OVERCOMING THE COMPLEXITY OF EXCITED-STATE DYNAMICS OF COLLOIDAL CDSE NANOCRYSTAL ENSEMBLES BY EXPLOITING PHOTOINDUCED CHARGE-AND ENERGY-TRANSFER PROCESSES

By

Chenjia Mi

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ABSTRACT

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Semiconductor nanocrystals (NCs) are inorganic materials with fascinating electrophysical and photophysical properties, such as tunable band gaps, high extinction coefficient, bright photoluminescence (PL) emission, accessible to optical orientation effects, etc., making them great and versatile candidates for next generation of materials in lighting, solar energy harvesting, photocatalysis, sensing, bio-imaging and spintronics applications. As these applications draw most of the interest to NCs ability to interact with light, the excited NCs are plagued by complex photodynamics, expressed as phenomena like multi-exponential PL decays, delayed PL emission, PL intermittency, etc. As these phenomena hinders the performance of NCs in applications discussed above, understanding the underlying photophysics is the key to rationally design NCs based devices. Air stable free radicals such as nitronyl nitroxides (NNs) are suitable probes for excited state NCs, as they can efficiently quench the PL of NCs through energy transfer process, with a rate comparable to the intrinsic recombination of NCs, making such a perturbation of PL decays easily measurable. Comparing the unquenched PL decays of NCs to the classical 2-states emitter PL formalism, an ultrafast trapping process is found necessary to explain the loss of intensity at t = 0. While the quenched PL can only be analyzed with complex models, a phenomenological log-normal model reveals a serial kinetics, which is interpreted as exciton trapping-detrapping-recombination/transfer. A trap "storage" model that describes such photophysics is proposed, of which the trap states with normal distribution of energies can "store" the trapped hole carrier that can be thermally re-populated to the band edge after delayed time.

Such a model can successfully fit/predict all the currently observed photophysics. Another similar system employing tetramethylpiperidine oxide (TEMPO) derivatives as a charge acceptor is studied and found to be able to undergo an ultrafast (sub-picosecond timescale) hole extraction from photoexcited NCs. These results and models lead to a better understanding of excited state NCs, a rethinking of NCs trap states, and a series of interesting future directions of research on NCs photophysics.

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KEY TO ABBREVIATIONS

NC: nanocrystal
LED: light emitting diode
PL: photoluminescence
QY: quantum yield
DCM: dichloromethane
NN: nitronyl nitroxide
FRET: Förster resonance energy transfer
EPR: electron paramagnetic resonance
CPNN: 4-carboxy-phenyl NN
PNN: phenyl NN
APNN: 4-aminophenyl NN
NPNN: 4-nitrophenyl NN
TEMPO: 2,2,6,6-tetramethyl-piperidine-1-oxide
AT: 4-amino-TEMPO
CT: 4-carboxy-TEMPO
TOP: trioctylphosphine
TOPSe: trioctylphosphine selenide
TOPO: trioctylphosphine oxide
ODE: 1-octadecene
PMT: photomultiplier tube
CCD: charge-coupled device

TCSPC: time-correlated single photon counting

- D-A: donor-acceptor
- Q: quencher
- E: emitter
- IRF: instrument response function
- TA: transient absorption
- uPL: up-conversion photoluminescence
- PDF: probability density function

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Chapter 1. Introduction

1.1. Properties, Advantages and Applications of Semiconductor Nanocrystals

Semiconductor nanocrystals (NCs), as their name implies, are nanometer-sized crystals. The signature characteristic of these materials is their size-dependent optical bandgaps (the minimum energy required to excite an electron from the valence band to the conduction band). Many types of NCs experience "quantum confinement" below a critical size, which is defined by their excitonic Bohr radius. Thus, their bandgap is inversely related to their diameter (for spherical NCs), as described by the Brus equation (eq. (1.1.1)).^{1,2}

$$E_g^{NC} \cong E_g^{bulk} + \frac{h^2}{8r^2} \left(\frac{1}{m_e} + \frac{1}{m_h}\right) - \frac{1.8e^2}{4\pi\varepsilon_{NC}\varepsilon_0 r}$$
(1.1.1)

where E_g is the bandgap (for NC and bulk, respectively); *r* is the NC radius; ε_{NC} is relative optical dielectric constant of the NC; m_e and m_h are the effective masses of conduction band electron and valence band hole, respectively; *h*, *e*, ε_0 are Planck's constant, electron charge and vacuum permittivity, respectively. For example, bulk CdSe has a bandgap of 1.74 eV.³ CdSe NCs, however, have their band edge emission covering the entire range of the visible spectrum (from 700 nm, 1.77 eV to 400 nm, 3.10 eV), for diameters ranging from >10 nm to 1.3 nm.^{4,5} Such tunable bandgap allow semiconductor NCs to cover a continuous spectrum of excitation/emission using materials with the same chemical composition and using similar synthetic protocols. Devices such as light-emitting displays and diodes (LEDs) would benefit from such great tunability.^{6–9} Another fascinating property of NCs is their high optical absorptivity. Colloidal CdSe NCs suspensions typically exhibit band edge molar absorptivity more than one order of magnitude higher (2 nm CdSe NCs have an extinction coefficient of 156000 M⁻¹cm⁻¹ in colloidal suspension at 458 nm)^{4,5} than most molecular dye species (for instance, ruthenium(II) tris-bipyridine's extinction coefficient of 14600 M⁻¹cm⁻¹ in aqueous solution at 452 nm)¹⁰. Because of such

extraordinary optical properties, NCs have much potential to be used in light-harvesting applications for solar energy conversion, among others.¹¹

