dynamics measured for 3.6 nm CdSe QDs + 4-amino TEMPO. The dashed lines are guide to the eyes, the y-axes in logarithmic scale. The arrows indicate the respective axes

Figures 4.8 and 4.9 display TA and uPL time transients (collected at 570 and 585 nm, respectively) for the QD solution (Figure 4.8) and QD-AT mixture (Figure 4.9). In the case of QD-only solution, uPL relaxation is slightly faster than TA relaxation, suggesting more efficient surface trapping of holes compared to electrons.⁴⁰ Similar observations have been reported earlier and have been assigned to trapping at chalcogenide surface dangling bonds.⁴²

While electron dynamics (probed by TA) remain almost unchanged in the mixture, the hole dynamics change dramatically indicating fast depopulation of QD hole states. This process suggests that the PL quenching observed in QD-AT mixture is as a result of hole transfer (HT) from the photo-excited QD to the nitroxide radical. Similar results (Figure 4.11) are observed for the 5nm CdSe QDs. Absorbance and PL spectra for 5 nm QD and QD+AT are shown in Figure 4.10. The concentration of the radical added to the 5 nm CdSe samples was same as that in case of 3.6 nm CdSe QDs.

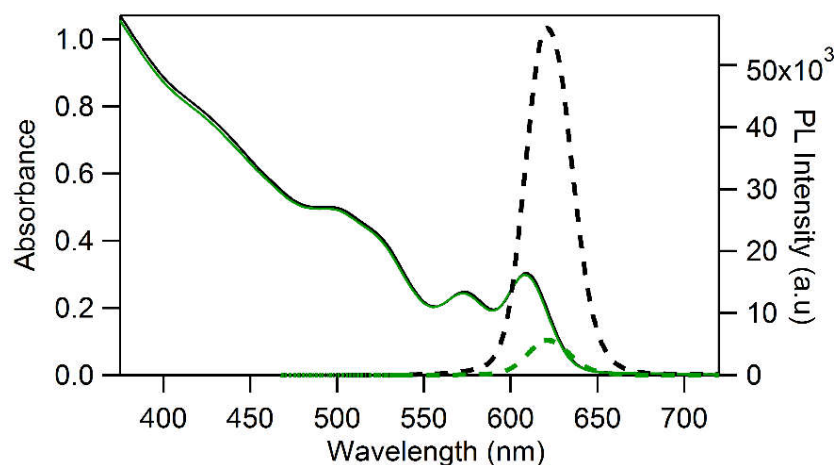


Figure 4.10: Absorbance and PL spectra of 2 μ M 5.0 nm CdSe QDs + 6 mM 4-amino TEMPO

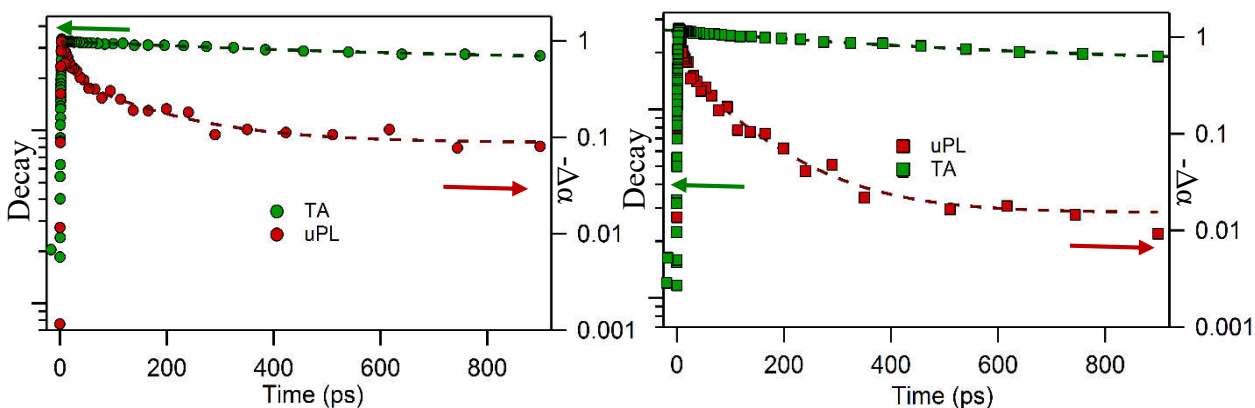


Figure 4.11: Comparison of the TA (normalized at $t = 0$) and uPL dynamics measured for 5.0 nm CdSe QDs + 4-amino TEMPO. The dashed lines are guide to the eyes, the y-axes in logarithmic scale. The arrows indicate the respective axes

4.3 B: Ultrafast hole transfer from photo-excited QDs to radicals

Comparison of the TA and uPL spectra clearly demonstrates that hole transfer process is responsible for the PL quenching of CdSe QD with AT. Another remarkable observation from the uPL measurement was that there is a drop in PL intensity at time zero with addition of the radical (Figure 4.12). This indicates that there is an ultrafast (faster than ~ 1 ps resolution of the uPL set up) component to the hole transfer process occurring from the QD to the radical.

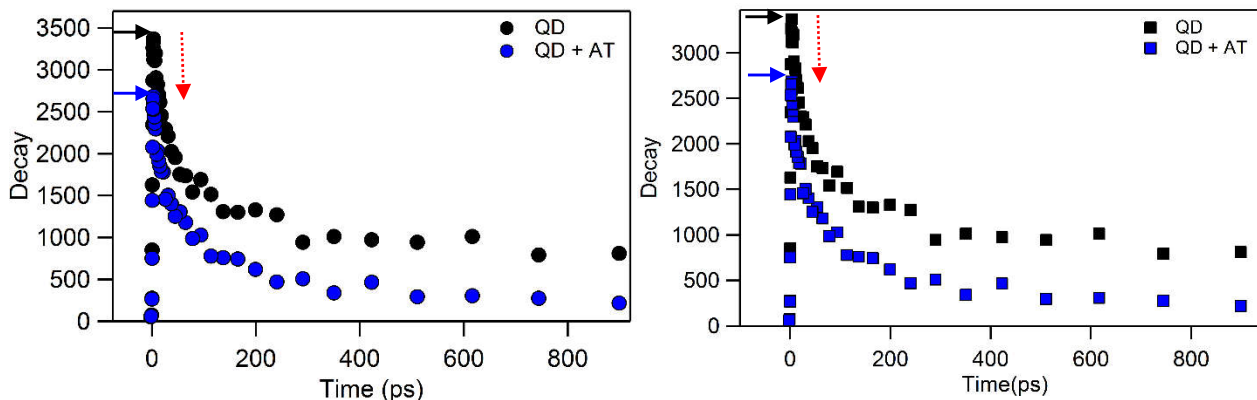


Figure 4.12: uPL decay of 3.6 nm CdSe QDs (panel a) and 5.3 nm CdSe QDs (panel b) showing the drop in PL intensity at time zero. The black and blue arrows indicate the intensity at time zero for the QD and the QD+AT solution respectively and the red arrow denotes the drop in PL intensity

4.3 C: Exciting at the band edge vs. exciting with higher energy

The TCSPC measurement (in the picosecond timescale with 50 ps time resolution and a tunable laser) was conducted on the CdTe QDs (Figures 4.13 and 4.15) by exciting at the band edge vs. exciting at 430 nm to see if the quenching efficiency differed in the two cases. Excitation at 430 nm, leads to formation of hot electrons and hot holes which subsequently thermalizes to cold electrons and holes, however exciting at the band edge produces cold electrons and holes only. Since, the thermalized hole transfer was found to be ultrafast ($< \text{few ps}$), the excitation wavelength was varied to see if the hot holes played a role in the quenching mechanism. The I_0/I values are calculated by integrating the PL decay and then dividing the integrated intensity of each sample (QDs with different AT concentrations) by the intensity of the QD sample.

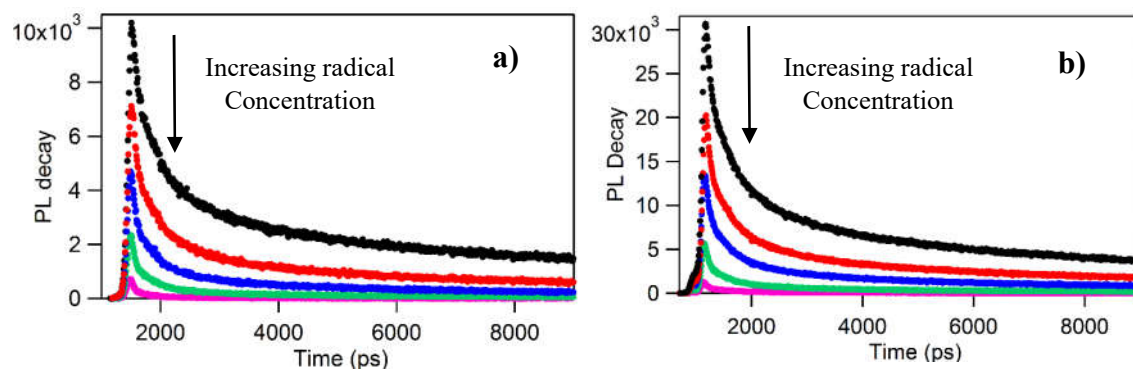


Figure 4.13: PL decay of 5 nm CdTe QDs with increasing concentration of 4-amino TEMPO radical (panel a: 650 nm excitation, panel b: 430 nm excitation). The concentrations are listed in Table 4.1

Table 4.1: Comparison of the (I_0/I) values of 5 nm CdTe QDs + AT for the two different excitations

[AT] (mM)	I_0/I (430 nm)	I_0/I (650 nm)
0	1	1
0.17	1.9	2.0
0.35	3.5	4.2
0.88	11.8	12.3
1.91	70.0	68.3

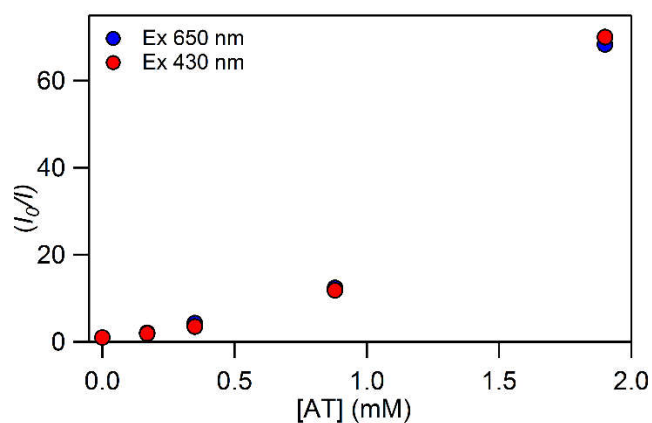


Figure 4.14: (I_0/I) of 5 nm CdTe QDs with increasing concentration of 4-amino TEMPO radical. The concentrations are listed in Table 4.2

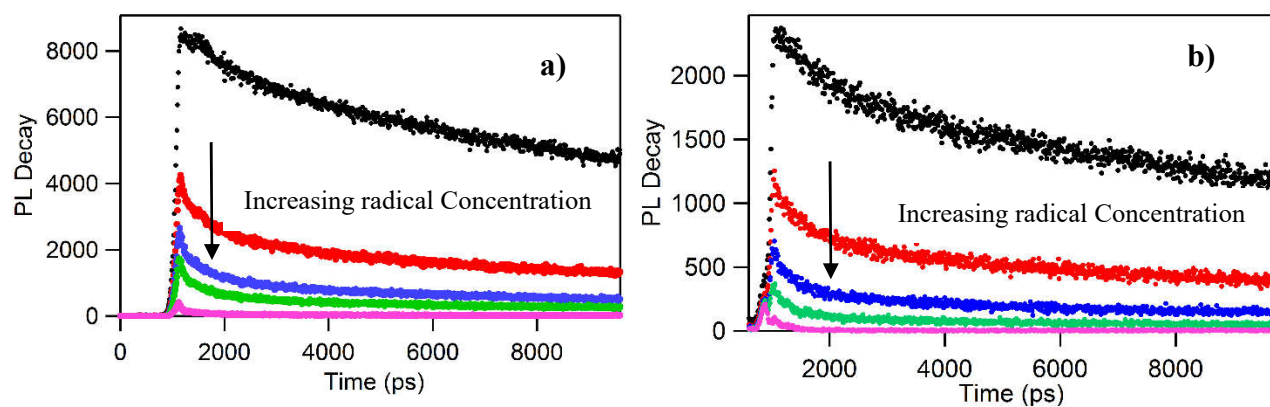


Figure 4.15: PL decay of 4 nm CdTe QDs with increasing concentration of 4-amino TEMPO radical (panel a: 630 nm excitation, panel b: 430 nm excitation)

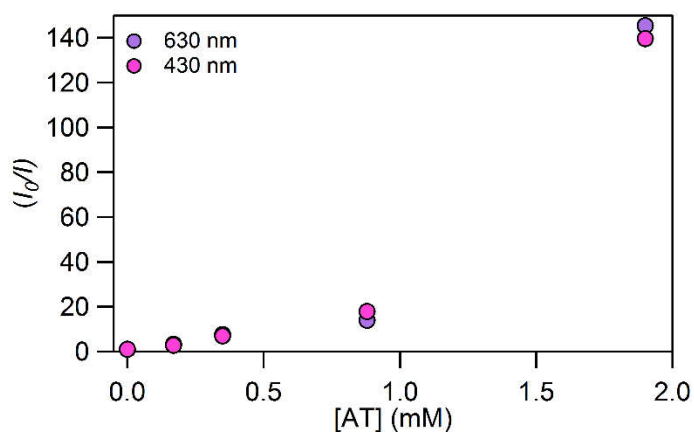


Figure 4.16: (I_0/I) of 4 nm CdTe QDs with increasing concentration of 4-amino TEMPO radical

Table 4.2: Comparison of the (I_0/I) values of 4 nm CdTe QDs + AT for the two different excitations

[AT] (mM)	I_0/I (430 nm)	I_0/I (650 nm)
0	1	1
0.17	2.8	3.3
0.35	7.0	7.6
0.88	17.9	13.9
1.91	139.6	145.4

Similar results are obtained for CdSe QDs as well. This indicates that either hot holes are not involved in the quenching process or that the thermalization of the hot holes are faster than the ultrafast hole transfer to the radicals.