Colloidal NCs also have large surface-to-volume ratios compared to bulk semiconductors, providing binding sites on their surface that can accept a variety of ligands. ^{12–14} The coupling with guest species opens the door to many interesting phenomena, allowing NCs to transfer/accept energy or charge carriers to/from molecular species or other semiconductors. These photophysical processes enable important applications such as bio-sensing, bio-imaging and photocatalysis, as well as any process that requires a flow of energy.^{15,16}

Generally, NCs that are formed of heavy elements such as Cd possess large spin-orbit coupling, which helps to translate the orbital angular momenta of photons to spin angular momenta of electrons (in the form of electron-hole pair, or exciton). These so-called optical orientation mechanisms allow the selective excitation of an electron with a specific spin. When coupled with paramagnetic species, this spin-spin coupling can be used to pass information and potentially to build logic circuits.^{17–19}

Moreover, the synthetic protocols of many kinds of NCs are mature and easy to be adopted to infrastructures with low cost.^{14,20–22} In the case of colloidal CdSe, high quality NCs with narrow size distribution (<5%) can be synthesized by simple and low-cost heat-up methods.^{14,22,23} The product NCs are generally chemically stable with the presence of oxygen/moisture (as observed in laboratory environments).

1.2. The Complexity of NC Photophysics

As described above, most of the attention given to NCs come from their ability to interact with light: in other words, their excited-states are at the center of interest. Thus, understanding their photophysics is the key to rationally design electro-optical devices/systems based on NCs. However, excited NCs are plagued by complex photodynamics, such as highly multi-exponential photoluminescence (PL) decay,^{24–27} extremely delayed PL emission (more than 6 orders of magnitude longer than the NCs intrinsic radiative lifetime),^{25,27–29} "blinking" or "flickering" phenomena of single NC emission.^{30–34} These photodynamic effects hurt the PL quantum yield (QY) of the NCs and negatively impact the desirable charge/energy transfer processes that are essential to extracting work from NCs. Efforts have been dedicated over decades on solving these complications and great progress has been achieved. Some key results that help understanding and solving these problems are addressed below.

A typical absorption spectrum of CdSe NCs is shown in Figure 1.2.1. Several distinct bands are observable, including the band edge transition $(1S_{3/2}1S_e)$. Due to the quantum confinement, the transition energetics are discrete like those of molecules, rather than continuous bands like for bulk semiconductors.^{35–37} For spherical NCs, without considering band-mixing effects, each band gives rise to an independent series of quantized states that can be described using two quantum numbers, as similar to atomic orbital terms.



Figure 1.2.1. Typical absorption profile (top) and schematic molecular like band structures (bottom) of CdSe NCs. Absorption bands A, B and C in the spectrum are assigned to $1S_{3/2}1S_e$, $2S_{3/2}1S_e$ and $1P_{3/2}1P_e$ transitions, respectively.

The excitonic PL stems from the lowest-energy band edge transition, namely the $1S_{3/2}1S_e$ transition. While simple orbital terms can be used to express the absorption spectra of NCs, such models fail to capture some of the most important characteristics of PL. Based on experimental absorption spectra, the oscillator strength of CdSe NCs suspended in dichloromethane (DCM) is calculated to be in the order of 1, using eq. (1.2.1):

$$f = \frac{4\varepsilon_0 m_e c^2 n}{N_A e^2} \left(\frac{E_{loc}}{E}\right)^2 10 \ln 10 \int \varepsilon(\overline{\nu}) d\overline{\nu}$$
(1.2.1)

where *f* is the oscillator strength; m_e is the electron effective mass; *n* is the refractive index of the system; $(E_{loc}/E)^2$ is local field correction factor that has an approximate value of $(n^2+2)^2/9$; $\varepsilon(\bar{v})$ is the molar absorptivity in M⁻¹cm⁻¹ and \bar{v} is the energy in wavenumbers (cm⁻¹); ε_0 , *c*, N_A , *e* are vacuum permittivity, speed of light, Avogadro's number and electron charge, respectively. Having oscillator strength, one would then be able to predict the radiative lifetime with eq. (1.2.2):

$$k_r = \frac{g_0}{g_1} \frac{2\pi n e^2 v_{em}^2}{\varepsilon_0 m_e c^3} \left(\frac{\boldsymbol{E}_{loc}}{\boldsymbol{E}}\right)^2 f$$
(1.2.2)

where k_r is the spontaneous emission rate constant; g_0 and g_1 are the are the degeneracy of ground and excited-state, respectively; and v_{em} is the emission frequency. The predicted radiative lifetime of NCs is approximately 1 ns, much shorter than the experimental observations of 20 - 40 ns.^{38–41} Moreover, NCs exhibit temperature-dependent radiative lifetimes, which lengthens drastically at cryogenic temperatures (<10 K).^{42–44} Thus, the electronic fine structure introduced by the electronhole exchange interaction must be taken into consideration. Scheme 1.2.1 shows this electronic fine structure splitting of the 8-fold degenerate band edge transition ($1S_{3/2}1S_e$) caused by electronhole exchange interactions, and further by crystal-field splitting and distortions caused by asymmetry of the NC shape.⁴⁵ The Boltzmann distribution between lowest-energy dark states ($\pm 2^U$) and higher-energy bright sates ($\pm 1^L$, $\pm 1^L$, 0^U) leads to a significantly longer observed radiative lifetime. Decreasing temperature will decrease the population of the bright states and thus significantly extent the radiative lifetime of NCs.



Scheme 1.2.1. Electronic fine structure of the $1S_{3/2}1S_e$ transition of CdSe NCs.

With the electronic fine structure taken into consideration, the time-resolved PL decay is still predicted as a single-exponential decay, given the fact that thermal equilibrium is quickly established (sub-picosecond timescale) among these bright and dark states (the energy splitting is only a few tens of millielectronvolts). In principle, treating the NCs energetics as a pseudo-2-states model would still be valid. However, the ensemble PL decay of CdSe NCs practically always display highly multi-exponential features, which is necessarily associated with a distribution of recombination rate constants with the timescale ranging from sub-nanosecond to microseconds. A first possible hypothesis to explain the distributed nature of the PL dynamics would be the heterogeneity of sizes/shapes of the ensemble NCs. Nevertheless, whereas batches of CdSe NCs usually have 5 - 10% size distribution, this cannot explain such broad a range of exciton recombination lifetimes. Because such a distribution leads to a broadening of <5% from the mean value of emission energy on the PL spectrum, of which the impact on radiative lifetime would be negligible.

Moreover, for an excited-state emitter with 2-states (ground state and first excited-state), the slowest observable recombination process is the radiative recombination, which, in the case of NCs, has a common timescale of several tens of nanoseconds (depending on the NCs composition/size/shape).³⁸⁻⁴¹ However, extremely delayed PL emission can still be detected even seconds after the excitation event.^{27,28,46} The "delayed" PL emission, defined as the emission that has a time constant that are slower than the radiative lifetime, contributes to a significant (can be > 10%) portion of the total PL emission that cannot be overlooked.^{27,29,47} Thus, it is concluded that the pseudo-2-states model of NCs fails to explain such a phenomenon. Figure 1.2.2 shows an experimentally measured PL decay of NCs (see Chapter 2 for details) on top of two simulated single exponential decays that have decay time constants of 40 ns and 20 ns (corresponding to the

currently debating PL lifetime of CdSe NCs of this specific size), with all three decays normalized to the intensity of t = 0. While the slowest component of the NCs PL decay should fall in the range of the two simulated curves, over 10% of emitted photons apparently reach the detector at a much slower rate than the radiative process: such a phenomenon is defined here as "delayed" PL emission. Understanding the mechanism of "delayed" PL can make a huge difference on tasks of extracting useful work from photoexcited NCs.



Figure 1.2.2. Experimental (red) PL decay of CdSe NCs (3.0 nm diameter with ensemble PL QY of 0.16) compared to simulated single exponential decays with time constant τ of 40 ns (blue) and 20 ns (black).

Another puzzling phenomenon is the PL "blinking" of NCs. "Blinking" is the PL intermittency that is typically observed for single NCs under continuous wave photoexcitation.³⁰ This PL intermittency is not solely due to natural non-radiative recombination of NCs, but rather to a switching behavior between "bright" and "dark" states of the NC, of which the statistics typically obeys power law,^{28,48–50} so that the "bright" (or "dark") state of the NC can last milliseconds to seconds timescale before switching to the opposite state. Such "blinking" behavior indicates that even single NCs do not behave homogeneously over time. Hence, a colloidal NCs ensemble is necessarily a complex distribution, in terms of photophysics, at any given time. The "dark" states of NCs also significantly hurts the overall PL QY of NCs, which negatively impacts the potential applications mentioned above. Thus, understanding the physics behind the "blinking" behavior would enlighten the way to cure the PL QY of NCs.

The "delayed" PL emission and PL "blinking" behavior are proposed to be related, as they can possibly originates from the same chemical property of NCs.²⁷ As discussed above, a simple 2-states model cannot explain the NCs photophysics very well. It is also well known that the surface of materials often has vastly different chemical properties compared to the bulk part, as surface atoms are usually under-coordinated and may have vacancies, dangling bonds, or interactions with a guest moiety, which can all possibly act as trap states for charge carriers. Compared to bulk extended materials, NCs have much larger surface-to-volume ratio, which significantly increases the impact of surface trap states.