4.3 D: Analysis of the TCSPC PL dynamics and TA

In order to understand the nature of the charge transfer, detailed analysis of the TCSPC PL dynamics in the ps and ns time range and the ps TA spectra was conducted.

4.3 D.1: CdSe QDs

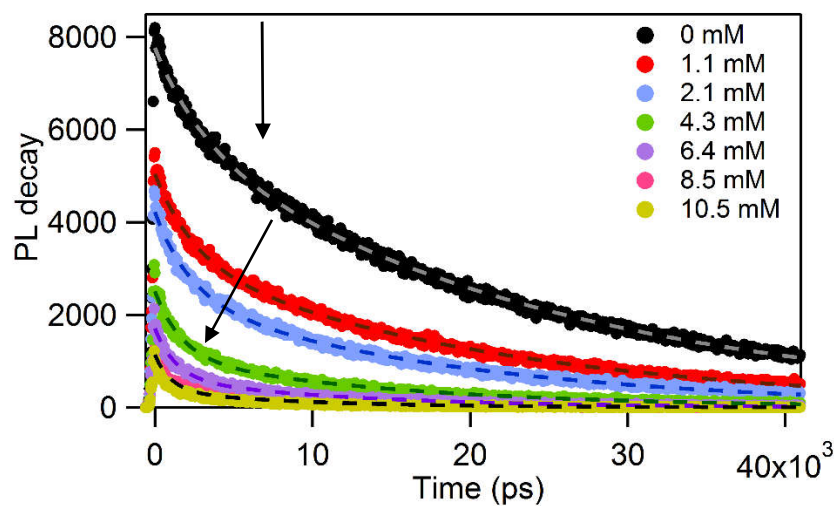


Figure 4.17: TCSPC decay of 3.8 nm CdSe QDs with increasing concentration of 4-amino TEMPO radical. The dashed lines are guide to eyes. The arrows show the change in the PL intensity and change in PL decay with increasing concentration of radical (listed in Table 4.3)

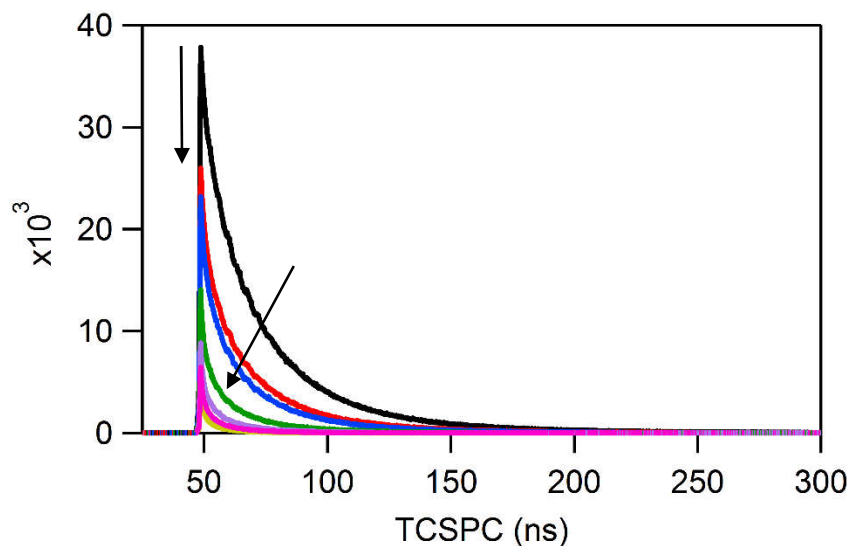


Figure 4.18: TCSPC decay of 3.8 nm CdSe QDs with increasing concentration of 4-amino TEMPO radical. The arrow shows the change in the PL decay with increasing concentration of radical. (The concentrations are same as in Figure 4.17 and the graphs have the same color code, the values are listed in Table 4.3)

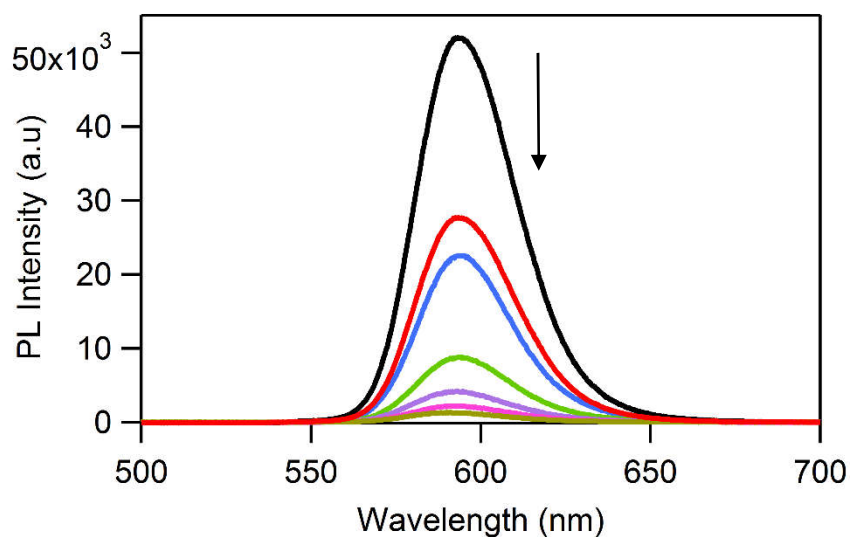


Figure 4.19: PL spectra of 3.8 nm CdSe QDs with increasing concentration of 4-amino TEMPO radical. (The concentrations are same as in Figure 4.17 and the graphs have the same color code, the values are listed in Table 4.3)

As observed in the ps TCSPC measurement with the 4 nm (Figure 4.15) and 5 nm CdTe QDs (Figure 4.13), the 3.8 nm CdSe QDs show similar quenching behavior (Figure 4.17) where there is an instantaneous quenching observed in the TCSPC measurement. The TCSPC spectra (ns and ps set up) and the CW PL spectra are used to calculate the I_0/I value. As mentioned earlier the spectra are integrated for the QD and QD+AT mixtures to obtain the I_0/I . The fact that the I_0/I values are close to each other suggests that though these measurements were conducted using different setups and sometimes at an interval of 4-5 hours, they are still consistent with each other and hence can be used to extract meaningful information.

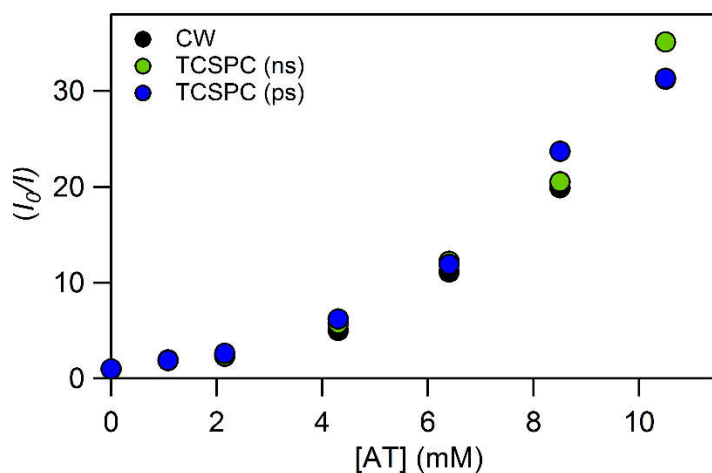


Figure 4.20: Comparison of (I_0/I) of 3.8 nm CdSe QDs with increasing concentration of 4-amino TEMPO radical, the values are listed in Table 4.3

Table 4.3: Comparison of the (I_0/I) values of 3.8 nm CdSe QDs + AT for CW measurement, TCSPC (ns and ps) measurements

[AT] (mM)	TCSPC(ns)	TCSPC(ps)	$(I_0/I)^{CW}$
0	1	1	1
1.1	1.9	1.9	1.9
2.1	2.4	2.6	2.3
4.3	5.7	6.2	5.0
6.4	12.2	11.9	11.1
8.5	20.5	23.7	19.9
10.5	35.1	31.3	31.2

As discussed earlier in chapter 3 (Section 3.B), the 1st exciton peak in the TA spectra effectively measures of population of the 1S_e state by the electron. The first exciton decay from the TA spectra (Figure 4.21) of the 3.8 nm CdSe QDs does not change effectively on addition of the 4-amino TEMPO. This suggests that the electrons are not involved in the quenching mechanism of the CdSe QDs studied here. The first exciton decay can be fit with a bi-exponential fitting function with the fast component ~ 26 ps (amplitude 0.8) and a longer component ~ 400 ps (amplitude 0.2). The 26 ps component of the bleach recovery kinetics of the QD can be attributed to electron trapping and the 400 ps long component to recombination of the charge carriers.^{22,43}

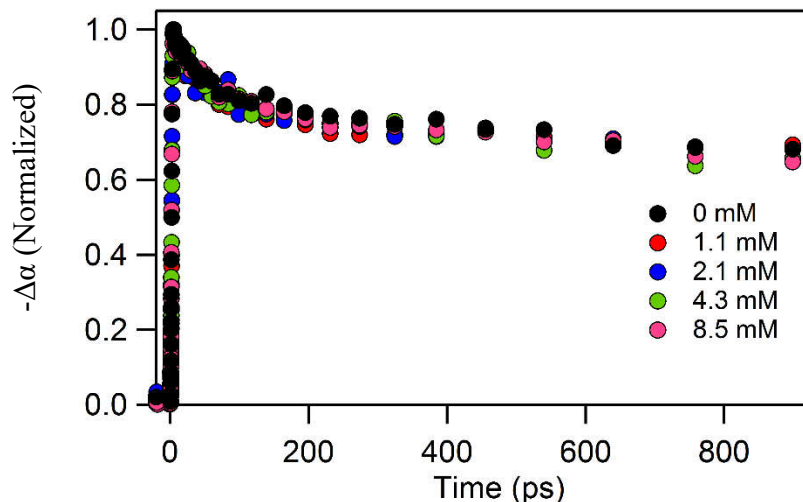


Figure 4.21: The decay of the first exciton of 3.8 nm CdSe QDs with increasing concentration of 4-amino TEMPO radical

On the other hand, the TCSPC (ps) spectra (Figure 4.17) needed to be fit with a multi-exponential function (typically 3 components could be extracted). It was observed that with increasing radical concentration, there were three components in the decay that was affected. The longest component ($\sim 10\text{-}20$ ns lifetime; $k_q \sim 10^{10} \text{ s}^{-1}$) mostly reflects the diffusion related quenching effects. In order to study effect of the radical on the faster component of the decay, the long component of the spectra was first fit with a single exponential and then subtracted from the decay. The remainder was fit with a bi-exponential fit. Table 4.4 lists the parameters obtained from this fitting procedure. This procedure was used to extract the effect of the radicals on the shorter components of the decay.

Table 4.4: Fitting parameters of the TCSPC (ps) decay of 3.8 nm CdSe QDs. The last two columns depict the amplitude averaged and intensity averaged lifetime calculated from

$\tau_{\text{short}(1)}$ and $\tau_{\text{short}(2)}$

[AT] (mM)	τ_{long} (ps)	A ₁	$\tau_{\text{short}1}$ (ps)	A ₂	$\tau_{\text{short}2}$ (ps)	$\tau_{\text{avg,short}}$ (Amp.) (ps)	$\tau_{\text{avg,short}}$ (Int.) (ps)
0	20017	0.41	770	0.59	2976	2072	2640
1.1	17463	0.42	671	0.58	2743	1873	2431
2.1	15786	0.38	2.3	0.62	2520	1767	2254
4.3	12530	0.44	5.0	0.56	2153	1380	1930
6.4	11077	0.42	11.1	0.58	1946	1257	1779
8.5	9760	0.52	19.9	0.48	1896	1062	1667
10.5	9133	0.49	31.2	0.51	1685	981	1487

It is observed that the long component of the decay decreases with the radical concentration (Table 4.4, column 2). The time constant from this was used to plot the τ_0/τ as reported in Figure 4.22.

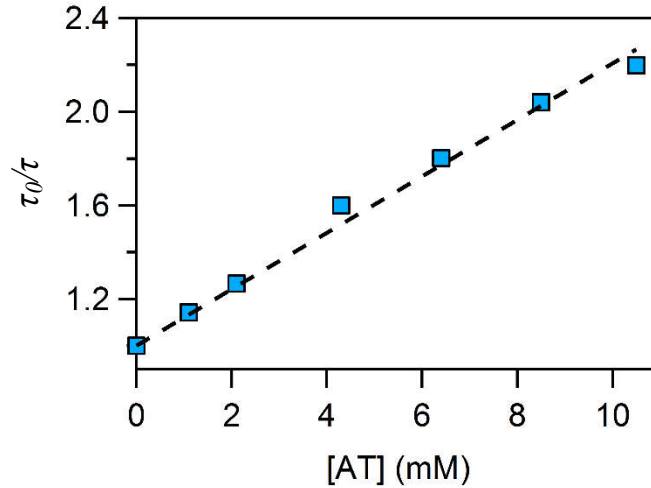


Figure 4.22: Plot of τ_0/τ of 3.8 nm CdSe + AT obtained from the long component of the TCSPC (ps) fit

$$\frac{\tau_0}{\tau} = 1 + k_q \tau_0 [AT] \dots \dots \dots \text{Eq. (4.2)}$$

From the fit in Figure 4.22, k_q was calculated to be $0.5 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ which is close to the diffusion limited value $10^{10} \text{ M}^{-1} \text{ s}^{-1}$.^{11,44}

A closer look into the short decay parameters listed in Table 4.4 ($\tau_{\text{short}(1)}$, $\tau_{\text{short}(2)}$) reveals that the individual lifetime changes as the concentration of the radical increases, the decrease in the lifetimes being more drastic for $\tau_{\text{short}(2)}$.