Taking the surface trap states into consideration, a 3-states model of excited-state NCs can be built and actually helps explaining both "delayed" PL and "blinking". Let's consider the fate of an exciton: after photoexcitation, this electron-hole pair is generated and quickly relaxes to the band edge (with a small chance of hot carrier trapping/transferring), populating the lowest-energy excitonic state $(1S_{3/2}1S_e)$. Then, as shown in Scheme 1.2.2, the exciton can undergo five pathways as follows:

1) radiative recombination to release a photon of energy equal to the optical bandgap;

2) non-radiative recombination, converting the energy of excitation into the creation of phonons;

3) energy transfer to an energy acceptor species (e.g. surface bound molecules or neighbor NCs);

4) one or both of the carriers can be transferred to an acceptor species;

5) one or both carriers can get trapped on surface defect states.

Of all five pathways, 1), 3) and 4) can be used to extract work from excited NCs. Pathway 5) can further be branched into three mechanisms:

a) the trapped carrier(s) repopulates the band edge states, through thermal or tunneling mechanism, and forms a new "exciton";

b) the trapped carrier finds its counterpart and recombines, either through trap emission or through phonon-assisted processes;

c) the trapped carrier(s) remains in the long-lived trap states until the next excitation event happens.

Mechanism a) has been invoked to explain the "delayed" emission,^{29,47} as once the carrier(s) are trapped, it may take a long time for the new "exciton" to generate, as both valence and conduction band edge need to be repopulated. These trap states are not necessarily degenerate in energies, and such a distribution of trap energies can potentially explain the highly multi-exponential feature of the ensemble NCs PL decay. Mechanism b) is considered as a "leakage" process, as it usually cannot lead to extract work, at least not with the same potential compared to the exciton states.

From an external point of view, this mechanism is indistinguishable from the intrinsic nonradiative recombination of the exciton. Together they are proposed as a single mechanism that leads to the "dark" states of a "blinking" NC when such channels are activated. Mechanism c) leads to the formation of trion states in NCs and is proposed as another mechanism of "blinking". Due to NCs quantum confinement, the delocalized band edge electron and hole wave functions have much better overlap than bulk materials. Thus, when a trion is formed by re-exciting a chargeseparated NC, Auger recombination happens in picosecond timescale^{51,52} and the PL of such a NC is efficiently quenched, giving rise to the "dark" periods in "blinking" NCs.



Scheme 1.2.2. Fates of NCs in excitonic states (left) with five possible pathways, and in carrier-trapped states (right) with three following mechanisms.

1.3. Probing Excited NCs

Considerable efforts have been invested in the study of the NCs photophysics in order to understand and solve the problems stated above. At the moment, the simple 3-states picture involving trap states is a key to understand the excited-state NCs. Although PL, PL excitation and transient absorption (TA) spectroscopies are all powerful tools to monitor the photophysics of excited-state NCs, the problems remain challenging as many experimental conditions are hard to control. As for colloidal NCs, size and shape distribution contribute to the complexity of the intrinsic exciton recombination dynamics, despite being small. More critically, variations in surface trap states, which are proposed to be responsible for the "delayed" PL and "blinking" behaviors,^{27,29,32,47} can lead to a much broader distribution of the observed dynamics of excited NCs. In fact, this distribution is necessary to explain the highly multi-exponential feature of the NCs PL decay, as will be demonstrated in Chapter 4. Spectroscopic measurements on the ensemble colloidal NCs only yield average values of these complex distributions. To probe the underlying recombination rate constants that leads to the multi-exponential decay, a hybrid inorganic-organic system that employs organic free radicals to quench the PL of the NCs is designed. These freeradical probes perturb the excited-state NCs by shifting the entire rate constant distribution. In such a system, the excited NCs is self-revealing, as the PL intensity is directly proportional to the population of excitonic states at any time. Thus, a suitable quenching efficiency is desired so that an observable PL emission intensity still remains for the quenched NCs, but the reduction on PL QY is large enough to be differentiated from that of the unquenched NCs.

One possible type of quencher is energy acceptor, as energy transfer is a typical way of quenching the PL of NCs. Nitronyl nitroxide (NN) free radicals are a kind of suitable PL quenchers that undergo dipolar (Förster) resonance energy transfer process (FRET), as will be discussed in detail in Chapter 3. These stable free radicals were first described by Ullman,^{53,54} and are commonly known as "spin labels".⁵⁵ Their signature electron paramagnetic resonance (EPR) spectra⁵⁴ allows to monitor their physical/chemical state. The paramagnetism of these radicals also allows a potential design of spin-coupled transfer system. Moreover, the chemical stability and the ability of synthetically tuning substituents make them extraordinarily versatile probes. One specific type of NN that has a 4-carboxy-phenyl group, namely CPNN, is mainly used here as a probe PL quencher. Others such as phenyl NN (PNN), 4-aminophenyl NN (APNN), and 4-nitrophenyl NN (NPNN) are also tested with CdSe NCs for comparison. CPNN is chosen mainly due to its binding affinity to the NCs surface, its "Goldilocks" quenching efficiency, and also its ease of synthesis, purification and storage. Aside from probing the excited-state NCs photophysics, the FRET processes undergone within this system is also fundamentally interesting, as such a mechanism is involved in many natural and artificial process to extract useful work form a photoexcited systems.^{23,56–63}

Another candidate family for probing excited-state NCs through PL quenching is 2,2,6,6-tetramethyl-piperidine-1-oxide (TEMPO) derivatives, which are another type of air stable free radical. Because of their much smaller optical cross section compared to NNs, FRET is not an efficient process in NC-TEMPO hybrid system.⁶⁴ However, a surface-bound TEMPO molecule, such as 4-amino-TEMPO (AT) or 4-carboxy-TEMPO (CT) lead to PL quenching efficiencies comparable to CPNN, which is shown to arise from a charge transfer mechanism, as will be described in Chapter 5. With the ability of extracting charge carriers from excited-state NCs, this hybrid system can potentially be designed as a solar energy harvesting system, photocatalytic system, or spin-valve system.^{65,66}
1.4. Structure of this Dissertation

In this dissertation, after introduction of Chapter 1, all experimental details are given in Chapter 2. Key results of CdSe NCs-CPNN FRET system are shown in Chapter 3. The analysis of complex PL decays and a 3-states kinetic models providing satisfactory depiction of the photodynamics of the NCs in the quenching experiment are shown in Chapter 4. The PL quenching results of charge transfer system CdSe NCs-AT and CdSe NCs-CT with interesting discoveries on ultra-fast hole transfer process are discussed in Chapter 5. (Per request of the administrative formatting requirement and the pressure of the deadline Chapter 6 lists several Igor Pro programs used in data analyses which is supposed to be the appendices of the thesis. The reshaping is counterproductive and is not appreciated). All results and importance of the works are again briefly summarized in Chapter 7 with proposed future directions.

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Chapter 2. Synthesis and Characterization

2.1. Wurtzite CdSe NCs: Hot Injection Method

In general, the hot injection method can be described simply as injecting cold selenium precursor into hot cadmium precursor.^{1,2} Very shortly after the injection, the monomers of CdSe are formed and the nucleation of the crystals is triggered. The temperature sharply drops due to the introduction of cold Se precursor, while the concentration of monomers drops below the critical concentration due to nucleation and consumption of the monomers. As a result, no new nucleation processes should happen. Under stable heating and low monomer concentration the growth process is controlled to be slow, ensuring narrow size distribution of the product NCs.^{3,4}

Se precursor preparation: 1.579 g Se (20.00 mmol) powder is added to a round bottom flask with a stir bar. The flask is then sealed with a rubber septum and degassed with standard Schlenk technique. In detail, the sealed flask is pulled vacuum below 3 Pa and the pressure is maintained for 5 min. For syntheses of larger scale, the time to maintain vacuum should be extended (to 15 - 30 min) to achieve an oxygen free environment. Then the flask is filled with purified nitrogen (as a cost-effective option. Argon can be used as a cleaner air-free protection gas, similar as below.) carefully. This vacuum – nitrogen cycle is repeated 3 times to remove oxygen from the flask. Then, under nitrogen environment, 50.0 mL of trioctylphosphine (TOP) is added with a syringe. The mixture is stirred at room temperature for 12 h, until a clear light brown solution (0.4 M trioctylphosphine sclenide, TOPSe solution) is formed. The Se precursor can be used immediately after preparation or stored in a fridge. Note that with the presence of oxygen (either from unsatisfying degassing, leaking, or long-time storage), the solution become more viscos and finally turns into a white waxy solid, indicating the formation of trioctylphosphine oxide (TOPO). This TOPO formation should be avoided.

Cd precursor preparation: 0.0128 g CdO (0.1 mmol), 0.125 mL oleic acid (0.4 mmol) and 3.0 mL 1-octadecene (ODE, 90% purity ODE does not notably affect the result) are added to a threeneck round bottom flask with a stir bar. A condenser is mounted onto the flask, and a thermal couple pierced through an air-tight septum is mounted onto the flask to probe the temperature of the solution. All open necks are sealed with rubber septa and the top of the condenser is connected to a Schlenk line. The system is degassed with standard Schlenk technique for 5 min \times 3 times while the condensing water is kept off. The mixture is heated up to 100 °C and carefully degassed one more time until no obvious bubbling forming from the liquid to remove water. Then the system is kept under (slightly overpressure) nitrogen and the condensing water is turned on. The mixture is heated to 220 °C under stirring until a clear solution is formed. Then the flask is cooled down to room temperature, and quickly opened to add 0.070 g (0.18 mmol) TOPO and 0.20 g (0.74 mmol) octadecylamine. The system is then sealed again and degassed for 3 times while the condensing water is turned off, and then heated to 100 °C and degassed 1 more time. The condensing water is then turned on and the flask is heated to 240 - 300 °C (depending on the desired size) under nitrogen and under constant stirring.