$\tau_{\text{short}(1)}$ can be ascribed to the exciton recombination while $\tau_{\text{short}(2)}$ can be attributed to shallow hole trap states.^{45,46} $\tau_{\text{short}(1)}$ is close to the charge recombination rates observed in TA (though in TA these would only reflect the electron dynamics whereas here we are sensitive to the exciton dynamics). The shallow traps would provide a temporary reservoir for the holes to shuttle between them and the band edge, eventually decaying across the band edge therefore the quenching

occurring through the trapping mechanism $\tau_{\text{short}(2)}$ has a much slower rate compared to the direct band edge transfer $\tau_{\text{short}(1)}$.^{46,47}

As for the presence of two components responsible for hole transfer (one with time constant < 1 ps and the other $\tau_{\text{short}(1)}$), it can be hypothesized that there might be two possible orientation of the radical around the QDs, one such that the NO $\cdot$ is in closer proximity to the QDs and hence leads to an ultrafast hole transfer. The other orientation, might not have such close proximity resulting in the slower hole transfer rate as observed in the ps TCSPC time scale ($\tau_{\text{short}(1)}$). However, more detailed experiments would be necessary to substantiate this hypothesis. The results obtained with CdTe QDs are discussed next.

4.3 D.2: CdTe QDs

The same analysis was conducted for the quenching of 5 nm CdTe QDs with 4-amino TEMPO. The TCSPC (ps) decay for the 5 nm CdTe has already been shown in Figure 4.13. The decay was fit in the same manner as for the CdSe QDs in Section 4.3 D (I). The values obtained are listed in Table 4.5.

Table 4.5: Fitting parameters of the TCSPC (ps) decay of the 5 nm CdTe QDs with 4-amino TEMPO

[AT] (mM)	τ_{long} (ps)	A_1	τ_{short1} (ps)	A_2	τ_{short2} (ps)
0	2267	0.22	74	0.78	380
0.17	2240	0.25	71	0.75	370
0.35	2218	0.44	58	0.56	350
0.88	1993	0.49	50	0.51	203
1.90	1796	0.57	41	0.43	260

Similar to the CdSe QDs, it is observed that the long component of the decay in case of the CdTe QDs decrease with the radical concentration (Table 4.5, column 2). The time constant from this was used to plot the τ_0/τ as reported in Figure 4.23.

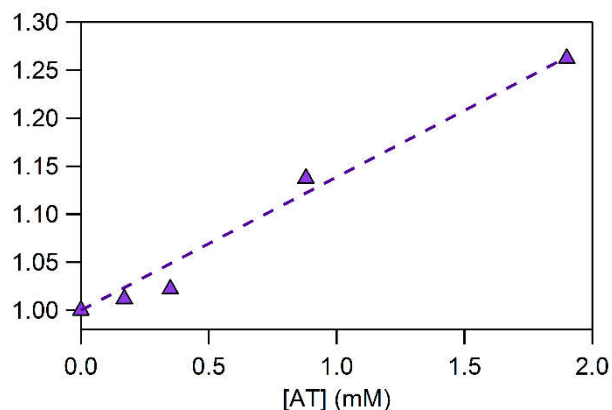


Figure 4.23: Plot of τ_0/τ obtained from the long component of the TCSPC (ps) fit for 5 nm CdTe QDs and AT

The k_q was calculated from Figure 4.23 and was found to be $1.2 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ which is again close to the diffusion limited value.

The TA spectrum of the 5nm CdTe QDs without any radical added (Figure 4.24, black circles) shows a very fast decay (within the first 100 ps). This can be attributed to electrons getting trapped into the surface electron traps. A similar approach was adopted for fitting the TA 1S exciton decay. The long component of the first exciton decay was fit with a single exponential and then subtracted from the decay to fit the rest of the decay with a bi-exponential. The fitting parameters are listed in Table 4.6. There are two short components (equal amplitudes) in the TA decay, both are found to remain constant with increasing radical concentration. These probably depict the surface electron trapping processes (shallow and deep trapping, since the time constants are quite different) which are not affected by the hole transfer process occurring from the QDs to the radical. The long component can be attributed to the electron recombination. Further studies would be required to validate these assertions, where different samples could be prepared with better surface coverage/ with inorganic shells on the QD cores to minimize these trap states and see how that affects the hole transfer process.

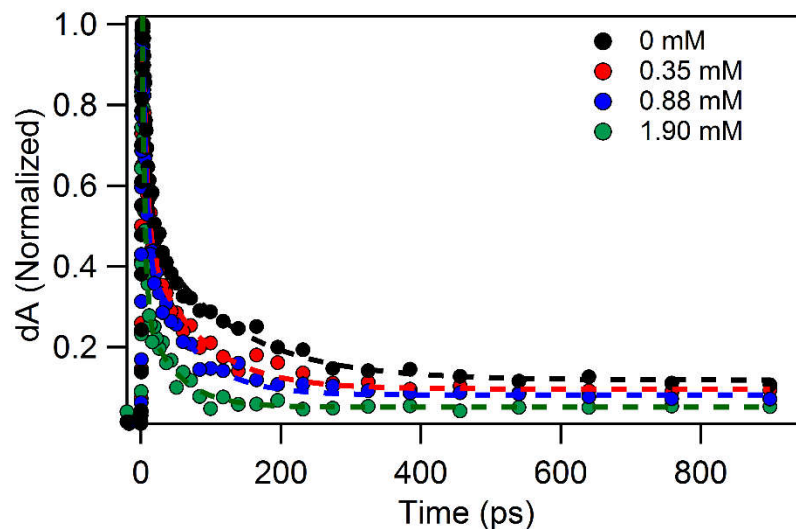


Figure 4.24: The decay of the first exciton (normalized at time zero) of 5.0 nm CdTe QDs with increasing concentration of 4-amino TEMPO radical. The dashed lines are the guide to the eyes

Table 4.6: Fitting parameters of the TA first exciton decay of the 5 nm CdTe QDs with 4-amino TEMPO

[AT] (mM)	τ_{long} (ps)	A_1	τ_{short1} (ps)	A_2	τ_{short2} (ps)
0	470	0.50	4.5	0.50	35.0
0.17	450	0.51	3.9	0.49	34.8
0.35	401	0.51	3.7	0.49	33.3
0.88	345	0.58	3.7	0.43	36.1
1.90	320	0.74	3.5	0.26	33.8

There are few conclusions that can be drawn from the analysis conducted in Section 4.3. First of all, comparison of the TA 1S exciton bleach and the upconversion and TCSPC measurements clearly demonstrates that the charge transfer occurring in CdSe and CdTe QDs in presence of

4-amino TEMPO is a hole transfer process. There is an instantaneous drop in intensity observed in the uPL and TCSPC PL decay, which represents a very fast hole transfer process (< 1 ps). Further, the TCSPC decay analysis shows a distribution of rate constants that become shorter with increasing radical concentration. A closer look at the change in the decay curves reveal a fast transfer occurring from the band edge, a slower transfer occurring via the surface trap states and contribution from another diffusion-limited transfer. Though, this analysis gives an insight into the underlying mechanism of transfer, using multi-exponential fits for extracting meaningful rate constants can always be tricky. In view of this, for the proper explanation of the ensemble measurements; a model is required; where the distribution of decay rates are explicitly defined. Such a model was proposed by van Driel⁴⁸ and has also been successfully employed in the quantum efficiency studies of core-shell CdSe/ZnS colloidal QDs.⁴⁹ The basic principles and details of this theory has been is mentioned in the next section (4.4).⁵⁰

Finally, a comparison of the quenching by CdSe and CdTe QDs was conducted. On comparing the ultrafast quenching observed for the CdSe and CdTe QDs with 4-amino TEMPO (by analysing the instantaneous drop observed in the ps TCSPC) , it is found that $(I_0/I)^{\text{instant}}$ obtained from the instantaneous drop in the uPL and TCSPC measurements is faster in case of CdTe QDs as compared to the CdSe QDs (Figure 4.25). The band alignment of the VB²² of CdSe, CdTe and the oxidation potential of the 4-amino TEMPO radical⁵¹ hints towards a larger driving force for the hole transfer from the CdSe QDs. The lower transfer rate in this case might mean that the transfer falls in the inverted regime of the Marcus theory. However, owing to the uncertainty in the VB alignments of the CdSe and CdTe QDs, this is more difficult to ascertain at this point. more detailed comparison of the surface nature of both the QDs are required in order to prove that this observed effect is owing to the difference in the electronic properties of the CdSe and CdTe QDs or due to

any difference in their surface properties (leading to one having more anion/cation-rich surface compared to the other, which would influence the quenching process).

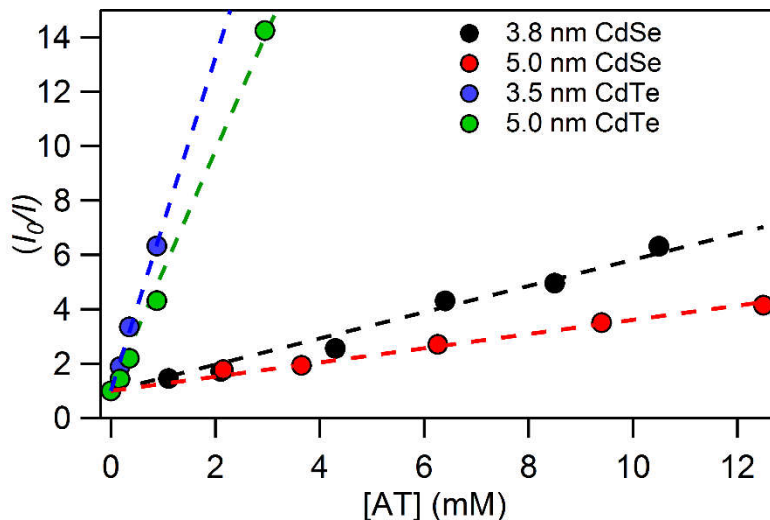


Figure 4.25: Plot comparing the $(I_0/I)^{\text{instant}}$ of CdSe and CdTe QDs with increasing radical concentration of 4-amino TEMPO

4.4: Modeling the distribution of decay rates

The decay curve obtained from the PL measurements consists of a histogram of the distribution of arrival times of single photons after many excitation-detection cycles. The histogram is modeled with a decay-function from which the decay time of the process can be deduced. It is a general problem to model these complex multi-exponential decay processes in QDs. In many cases the decay is much more complex and strongly differs from single-exponential decay, as is observed consistently in this thesis. This usually means that the decay is characterized by a distribution of rate constants instead of a single rate.⁴⁸ Double- and triple-exponential functions or models with a particular distribution of single-exponentials are often used.⁵²⁻⁵⁴ Sometimes double- and triple-

exponential models can be explained,⁵⁵ however, in many cases no particular multi-exponential model can be anticipated on the basis of physical knowledge of the studied system.

The density of excited emitters $c(t)$ and the intensity from the emission decay curve ($g(t)$) are not proportional, but the density is a time-integral of the intensity⁴⁸ (as depicted in Eq. 4.4).

$$I_{PL} \propto \frac{d[emitter]}{dt} \dots\dots\dots \text{Eq. (4.3)}$$

$$[emitter] = \int I_{PL} dt \dots\dots\dots \text{Eq. (4.4)}$$

The integral relation is crucial to correctly interpret non-single-exponential decay. The proper normalization for a distribution of rates has been developed by van Driel, et al.⁴⁸ yielding a practical description of non-single-exponential emission decay curves in terms of the distribution of total decay rates weighted with the radiative rates. The analysis of decay curves in terms of distributions of decay rates yields valuable information on physically interpretable rates, as opposed to analysis in terms of multi-exponential fitting of the lifetimes.

For a better understanding of the analysis of charge transfer process, the mathematical form of the model as described by van Driel and co-workers is summarized here.

The PL decay curve is a probability density of emission which has therefore to be modeled with a so-called probability density function.⁵⁶ At $t \rightarrow \infty$, this function tends to zero. The decay of the

fraction of excited emitters $\frac{c(t')}{c(0)}$ at time t' is described with a cumulative distribution function

$1 - \frac{c(t')}{c(0)}$ where $c(0)$ is the concentration of excited emitters at $t' = 0$.⁵⁶ This function tends to 1 in

the limit $t' \rightarrow \infty$ since $c(t') = 0$ and to 0 in the limit $t' \rightarrow 0$ where $c(t') = c(0)$. The fraction of excited

emitters and the decay curve, i.e., the cumulative distribution function and the probability density function,⁵⁶ are related as follows:

$$\int_0^t g(t)dt = 1 - \frac{c(t)}{c(0)} \dots\dots\dots \text{Eq. (4.5)}$$

Thus, the decrease of the concentration of excited emitters at time t' is equal to the integral of all previous decay events or the total intensity $g(t)$ is proportional to the time-derivative of the fraction of excited emitters.