Hot injection: A syringe is purged with nitrogen 3 times, and 0.5 mL previously prepared 0.4 M TOPSe solution is transferred into the syringe and then quickly injected into the Cd precursor flask. A sudden color change from clear colorless solution to red is observed, indicating the nucleation and initial growth of the NCs. The temperature drops down to ~ 180 °C and is slowly raised back to the original temperature in 10 min. 0.20 mL of the reaction mixture is taken as aliquots at every 5 min after injection and dissolved into 2 mL of toluene. The absorption profile of the aliquots is monitored to determine the size of the NCs. As desired size achieved, the heating is stopped, and the flask is quickly cooled to room temperature to quench the reaction.

An alternative method of preparing Cd precursor employs the combination of stearic acid and oleylamine instead of oleic acid and TOPO. In detail, 0.0128 g (0.1 mmol) CdO, 0.717 g (2.25 mmol) stearic acid, 3.50 mL (10.6 mmol) oleylamine and 2.25 mL ODE are added to a three-neck round bottom flask with a stir bar. After standard Schlenk degassing procedure, the mixture is heated to 250 °C until a clear colorless solution is formed. TOPSe solution is diluted with 0.85 mL ODE and 1.25 mL oleylamine under nitrogen and swiftly injected into the hot Cd precursor. Heat is maintained while aliquots are taken similarly as described above. Upon reaching the desired size of NCs, the heat is removed, and the flask is cooled to room temperature to quench the reaction.

2.2. Zinc Blende CdSe NCs: Solvothermal Method

The solvothermal (heat-up) method involves no injection. In general, both Cd precursor and Se precursor are pre-mixed, and CdSe monomers form in the course of heating. Once the critical concentration is reached, the nucleation process starts and followed by growth of NCs. This method is adopted from Cao et al⁵ and modified in our own lab⁶ to better fit the needs on the sample.

Cadmium myristate preparation: 4.63 g (15.0 mmol) cadmium nitrate monohydrate is dissolved in 150 mL anhydrous methanol. 1.20 g (30.0 mmol) sodium hydroxide is crushed and mixed with 6.85 g (30.0 mmol) myristic acid and dissolved in 1.50 L methanol in a 2 L beaker with a large stir bar to form sodium myristate solution. To the sodium myristate solution under vigorous stirring, the cadmium nitrate solution is added dropwise with an addition funnel over 3 h. White precipitate will form over the course of addition of cadmium nitrate solution. After the addition is completed, the reaction mixture is filtered with reduced pressure, and the filter cake is washed with a total of 200 mL anhydrous methanol 5 times (40 mL each portion). Then the white solid product cadmium myristate is collected in a 1 L round bottom flask and dried under vacuum (<20 Pa) for 24 h, then filled with purified nitrogen and sealed for future use. The dried product is characterized with melting point of 103.6 – 105.0 °C and the yield is typically above 80%.

Solvothermal synthesis of CdSe NCs: 5.67 g (10 mmol) cadmium myristate and 1.11 g SeO₂ (10 mmol, 99.9999% purity) is added to a 2 L three-neck round bottom flask with 630 mL octadecene and a large magnetic stir bar. A bottle of oleic acid (90% purity) is degassed with standard Schlenk technique in the meantime. The flask is then degassed for 3 cycles using standard Schlenk technique to remove oxygen and water, and then warmed up to 100 °C under nitrogen with continuous stirring followed by one extra cycle of vacuuming process to thoroughly remove water

and other low-boiling-point impurities. The flask is then filled with purified nitrogen and the temperature is ramped to 240 °C in 7 min under refluxing condenser under vigorous stirring. As the temperature rises the reaction mixture turns in to a clear solution with slight yellow color, then turns red as the temperature ramps above 200 °C. As the reaction proceeds, several 0.2 mL aliquots are taken every 1 min with a syringe and diluted with toluene, and their absorption spectra are measured simultaneously to monitor the size of the NCs (based on an empirical sizing curve from literature⁷). Upon NCs reaching the desired size, heating source is removed. Under continuous stirring, the reaction mixture is injected with 10.00 mL degassed oleic acid over 10 min using a syringe. The resulting CdSe NCs suspension is then allowed to cool to room temperature followed by cleaning process described below.

2.3. Cleaning

To obtain clean colloidal NCs suspension without excess free ligands, the as-synthesized NCs ODE suspension is distilled under reduced pressure (6 - 10 Pa) at 130 °C to concentrate. The mixture is heated with caution as if the temperature rises above 150 °C there would be possible Oswald ripening that occurs, which would significantly broaden the size distribution of the NCs. After 600 mL of ODE is distilled out, the remainder NCs suspension is added with 20 mL toluene, followed by centrifuge under 6000 rpm for 20 min. This centrifuge step is to remove excess ligands and NCs with poor surface coverage that crash out from the suspension. After centrifuge, the supernatant is divided to 1 mL portions and transferred to 4-inch test tubes. To each test tube is 10 mL ethyl acetate added to crash out the NCs. These test tubes are then centrifuged under 6000 rpm for 20 min, then the supernatant is discarded. The NCs pallet is then re-dissolved with 1 mL of pentane, followed by crashing out with 10 mL ethyl acetate and centrifuge. This washing cycle is repeated 4 to 8 times and simultaneously monitored with NMR, until no observable free ligand signal on the NMR spectra. The NMR sample is prepared by dissolving the resulting NCs pallet after each washing cycle in deuterated toluene to make 85.8 µM suspension. Finally, the clean NCs pallet is mixed with 10 mL ethyl acetate and sonicated for 15 s, then dried under nitrogen flow for 24 h. The pallets are then re-dissolved in desired solvents (toluene, DCM, etc.) for future use.