When a non-single-exponential decay curve is modelled with a series of single-exponentials, the decay curve has the following form:

$$g(t) = \frac{1}{c(0)} \sum_{i=1}^n c_i \Gamma_{rad,i} \exp(-\Gamma_{tot,i} t) \dots\dots\dots \text{Eq. (4.6)}$$

where n is the number of different emitters (in case of QDs which have an ensemble of different emitters with different quantum efficiencies and trap states which trap the exciton but these can de-trap and emit radiatively eventually), c_i is the concentration of emitters that has a radiative decay rate $\Gamma_{rad,i}$ (at $t = 0$) and $c(0)$ is the concentration of all excited emitters at $t = 0$, i.e., the sum of all concentrations c_i . In QDs, the trap states generally have a distribution of energies. When the different fractions (or environments) are distributed in a particular way, a distribution function $\rho(\Gamma_{tot})$ has to be used. This function would describe the distribution or concentration of the emitters over the emission decay rates at time $t=0$. The fraction of emitters $\frac{c_i}{c(0)}$ with a total decay rate $\Gamma_{tot,i}$ is given by Eq. 4.7.

$$\frac{c_i}{c(0)} = \rho(\Gamma_{tot,i}) \Delta\Gamma_{tot} \dots\dots\dots \text{Eq. (4.7)}$$

where $\rho(\Gamma_{tot,i})$ expresses the distribution of the various components i over the rates $\Gamma_{tot,i}$ and has units of inverse rate. $\Delta\Gamma_{tot}$ is the separation between the various components i in the sum. The decay curve now has the following mathematical form:

$$g(t) = \sum_{i=1}^n \Delta\Gamma_{tot} \rho(\Gamma_{tot,i}) \Gamma_{rad,i} \exp(-\Gamma_{tot,i} t) \dots\dots\dots \text{Eq. (4.8)}$$

In Eq. 4.4 every component in the sum is correctly normalized as every component is multiplied with its radiative decay rate ($\Gamma_{rad,i}$). For infinitesimal values of $\Delta\Gamma_{tot}$ Eq. (4.8) could be expressed as an integral:

$$g(t) = \int_0^{\infty} \Gamma_{rad}(\Gamma_{tot}) \rho(\Gamma_{tot}) \exp(-\Gamma_{tot} t) d\Gamma_{tot} \dots\dots\dots \text{Eq. (4.9)}$$

It is assumed here that for every Γ_{tot} there is one Γ_{rad} , however in general both Γ_{tot} and Γ_{rad} vary independently. Thus, $\rho_{tot}(\Gamma_{rad})$ is used as the normalized distribution of Γ_{rad} at constant Γ_{tot} . For every Γ_{tot} the integration is performed over all radiative rates; a distribution of Γ_{rad} is taken into account for every Γ_{tot} . The general form of the equation turns out to be:

$$g(t) = \int_0^{\infty} \left[\int_0^{\Gamma_{tot}} d\Gamma_{rad} \rho_{\Gamma_{tot}}(\Gamma_{rad}) \Gamma_{rad} \right] \rho(\Gamma_{tot}) \exp(-\Gamma_{tot} t) d\Gamma_{tot} \dots\dots\dots \text{Eq. (4.10)}$$

An ensemble of emitters as in QDs, a distribution of rates Γ_{tot} is not completely characterized by a single value of the quantum efficiency. In such an ensemble, the quantum efficiency is

distributed, since each Γ_{tot} is associated with a distribution of radiative rates Γ_{rad} . The average quantum efficiency or the total PL intensity can be calculated by integrating Eq. (4.10) over time.

Since, detailed information on the relation between Γ_{tot} and Γ_{rad} is not available most of the times, modelling with a distribution of decay rates was applied by van Driel et al.^{52-54,57,58} Thus, the function used to model the non-single-exponential PL decay curve was:

$$g(t) = \int_0^{\infty} \sigma(\Gamma_{tot}) \exp(-\Gamma_{tot}t) d\Gamma_{tot} \dots\dots\dots \text{Eq. (4.11)}$$

Distribution functions that can be used for (are sums of normal, Lorentzian, and log-normal distribution functions).

A log-normal distribution function ($\sigma(\Gamma)$) of the rate Γ was used by van Driel.

$$\sigma(\Gamma) = A \exp \left[- \left(\frac{\ln \Gamma - \ln \Gamma_m}{\gamma} \right)^2 \right] \dots\dots\dots \text{Eq. (4.12)}$$

where A is the normalization constant, Γ_m is the median in the rate constant distribution and γ is related to the width of the distribution:

$$\Delta\Gamma = 2 \Gamma_m \sinh(\gamma) \dots\dots\dots \text{Eq. (4.13)}$$

where $\Delta\Gamma$ is equal to the width of the distribution at $1/e$. The median rate constant Γ_m and γ are adjustable fitting parameters.

It is widely assumed that $\sigma(\Gamma)$ is equal to the distribution of total rates,^{52,54,59-61} however, $\sigma(\Gamma)$ contains information about both the radiative and non-radiative rates. $\sigma(\Gamma)$ is actually the distribution of total decay rates weighted by the radiative rates.

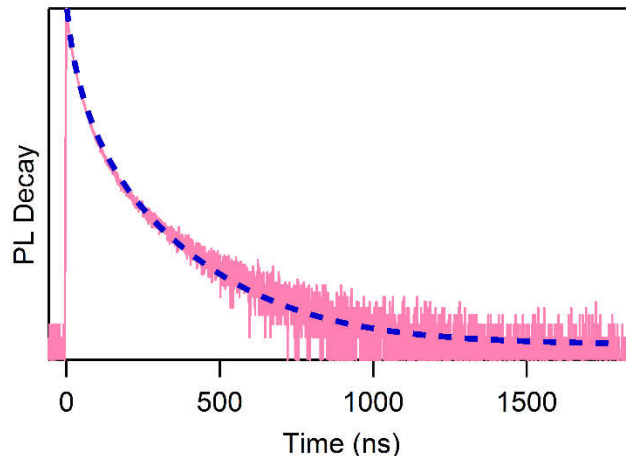


Figure 4.26: The PL decay of 3.6 nm CdSe QDs modeled with Eq. (4.11), the dashed line is the fit to the log normal rate constant distribution

The use of log normal distribution is justified in our case because of the multiplicative nature (multiplicative effects lead to log-normal distributions)⁵⁰ of the events occurring in photo-excitation of QDs and subsequent quenching event in presence of a suitable acceptor (radical). This will be discussed in details later in this section.

PL decay of the CdSe and CdTe QDs used in this work has been fit with the log-normal rate constant distribution, one such fit is shown in Figure 4.26. The log-normal distribution approach provides a good description of the experimental data (seen from how well the model fits the experimental decay curve). A good fit would not necessarily prove that this chosen distribution is unique, nevertheless, it helps us to extract direct physical information about the ensemble of emitters and their environment using the non-single exponential decays.⁶²

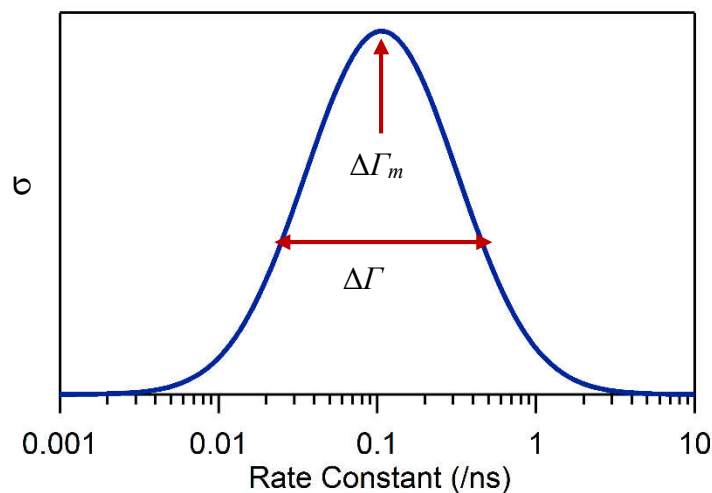


Figure 4.27: Log-normal distribution of rate constant (Γ). This distribution was modelled to the data of PL decay in Fig. 4.26 with Γ_m and γ (Eq. 4.12) as the adjustable fitting parameter. The x-axis is reported in logarithmic scale. Γ_m was found to be 0.106 ns^{-1} ($1/\Gamma_m = 9.4 \pm 1.4 \text{ ns}$) and the width of the distribution $\Delta\Gamma$ (calculated using Eq. 4.13) was found to be $0.54 \pm 0.08 \text{ ns}^{-1}$

This procedure has been applied to the series of PL decay curves collected for the CdSe and CdTe QDs in presence of 4-amino TEMPO.

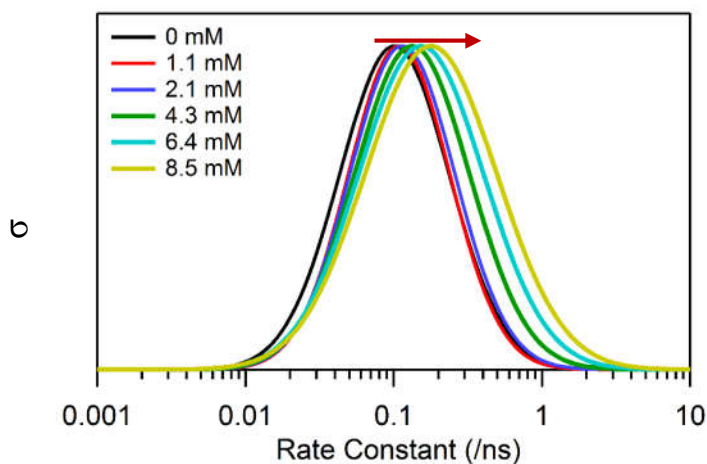


Figure 4.28: Log-normal distribution of rate constant (Γ) of 3.8 nm CdSe QDs with increasing concentration of 4-amino TEMPO. The arrow indicates the shift in Γ_m with increasing radical concentration

As evident from Figures 4.28 and 4.31, the most frequent decay rate (Γ_m) increases with increasing radical concentration. The same is noticed for all the samples measured here. Γ_m is a measure of the total decay rate and has two components: the radiative decay rate, k_{rad} , and the nonradiative decay rate, k_{nr} . k_{nr} depends on the microscopic mechanisms of the dominant nonradiative pathways and as discussed in the Chapter 1, the surface/ interface trap states would be one of the most important factors in this regard.

The increase in the Γ_m with increasing radical concentration, can be comprehended easily based on the behavior of the k_{tot} . A simple picture here might help in this regard.

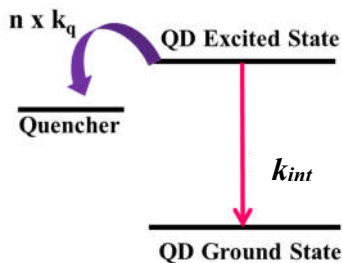


Figure 4.29: The recombination pathways in a photo-excited QD. Here k_{int} is the sum of all recombination rate constants in an excited QD

In presence of the quencher, there is an alternate pathway for recombination as depicted by the rate constant k_q . The total rate of transfer to the quencher also depends on the number of quencher, n . With increase in radical concentration, k_q increases and hence the k_{tot} ($k_{tot} = k_{int} + k_q$) increases. This explains the shift of Γ_m to higher values.

However, it is also observed that the width of the distribution increases with increase in radical concentration (depicted in Fig. 4.26 from the FWHM of the distribution). This increase in the width

of the distribution is more complex in nature. This means that the total decay rates are distributed more broadly in presence of higher concentration of radicals.

Γ_m consists of both k_{rad} and k_{nrad} but it is difficult to see how k_{rad} would be involved in observed the increase of the distribution width. However, there is always a range of trap state energies in QD ensembles. As depicted in Figure 4.30, the trapping and de-trapping rate constants (k_{tr} and k_{dt}) would differ significantly depending on the trap state energy level. For e.g. in this particular scheme k_{dt1} and k_{dt6} would be widely different owing to the energy difference of these two levels and hence the de-trapping is easier/faster from level 1 as compared to level 6. The electrons trapped in trap state 6 would have to cycle more number of times before it can get come back to the excited state.

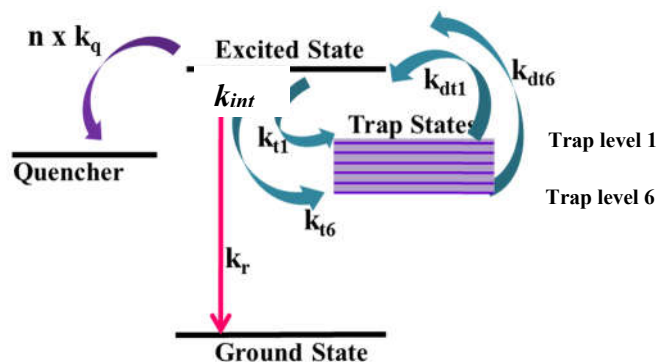


Figure 4.30: Schematic representation of the distribution of trap state energies in a QD

Now as more and more radicals are added to the system, the radicals have to diffuse to the QDs. Since, these radicals are not bound to the QDs, they can diffuse away from the QDs after some time. The charges which are trapped very close to the excited state (in energy, as for e.g. charges trapped in level 1 in Figure 4.30) have a better chance of getting quenched since they can de-trap more easily compared to the trap 6. The deeper traps are cycled much slower and hence do not get

a chance to be quenched and do not contribute towards the quenching but decay radiatively, with a longer lifetime. This would explain the increase in the width of the rate constant distribution with increasing radical concentration.