Figure 2.3.1. NMR spectrum of clean CdSe NCs. Methyl (Me), ethylene (Et), olefin (Ol) and α hydrogens are labeled respectively. Ferrocene (Fc) is used as internal standard. The solvent residues from washing steps and from d-toluene are labeled with star (*).



Figure 2.3.2. Absorption spectra of clean zinc-blende CdSe NCs with different diameters in DCM. The sample information can be found in Chapter 3, Table 3.2.1.

2.4. Annealing

Annealing NCs with excess ligands can increase the surface ligand coverage and significantly increase the PL QY of the as synthesized NCs. As the zinc blende NCs resulting from solvothermal synthesis are usually of high PL QY for spectroscopic studies, the wurtzite NCs sometimes require annealing. In detail, the as synthesized NCs are cleaned for 3 cycles to remove the excess ligands, then re-dissolved in hexanes to be carried in a 125 mL 3-neck round bottom flask. 1.5 g hexadecylamine and 2.5 g TOPO are added to the flask with a stir bar. The flask is then mounted with a water condenser in the middle and a thermal couple on one side, and then all the openings are sealed with rubber septa and the condenser is connected to the Schlenk line through a needle. Heat is provided gently to the flask under vacuum to remove hexanes. It is advisable to set up an extra cold trap with liquid nitrogen between the condenser and the Schlenk line to trap the hexanes vapor. The temperature of the reaction mixture decreases as the hexanes evaporating and increases back once all hexanes are removed. The flask is heated to 100 °C (with a rate of 10 °C/min) under vacuum with the condensing water turned off to remove any trace amount of hexanes and water from the system. Then the system is degassed with standard Schlenk technique for 3 cycles, filled with nitrogen, and then the condensing water is turned on. The temperature of the mixture is then raised to 125 °C. 2.5 mL of TOP is degassed and transferred to the reaction flask with a syringe. The flask is maintained at 125 °C for 24 - 72 h. After the annealing is complete the product NCs is diluted with 5 mL of toluene, then crashed out with a total of 50 mL methanol in separated test tubes. The test tubes are then centrifuged and the resulting NCs pallets are washed with the cleaning procedure described above.

2.5. Syntheses of NN Radicals

The NN radicals used in PL quenching experiments are synthesized fresh. In general, the synthetic mechanism consists of an aldehyde-amine condensation followed by oxidation to free radicals.^{8–} ¹⁰ Starting materials are 2-nitropropane and benzaldehyde derivatives. An example scheme of synthesis of CPNN is shown in Scheme 2.5.1, and the detailed procedures are given as follows.



Scheme 2.5.1. Scheme of NN synthesis (R = H, NH₂, NO₂ or COOH).

2,3-dimethyl-2,3-dinitrobutane (1) synthesis: 85.0 mL of 6 M NaOH solution is cooled in a 1 L round bottom flask with a stir bar in an ice bath for 15 min. Under continuous stirring, 45.0 mL of 2-nitropropane is added to the NaOH solution dropwise using an addition funnel over 1 h. 14.0 mL of Br₂ is then added dropwise through an addition funnel to the reaction mixture over 1 h. The reaction flask is kept in ice bath during the addition. After the addition is complete, the reaction mixture is taken out from the ice bath and warmed to room temperature, followed by addition of 160.0 mL of ethanol. Then a water condenser is mounted on to the reaction flask and the reaction mixture is heated to boiling and refluxed for 3h. After the reaction is finished, the mixture is cooled to room temperature and poured into a 2 L Erlenmeyer flask that contains 250 mL of water and 250 g of ice. The reaction flask is rinsed with 20 mL of water for 3 times and the rinses are mixed with the product mixture. In the Erlenmeyer flask formed white crystalline. The crude product is filtered with reduced pressure and dried in air. 93% yield is obtained. A recrystallization procedure is then performed, by mix all crude product in 400 mL methanol in a 1 L Erlenmeyer flask and heat to slightly boiling. The hot methanol solution is then quickly filtered with reduced pressure and the filtrate is transferred in to a 1 L Erlenmeyer flask and cooled in an ice bath. As the flaky crystals form in the Erlenmeyer flask, the mixture is filtered with reduced pressure and the crystal product is collected with a yield of 62%. The melting point of this product is measured to be 214 -216 °C. This product is then stored in a desiccator for future use.