The quenching event actually depends on the probability of occurrence of three separate events: i) de-trapping of the charges from the trap states, ii) the diffusion of the radical towards the quencher, and iii) the transfer of charge. Thus the probability of the quenching process is a product of each individual probabilities leading to a lognormal distribution.⁵⁰

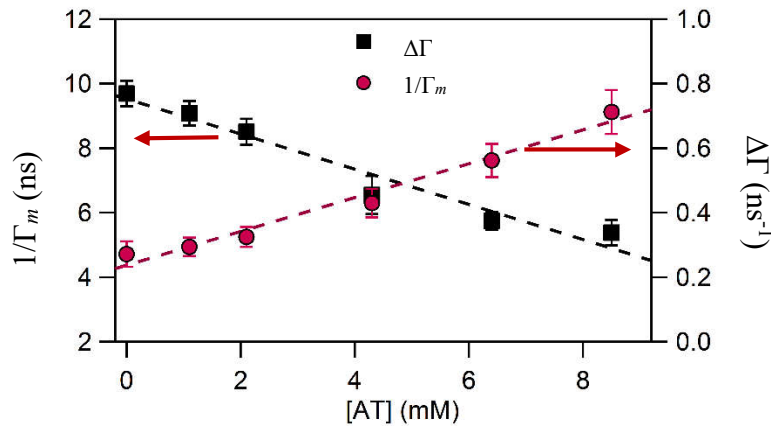


Figure 4.31: Plot showing the behavior of Γ_m and $\Delta\Gamma$ of the distribution of rate constants of 3.8 nm CdSe QDs with increasing radical concentration. The dashed lines are guide to the eyes

The $(I_0/I)^{TD}$ value obtained by integrating the PL decay after normalization was compared to the $(\tau_0/\tau)_m$ where $\tau=1/\Gamma_m$. Though, the modeling of the ensemble rate constant distribution provides insight into the statistical behavior of the QDs, some intrinsic properties still cannot be extracted from such averaged data. As for example, Γ_m is the most frequent rate constant in the distribution, however owing to the width of this distribution, Γ_m cannot be considered as a representative of the

total PL decay rate constant. Hence, τ_0/τ cannot not capture the whole picture, and is significantly different from the $(I_0/I)^{TD}$ as depicted in Figure 4.32.

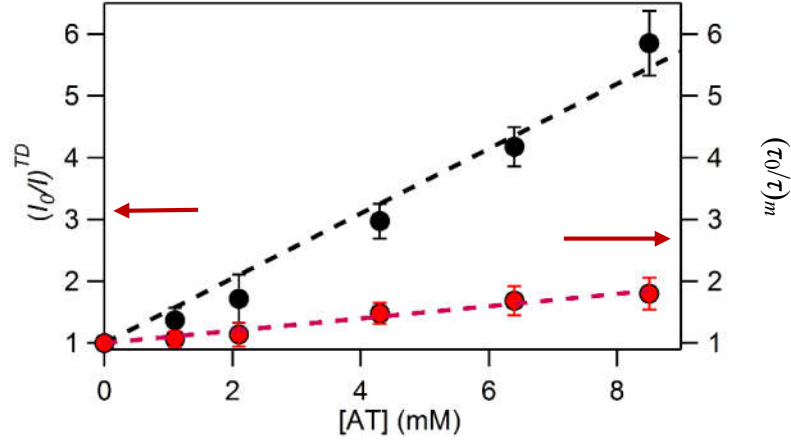


Figure 4.32: Plot showing the comparison of the $(I_0/I)^{TD}$ obtained by integrating the normalized TCSPC decay of 3.8 nm CdSe QDs with increasing radical concentration against the $(\tau_0/\tau)_m$ obtained from the lognormal model

The same analysis was conducted for the CdTe QDs and the results were found to be similar and can be explained using the hypothesis presented in Figures 4.30.

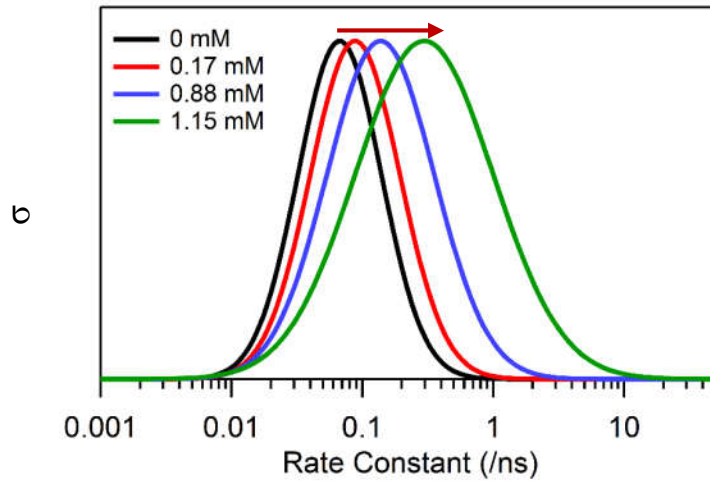


Figure 4.33: Log-normal distribution of rate constant (Γ) of 3.5 nm CdTe QDs with increasing concentration of 4-amino TEMPO. The arrow indicates the shift in Γ_m with increasing radical concentration

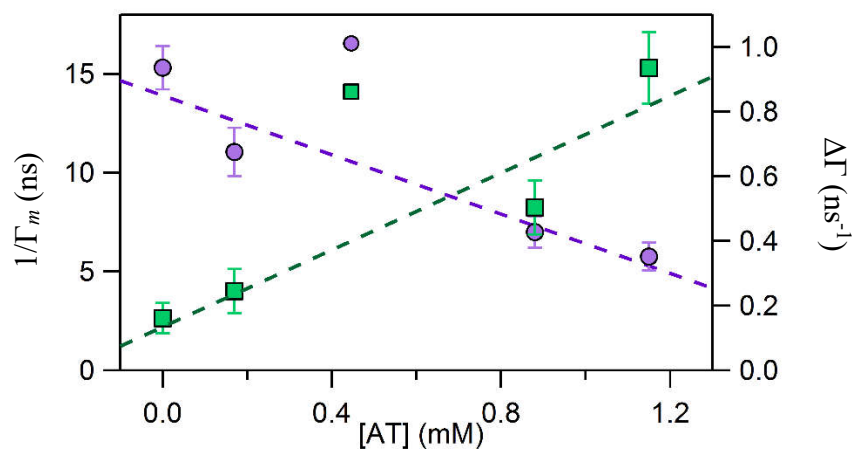


Figure 4.34: Plot showing the behavior of $1/\Gamma_m$ and $\Delta\Gamma$ of the distribution of rate constants of the 3.5 nm CdTe QDs with increasing radical concentration. The dashed lines are guide to the eyes

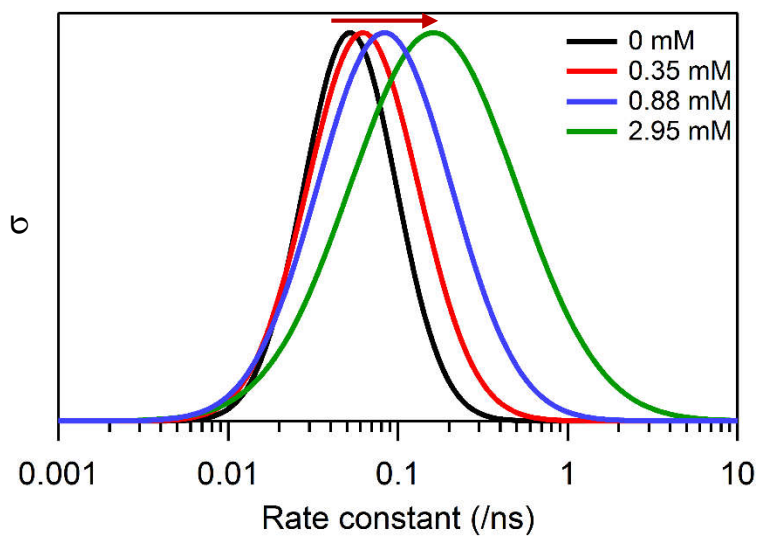


Figure 4.35: Log-normal distribution of rate constant (Γ) of 5.0 nm CdTe QDs with increasing concentration of 4-amino TEMPO. The arrow indicates the shift in Γ_m with increasing radical concentration

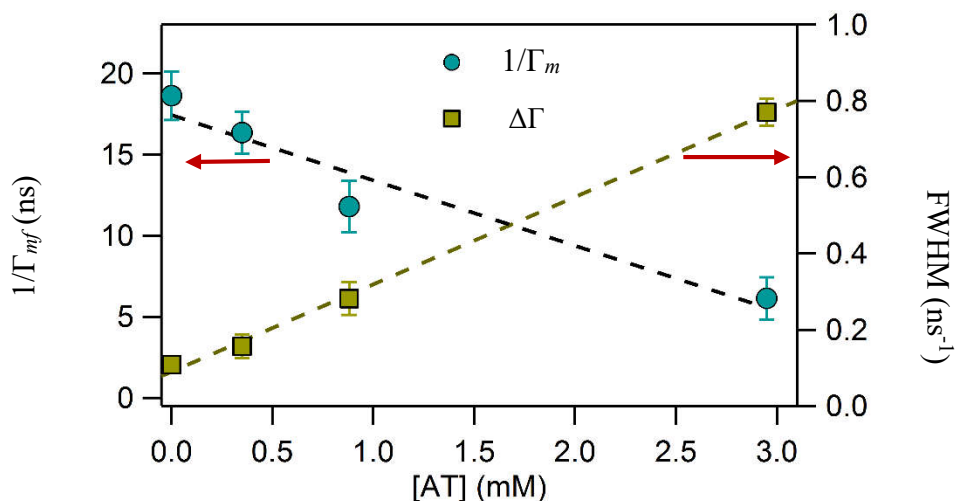


Figure 4.36: Plot showing the behavior of $1/\Gamma_m$ and $\Delta\Gamma$ of the distribution of rate constants of the 5 nm CdTe QDs with increasing radical concentration. The dashed lines are guide to the eyes

4.5: Conclusion

First of all, the comparison of the TA and uPL measurement clearly demonstrates that the PL quenching of the photo-excited QDs by the 4-amino TEMPO radical is due to a hole transfer process. Also, this hole transfer is found to be ultra-fast (faster than the ~ 1 ps resolution of the uPL measurement). 4-amino TEMPO can thus efficiently extract the hole with an ultrafast rate from photo-excited CdSe and CdTe QDs. These dyads would thus prove to be great systems for applications such as QD-sensitized solar cells utilizing the 4-amino TEMPO as a redox shuttle.

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REFERENCES

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Chapter 5: PL quenching of II-VI QDs with 4-carboxy TEMPO

5.1: Aim of this work

As seen in Chapter 2, the 4-amino TEMPO radical has low surface binding affinities for CdSe and CdTe QDs. However, the rate of hole transfer from the QD to this radical is found to be ultrafast (< 1 ps) which is very desirable for many applications like QD-sensitized solar cells. Higher binding affinities coupled with ultrafast hole transfer capabilities would make this QD-nitroxide radical dyads highly desirable. Moving forward with this idea, the TEMPO radical with a carboxy head group (Figure 5.1) was explored. It has been observed earlier that hard bases (for example ligands with oxygen-containing headgroups such as carboxylates) bind strongly to NCs with more ionic lattices and harder surface sites, such as CdSe.¹

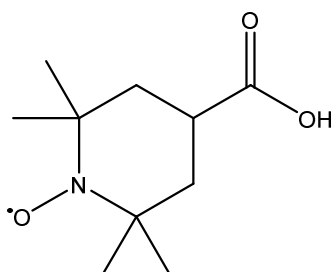


Figure 5.1: Structure of 4-Carboxy-2,2,6,6-tetramethylpiperidine 1-oxyl (4-Carboxy-TEMPO) radical

5.2: Experimental Section

5.2 A: Chemicals used

4-carboxy TEMPO free radical (97%), sodium myristate ($\text{CH}_3(\text{CH}_2)_{12}\text{COONa}$, $>98\%$), cadmium nitrate tetrahydrate ($\text{Cd}(\text{NO}_3)_2$, 98%) and oleic acid ($\text{CH}_3(\text{CH}_2)_7\text{CH}=\text{CH}(\text{CH}_2)_7\text{COOH}$, 90%)

were purchased from Sigma Aldrich. Ethyl acetate and pentane (ACS grade) were purchased from Macron Fine Chemicals and distilled before use.

5.2 B: Synthetic method

Owing to the greater polarity of the 4-carboxy TEMPO, toluene was not a good solvent for this radical. Dichloromethane (DCM) was a solvent that could disperse the QDs as well as the radicals efficiently and has been used for all the studies with this radical. In Chapter 2, it was observed that the free phosphonic acid traces in the solution could interact with the 4-amino TEMPO radical giving broad EPR peaks (Figure 2.29 panel c). To avoid any such complexities with the free amine ligands in the QDs used in all of our previous experiments, the QDs used for this study was synthesized in a different method as reported by Cao, et al.² This is a heat up method instead of the hot-injection method used previously. There are two advantages of using this method, (i) after synthesis, the QDs can be washed repeatedly to get rid of any free ligands in the solution and the resulting QD solution still has appreciably good QY (15-20%) and (ii) the surface bound ligands in this case are carboxylates (helping to avoid any unwanted interaction between the surface ligands and added radicals). The details of this method is described here. The precursor cadmium myristate was prepared from cadmium nitrate and sodium myristate. The sodium myristate solution was prepared by dissolving sodium hydroxide (15 mmol) and myristic acid (15 mmol) in anhydrous methanol (500 mL). Cadmium nitrate (5 mmol) was dissolved in anhydrous methanol (50mL) and was added drop wise (one drop per second) into the sodium myristate solution with vigorous stirring. The resulting white precipitate was filtered. For the CdSe NC synthesis, cadmium myristate (0.1 mmol), selenium dioxide (0.1 mmol) and ODE (6.3 mL) were mixed in a 25-mL three-neck flask. The resulting mixture was degassed under vacuum (30 mins) at room temperature. Under continuous nitrogen flow and stirring, the mixture was heated to the reaction

temperature (240 C) at a rate of 25 C/min. The time was counted as zero when the temperature reached 240 C. Aliquots were drawn at regular intervals to monitor the size of the resulting NCs. After 15 mins at the reaction temperature, oleic acid (0.1 mL) was added drop wise (6 drop/min) into the reaction solution to further stabilize the nanocrystals. The reaction temperature was maintained for an additional 25-45 min, and then the reaction solution was cooled to room temperature. The CdSe NCs were dissolved in small amount of pentane and precipitated out of the solution by adding ethyl acetate (non-solvent) and then centrifuged to remove the supernatant. This procedure was repeated 5-6 times until NMR spectra showed that there was no free oleic acid in the NC solution and all the oleic acid present were bound to the NC surface. Once the desired result was obtained, the NCs were dispersed in DCM and the quenching measurements were carried out. For the NMR experiments, relatively high concentration of QD solution (~ 0.1 M) are required, so the above synthetic method was scaled up 50-60 times. After the reaction was over, the ODE was extracted from the reaction mixture by vacuum distillation, before the NC work up process.

5.3: Results

5.3 A: Characterization of CdSe QDs

The NMR spectra of the QDs (Figure 5.2) in deuterated benzene (C_6D_6) was measured after 3 washes with ethylacetate. The peak ~ 5.5 ppm is the vinylic peak from the oleic acid. Presence of sharp peaks at ~ 5.5 ppm in the NMR spectrum suggests that there are some free oleic acid in the QD solution. The QD solution was washed thrice after this and NMR spectra measured again (Figure 5.3). The broad peak in Figure 5.3 shows that all the oleic acid are bound to the QD surface.

Same procedure was followed to obtain the two different CdSe QDs (3.6 nm and 5.1 nm) used in this chapter.

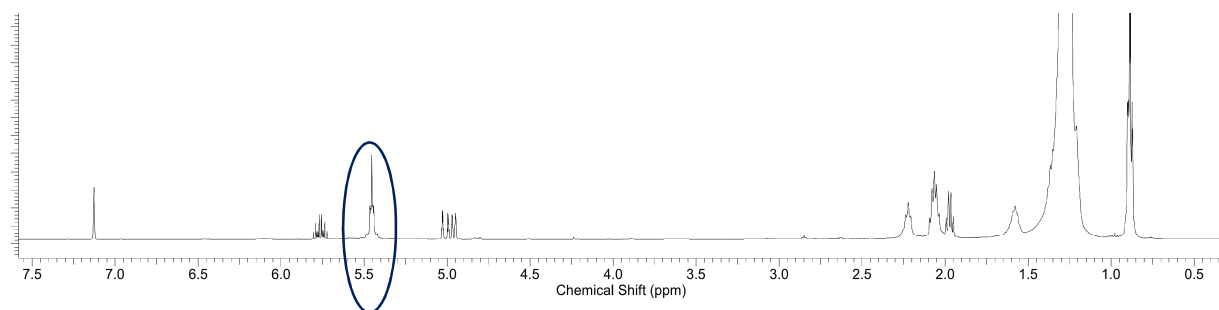


Figure 5.2: NMR spectra of the 5.1 nm CdSe QDs in benzene-d6 after third wash

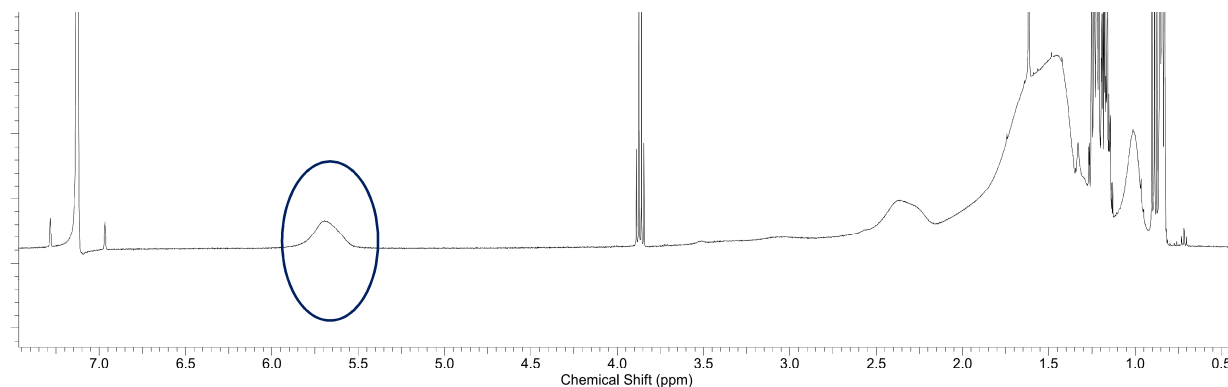


Figure 5.3: NMR spectra of the 5.1 nm CdSe QDs in benzene-d6 after sixth wash

The concentrations of nanocrystals and carboxylate ligands in benzene-d6 stock solutions were determined using a combination of NMR and UV-visible absorption spectroscopies. The concentration of the bound ligands in the QD solution was determined by using ferrocene. Ferrocene dissolved in benzene-d6 (10 μ L, 0.05 M) was added to a known volume of the nanocrystal stock solution and used as an internal standard. The concentration of ligands was

determined by integrating the ligand methyl and ferrocene resonances and normalizing for the number of hydrogens, respectively (3:10). The size and molar concentration of CdSe QDs in these stock solutions was determined by diluting to a known volume with toluene and measuring the absorbance and using the empirical equations as described in Chapter 2 (Eqs. 2.3 and 2.5). Using the diameter, number of ME (M = Cd; E = Se) units per NC were calculated (assuming a spherical shape). The ligand surface density was calculated from the number of ME units per NC, the molar concentration of ME, and ligands in the stock solution. By coupling the NMR and UV-vis absorbance of the QD samples, the ligand concentration was determined to be 2.7 ligand/nm² and 2.0 ligand/nm² for the 3.6 nm and 5.1 nm CdSe QDs respectively. The QY of the samples were found to be 20% and 15% respectively. The absorbance and the PL spectra of these samples are reported in Figure 5.4.

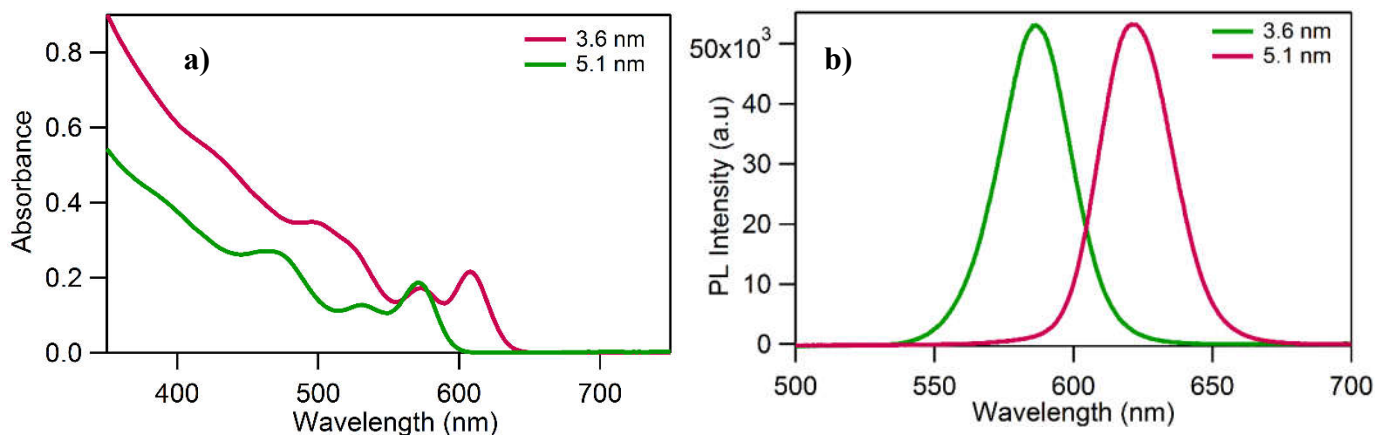


Figure 5.4: Absorbance spectra (panel a) and PL spectra (panel b) of the 3.6 nm and 5.1 nm CdSe QDs used in the study

5.3 B: Quenching experiments with CdSe and 4-carboxy TEMPO radicals

The quenching experiments were conducted with these QDs (2-3 μM concentration) and 4-carboxy TEMPO (4-CT) radical in DCM. The solubility of the radical in DCM was found to be ~ 0.1 M at room temperature. So, in all cases a stock solution of ~ 0.06 M was used for the quenching experiments.

The extinction coefficient of the radical in DCM was found to be $10.5 \text{ M}^{-1}\text{cm}^{-1}$ at 462 nm. The radical solution was always freshly prepared for the quenching studies and the exact concentration determined from the absorbance.

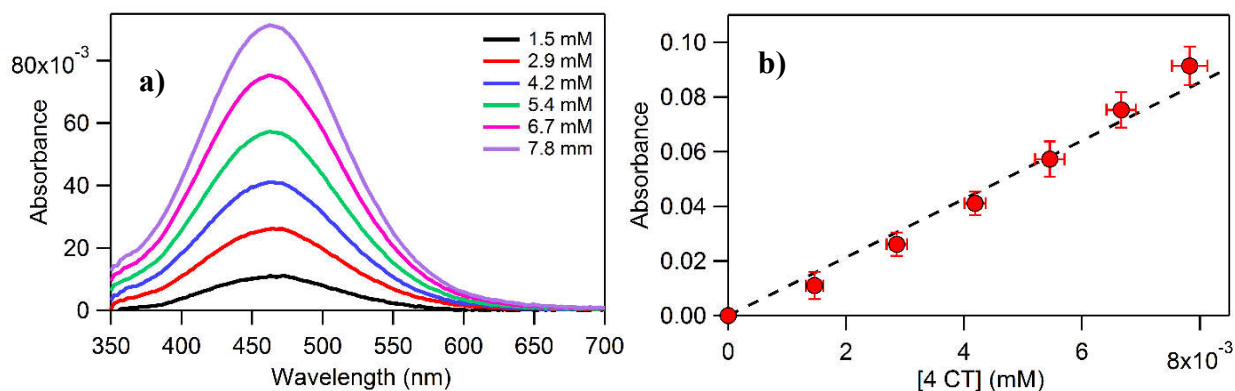


Figure 5.5: Absorbance spectra of 4-carboxy TEMPO radical in DCM (panel a) and determination of the extinction coefficient of the radical (panel b)

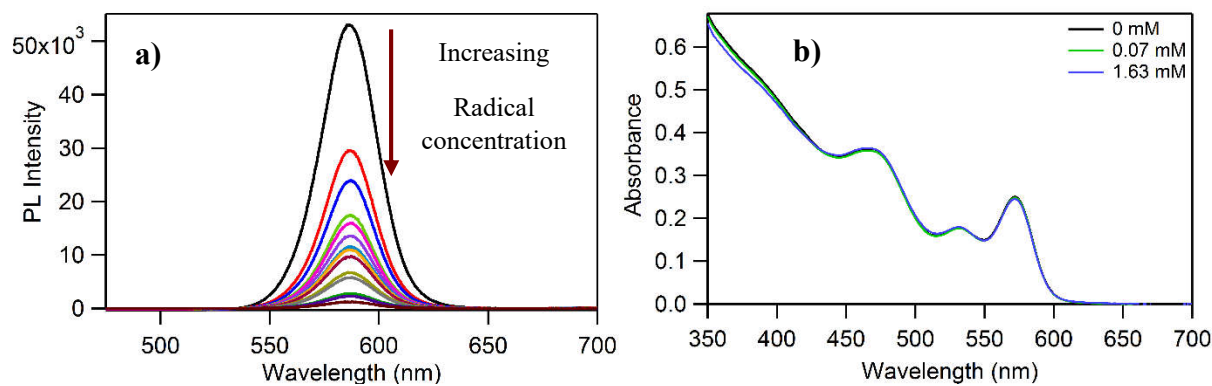


Figure 5.6: Decrease in PL intensity (PL quenching) (panel a), absorbance of the QDs (panel b) of 3.6 nm CdSe QDs with increasing concentration of 4-carboxy TEMPO radical. The concentration of the radicals in panel a) is varied from 0-2.3 mM. The $(I_0/I)^{CW}$ and concentration are listed in Table 5.1

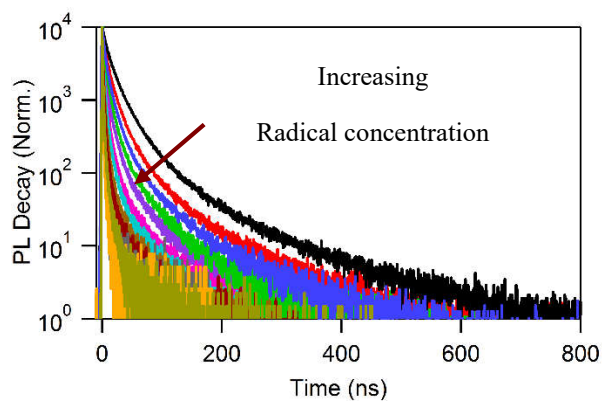


Figure 5.7: Change in PL decay of 3.6 nm CdSe QDs with increasing concentration of 4-carboxy TEMPO radical. The concentration of the radicals is varied from 0-2.3 mM. The $(I_0/I)^{CW}$ and concentration are listed in Table 5.1

Table 5.1: List of the $(I_0/I)^{CW}$ and concentration of 4-carboxy TEMPO for the quenching of 3.6 nm CdSe QDs

[4-carboxy TEMPO] (mM)	$(I_0/I)^{CW}$
0	1
0.005	1.69
0.01	2.17
0.015	3.28
0.02	3.40
0.04	5.72
0.07	7.47
0.13	10.70
0.24	13.89
0.94	27.00
1.63	35.81
2.29	44.96

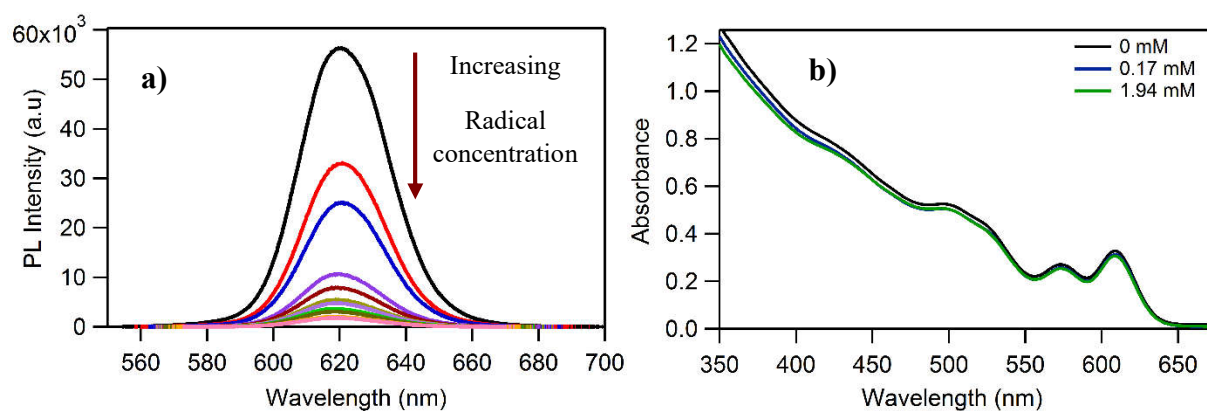


Figure 5.8: Decrease in PL intensity (PL quenching) (panel a), absorbance of the QDs (panel b) and change in PL decay of 5.1 nm CdSe QDs with increasing concentration of 4-carboxy TEMPO radical. The concentration of the radical [CT] is varied from 0-1.9 mM. The $(I_0/I)^{CW}$ and concentration are listed in Table 5.2

Figure 5.8 (Cont'd)

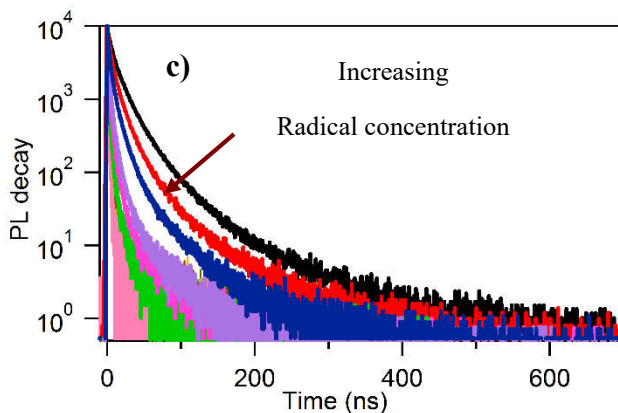


Table 5.2: List of the $(I_0/I)^{CW}$ and concentration of 4-carboxy TEMPO for the quenching of 5.1 nm CdSe QDs

[4-carboxy TEMPO] (mM)	$(I_0/I)^{CW}$
0	1
0.005	1.69
0.01	2.17
0.03	3.28
0.06	3.40
0.12	5.72
0.17	7.47
0.28	10.70
0.57	13.89
1.26	27.00

The PL intensity of the QDs is found to decrease (PL quenching) with subsequent addition of radicals (Figures 5.6 (panel a) and 5.8 (panel a)). The PL intensity and the decay are analyzed as in Chapter 2 to obtain the Stern Volmer plots. As before $(I_0/I)^{CW}$ was obtained by integrating the

PL intensity and obtaining the ratio for QD (I_0) and QD + radical (I). For the $(I_0/I)^{TD}$, the PL decay curve was normalized and integrated to obtain the change in the nature of the decay and the ratio calculated similarly.

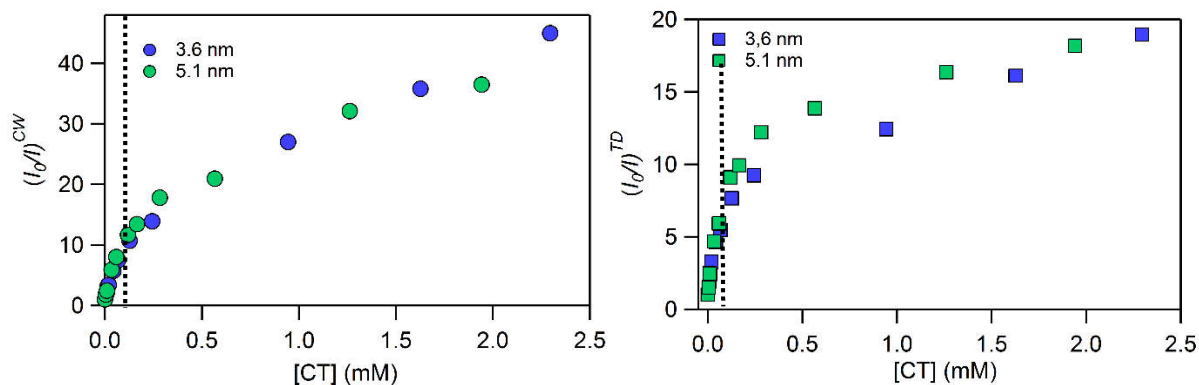


Figure 5.9: $(I_0/I)^{CW}$ (panel a) and $(I_0/I)^{TD}$ (panel b) with increasing concentration of 4-carboxy TEMPO radical. The dashed line demarcates the concentration from where saturation begins

A close look at the Stern Volmer plots for the CW and TD measurements reveal that at low concentrations, $(I_0/I)^{CW}$ and $(I_0/I)^{TD}$ values are similar. At higher concentrations both of these saturates, pointing towards the onset of the diffusion-mediated quenching. The Stern Volmer analysis cannot be conducted on this system as conducted in case of 4-Amino TEMPO because the dynamical and instant quenching processes are convoluted in this system.

Comparison of $(I_0/I)^{CW}$ values for similar dots with the 4-amino TEMPO and 4-carboxy TEMPO (Figure 5.10), shows that the quenching efficiency is higher in case of 4-carboxy TEMPO.

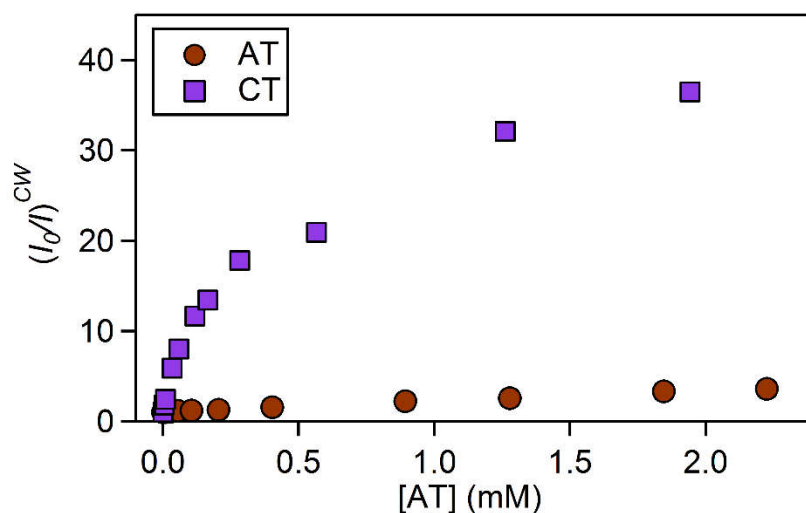


Figure 5.10: Comparison of $(I_0/I)^{CW}$ of 5 nm CdSe QDs with 4-carboxy TEMPO and 4-amino TEMPO

5.3 C: EPR measurement of the CdSe QDs with 4-carboxy TEMPO radicals

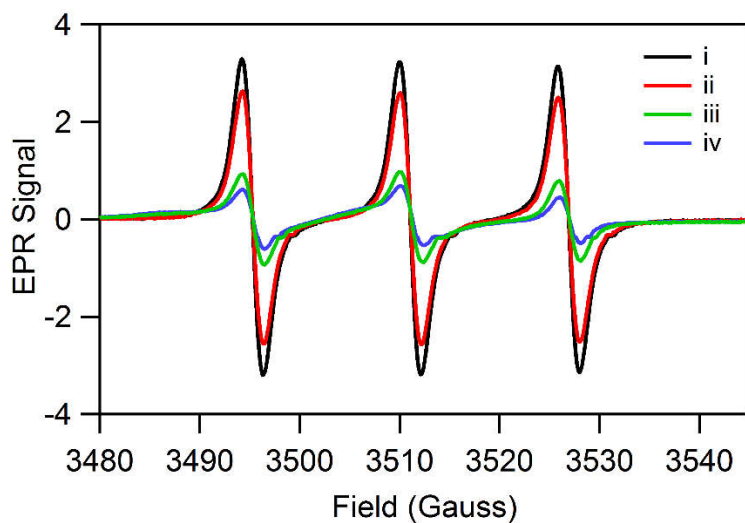


Figure 5.11: (i) EPR spectra of 40 μ M 4-carboxy TEMPO in DCM, (ii) 40 μ M 4-carboxy TEMPO + 0.3 μ M 3.6 nm CdSe QDs, (iii) 40 μ M 4-carboxy TEMPO + 4.4 μ M 3.6 nm CdSe QDs, (iv) 40 μ M 4-carboxy TEMPO + 13.8 μ M 3.6 nm CdSe QDs

The EPR spectra of the radical was measured in DCM in a 1 mm silica EPR tube. For the QD-radical mixtures, the QDs were mixed with the radical, transferred into the tube and degassed for 10 mins before measuring the EPR spectra. The spectra in Figure 5.11 have the same area under the curve (same integral values), the lower peak intensity with increasing radical concentration thus depicts the broadening of the EPR signal. With increasing concentration of 3.6 nm diameter CdSe QDs added to the solution of 4-carboxy TEMPO, the broadening of the EPR signals was found to be enhanced, accompanied by a reduction in peak-to-peak height, particularly at the high field peak. This broadening is indicative of restricted mobility and slow tumbling of the radical as a result of binding to the QD surface.^{3,4}

In case of 4-amino TEMPO, this broadening was not observed even at very high radical concentration (Chapter 2, Section 2.2 C). It can thus be concluded qualitatively that 4-carboxy TEMPO binds to the CdSe QDs better than that of 4-amino TEMPO. Owing to the higher quenching efficiency of 4-carboxy TEMPO as compared to 4-amino TEMPO, the ultrafast measurements were conducted to see if this radical had higher charge transfer rate than the amino radical. The results are presented in section 5.3 E.

5.3 D: Effect on the rate constant distribution with increasing radical concentration

As in Chapter 4 (Section 4.4), the lognormal rate constant distribution model was used here to understand how the Γ_m and the width of the rate constant distribution is affected in the quenching process. The TCSPC (ns) PL decay curve (Figure 5.7) was fit with a lognormal rate constant model (Chapter 4, Eq. 4.11). The result is shown in Figure 5.12.

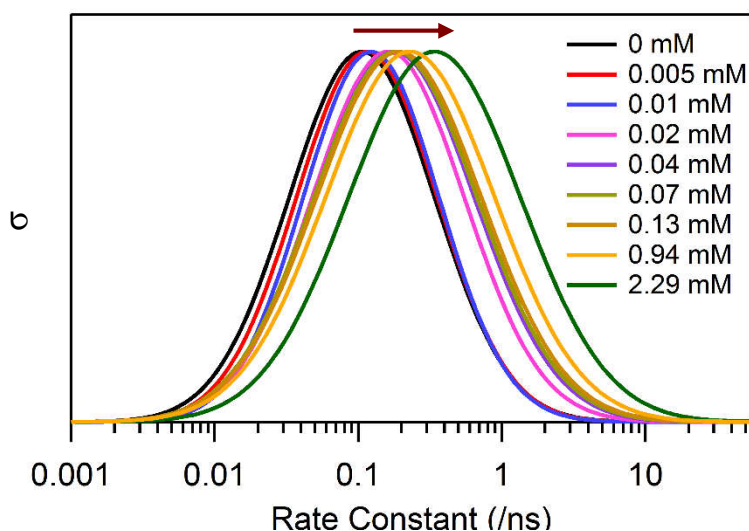


Figure 5.12: Log-normal distribution of rate constant (Γ) of 3.6 nm CdSe QDs (from TCSPC ns decay curves, Figure 5.7 with increasing concentration of 4-carboxy TEMPO. The x-axis is reported in logarithm scale. The arrow indicates the shift in Γ_m with increasing radical concentration

As observed in the case of 4-amino TEMPO, Γ_m shifts to higher values with increasing 4-carboxy TEMPO radical concentration, indicating that the PL decay becomes faster due to the charge transfer from the photo-excited QD to the radical (as explained in Chapter 4, Scheme 4.4).

Again, the width of the rate constant distribution ($\Delta\Gamma$) is also found to increase, pointing towards the involvement of the surface-detrapped charges in the quenching process as observed for 4-amino TEMPO. A closer look at the width of the distribution however suggests that at very small concentrations of the radical (linear region of the quenching, typically up to 0.02 mM 4-carboxy TEMPO), the width of the distribution practically remains the same. For these radical concentrations ($[QD]$ used in study = 3 μM), quenching does not occur by diffusion, and the quenching is mostly due to the charge carriers being quenched by the radicals bound to the QDs

or in very close proximity of the radicals, thereby leading to minimal/no effect on the width of the rate constant distribution.

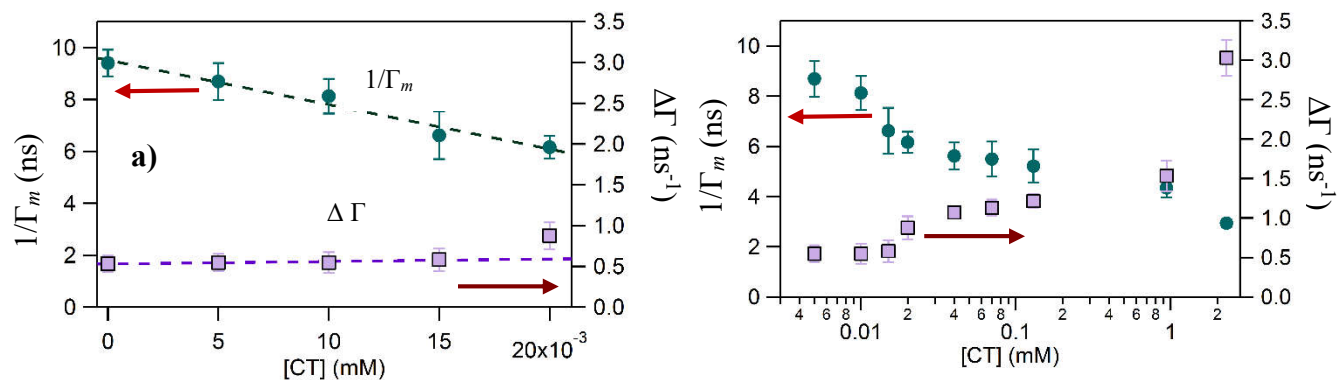


Figure 5.13: Plot showing the behavior of $1/\Gamma_m$ and $\Delta\Gamma$ of the 3.6 nm CdSe QDs with increasing radical concentration. (Panel a: concentrations below 0.02 mM, Panel b: the entire concentration range, the x-axis in panel b is changed to logarithm scale for better visual representation). The circles are the inverse of Γ_m in each case and squares represent $\Delta\Gamma$. The dashed lines are guide to eyes

However, above this concentration regime, the width of the distribution increases as seen in Figure 5.13 panel b, suggesting the involvement of the trapped charge carriers and diffusion of the radicals towards the QDs during the quenching process as discussed in Chapter 4 (section 4.5).

5.3 E: Upconversion PL measurements with 4-carboxy TEMPO radicals

The upconversion PL measurements (ps time scale) were conducted to extract the hole transfer rate in the CdSe-4-carboxy TEMPO system.

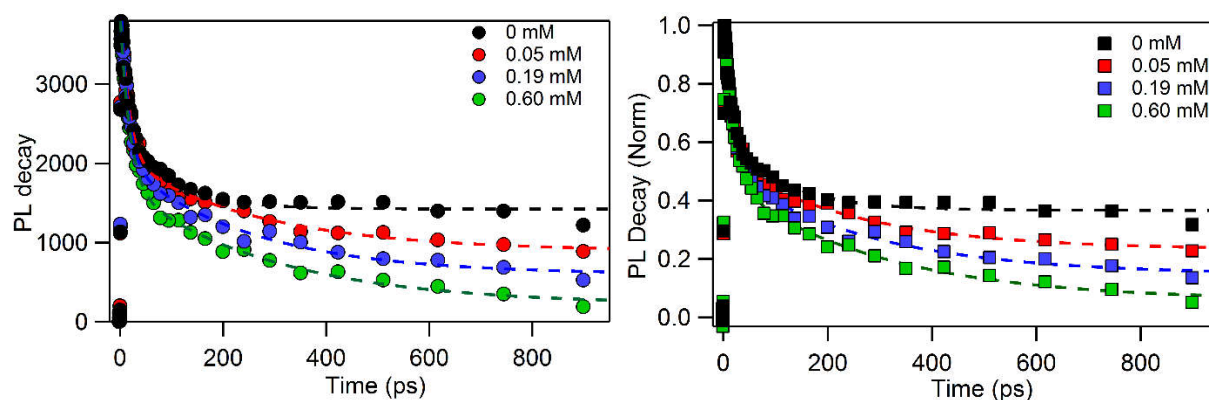


Figure 5.14: PL decay of the 3.6 nm CdSe QDs with 4-carboxy TEMPO (panel a), panel b shows the normalized decay. The dashed lines are guide to the eyes

From Figure 5.14, it is clear that the CdSe QDs in presence of 4-carboxy TEMPO do not show a decrease in the intensity of the PL at time zero unlike in case of the 4-amino TEMPO (Chapter 4, Figure 4.17). For 4-amino TEMPO, this indicated that the hole transfer rate was faster than the time resolution of the uPL measurement (~ 1 ps), however that is not the case observed with 4-carboxy TEMPO. Though the overall quenching is faster and the binding of the 4-carboxy TEMPO on the QD-surface is stronger, the rate of transfer in this case is not as fast as in the case of 4-amino TEMPO ($k_q = 5 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ and $K_a = 0.5 \times 10^3 \text{ M}^{-1}$ for a 3.6 nm CdSe QD and 4-amino TEMPO system).

This slower transfer rate might be due to the difference in the nature of the head group of both the radicals (carboxy vs. amino moiety) that results in a difference in orientation of the radicals as they approach the QDs, such that the $\text{NO}^\bullet$ moiety is closer to the surface of QDs in case of 4-amino TEMPO as opposed to that of 4-carboxy TEMPO. This might explain the slower transfer rate in case of the latter but further experiments are required to substantiate this hypothesis.

The uPL decay curve (Figure 5.15) of the 5.1 nm CdSe QDs show the same result on addition of 4-carboxy TEMPO.

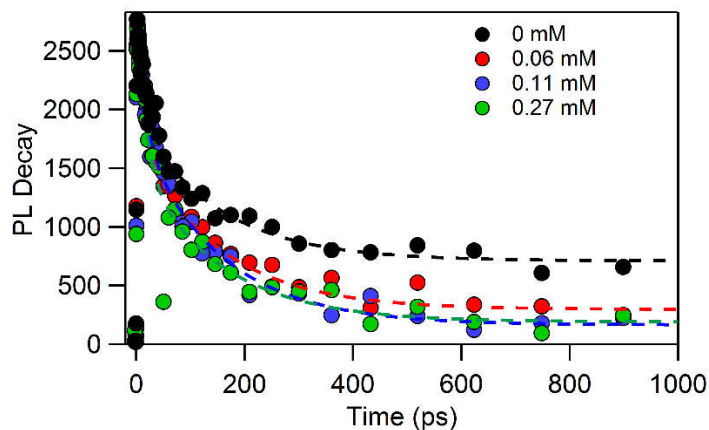


Figure 5.15: PL decay of the 5.1 nm CdSe QDs with 4-carboxy TEMPO. The dashed lines are guide to the eyes

Another striking observation in case of the quenching by 4-carboxy TEMPO was that this radical does not quench the CdTe QDs. In case of 4-amino TEMPO, the same CdTe QDs are quenched with an order of magnitude higher rate than that of CdSe QDs (Chapter 4, Figure 4.25). On the other hand, in case of the 4-carboxy TEMPO, CdTe QDs are not quenched as compared to the CdSe QDs (Figure 5.9). Since, the oxidation potential of the radicals⁵ are quite similar, this difference in hole transfer rate with CdTe QDs could be a result of difference in the electronic coupling of the QDs and the radical, however further investigation in this regard will be necessary.

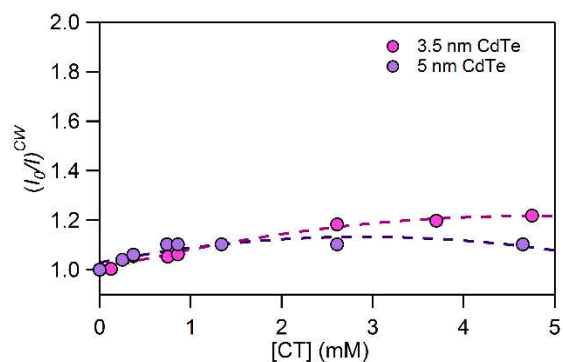


Figure 5.16: $(I_0/I)^{CW}$ plot for 3.5 nm and 5 nm CdTe QDs with 4-carboxy TEMPO. The dashed lines are guide to the eyes

5.4: Conclusion

The CT radical quenches the PL of CdSe QDs efficiently. The EPR measurements show that the radicals bind to the QDs effectively. In fact, comparing the quenching with 4-amino TEMPO on similar CdSe QDs, it is observed that 4-carboxy TEMPO quenches the PL of CdSe QDs more efficiently. However the ultrafast measurements depict that the rate of transfer is slower in case of 4-carboxy TEMPO.

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REFERENCES

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Chapter 6: Conclusion and Future work

The main goal of this work was to understand the electron dynamics at the interface of QDs by exploring the electronic communication between QDs and organic free radicals using spectroscopy and to investigate the effect of QDs size, surface properties and quantum yield on the electron dynamics. First, the details of the PL quenching of CdSe and CdTe QDs with two nitroxide free radicals, TEMPO and 4-amino-TEMPO was investigated. It was demonstrated that 4-Amino-TEMPO is an efficient PL quencher, but it is simultaneously limited by slow diffusion kinetics and low surface binding affinities whereas TEMPO does not quench the QDs appreciably. The key feature of this work was the use of the TD PL studies to examine the details of this quenching process. The results highlighted that the nature of ligand passivation of the QD surface played a significant role in controlling the interaction of nitroxide radicals with QDs, a key aspect to consider in future applications involving such dyads. It was also shown that amino-functionalized nitroxide radicals have very similar binding affinities as those of the HDA ligands used to cap the QDs in this study and that the QD size impacted very little, if at all, the equilibrium dynamics studied here. The PL quenching was then explored at cryogenic temperatures and it was observed that the efficiency of quenching decreases at first when the temperature is lowered below room temperature, however, the total quenching increases again below 250K and never shuts down even ~80 K. Further, ultrafast PL and TA measurements were conducted to explore the nature of this charge transfer process occurring in these CdSe, CdTe QD-4-amino TEMPO radical hybrid systems. The comparison of the TA and uPL measurement clearly demonstrated that the PL quenching of the photo-excited QDs by the 4-amino TEMPO radical was due to a hole transfer process taking place from the photo-excited QD to the radical. Also, it was found that this hole transfer was ultra-fast (faster than the ~1 ps resolution of the uPL measurement). 4-amino

TEMPO can thus efficiently extract the hole with an ultrafast rate from a photo-excited CdSe and CdTe QDs. This system would hence be a great one for applications such as QD-sensitized solar cells utilizing the 4-amino TEMPO as a redox shuttle. Owing to the ultrafast nature of the transfer observed in the case of 4-Amino TEMPO, the carboxy version of this radical (4-Carboxy TEMPO) was explored next. It was found that the binding between the QDs and this radical was stronger than that in case of 4-amino TEMPO and the overall quenching was more efficient as well. However, the rate of transfer was found to be slower than in QD-4-amino TEMPO system. Log normal rate constant distribution model was used to understand the underlying details of the observed quenching process occurring in the QD-nitroxide radical systems.

For the future work, this difference in the intrinsic rate of the charge transfer of the two studied radicals towards the same QDs has to be explored in details. Whether the difference in the structure/orientation of these radicals are responsible for the difference in the rate of charge transfer has to be verified. Also, the difference observed in quenching efficiency of the two radicals toward the CdTe QDs have to be investigated. Finally, the low temperature studies on the QD-4-carboxy TEMPO system might reveal important information. Looking at the nature of quenching at low temperatures, where the diffusion would be completely shut down would be interesting.

The highlight of this research is the observation of the ultrafast hole transfer from the QDs to the 4-amino TEMPO radicals. These type of nitroxide radicals have been demonstrated to be efficient redox shuttles for dye sensitized solar cells. The ultrafast hole transfer recorded here makes the CdSe/CdTe QD-4-amino TEMPO radical dyads promising candidates for QD-sensitized solar cells. Also, in case of QDs a lot of effort is put in order to increase the quantum yield of these materials. Often thick shells of higher band gap material are grown over the CdSe/CdTe QD cores to passivate the surface and confine the excitons to the cores. Though, this leads to brighter dots,

it also leads to slower charge transfer rates. In our system, traps are found to be involved in the quenching process. Thus the charges stored in the trap states are eventually de-trapped and participate in the charge transfer. Though the QDs used in our experiments have traps and hence do not have 100% quantum yields, they are in a way ideal for efficient communication with the radicals.