2,3-Bis(hydroxyamino)-2,3-dimethylbutane (2) synthesis (reduction): 3.09 g of Al foil is cut into 1 cm² pieces and submerged in DI water in a 500 mL round bottom flask with a stir bar. 60.0 mL of saturated HgCl₂ solution is added into the flask and stirred for 4 min. The resulting amalgam is filtered with reduced pressure and washed with 20 mL of DI water 5 times, with 20 mL of ethanol twice (to remove water), and then with 20 mL of THF twice (to remove ethanol). The

amalgam is then quickly transferred into a 500 mL flask and submerged with THF and cooled to 0 °C in an ice bath. 2.08g of **1** is dissolved in 20.0 mL of THF with 8.4 mL of DI water and added to the amalgam dropwise through an addition funnel over 45 min. The reaction mixture is kept at 0 °C under vigorous stirring. After the addition is completed, the reaction mixture is filtered through a silica plug and washed extensively with 500 mL of THF followed by 300 mL of methanol. All the filtrate is combined and dried *in vacuo* to yield a product of white crystalline. The product is then washed with 20 mL DCM for 3 times and filtered under reduced pressure and dried to give a final yield of 54%. The final product is then stored in a vial in a desiccator for immediate use, as it can react with air/moisture to form pink by-products.

1,3-Bis(hydroxyl)-4,4,5,5-tetramethyl-2-(4-carboxyphenyl)-imidazoline (3, R = COOH) synthesis (condensation): 0.4326 g (3 mmol) of **2** and 0.4504 g (3 mmol) of 4carboxybenzaldehyde are mixed in a vial with catalytic amount of 4-toluenesulfonic acid monohydrate. 10 mL of methanol is added to the vial to dissolve the reagents. The reaction solution is stirred under room temperature for 24 h and white precipitate formed. The reaction mixture is then filtered under reduced pressure, and the pallet is washed with 5 mL of methanol for 3 times and dried in air for future use.

4,4,5,5-Tetramethyl-2-(4-carboxyphenyl)-imidazoline-3-oxide-1-oxy (CPNN) synthesis (oxidation): the product **3** is directly dissolved in 10 mL of DCM. 5 mL of saturated NaIO₄ aqueous solution is then mixed with the DCM solution and the mixture is stirred vigorously for 30 min. The DCM layer turned dark blue while the aqueous layer turned pale violet. The DCM layer is then separated and washed with 20 mL of DI water for 3 times. The residue DCM solution is then dried with Na₂SO₄ powder and filtered. The filtrate is evaporated, and the resulting solid is recrystallized with DCM to obtain a product of dark blue crystals. The product CPNN is

characterized with elemental analysis and resulting C: 59.63% (theoretically 60.64%), H: 6.48% (6.18%), N: 9.74% (10.10%); single-crystal XRD (matching the known structure of CPNN); EPR (see Chapter 3, Figure S3.1.4) and NMR (no peak other than solvent residue is shown in 0 - 12 ppm chemical shift range) to confirm the composition and molecular structure.

Syntheses of PNN and NPNN are similar to that of CPNN except that commercially available benzaldehyde or 4-nitrobenzaldehyde are used in the condensation step, respectively. Synthesis of APNN requires 4-aminobenzaldehyde precursor, which tend to polymerize under the reaction condition and thus needs to be synthesized fresh.

4-aminobenzaldehyde synthesis: 30.0 g (0.125 mol) Na₂S·9H₂O, 15 g (0.47 mol) sublimed sulfur, 27 g (0.67 mol) NaOH are mixed with 600 mL distilled water in a 2 L round bottom flask with a magnetic stir bar. The flask is heated on a steam bath with occasional stirring. 50 g (0.36 mol) of 4-nitrotoluene is dissolved in 300 mL 95% ethanol in a 1 L round bottom flask and heated to slightly boiling. The hot ethanol solution is then poured into the 2 L flask with the aqueous solution. A water condenser is mounted on the flask and the steam bath is replaced with a heating mantle. The reaction mixture is then heated to boiling and refluxed for 3 h, resulting a clear dark red solution. Then the condenser is replaced with a steam-distillation tube. The reaction mixture is steam-distilled until 2 L of condensate is collected. The condensate should be clear and the residue in the reaction flask should be about 500 mL in volume. Insufficient residue volume can be made up with boiling water. A 2 L Erlenmeyer flask with 200 g of ice is prepared and settled in an ice bath. The residue from steam distillation is poured into this Erlenmeyer flask to rapidly chill the reaction mixture, and golden yellow crystals form in the flask. After 2 h kept in ice bath, the reaction mixture is filtered under reduced pressure and the filter cake is washed with a total of 500 mL ice cold distilled water to remove excess NaOH. The resulting golden yellow crystals are

collected in a vial, dried under vacuum overnight, and the vial stored surrounded by KOH in a container for future use. If chunky yellow solid (formed by self-polymerization) is mixed with the crystals with high melting point, the crude product can be dissolved in boiling water and filtered when the solution mixture is hot until the filtrate is clear. DCM is then added to the aqueous solution to extract 4-aminobenzldehyde twice. The combined organic layer is dried with anhydrous Na₂SO₄ and the DCM is evaporated with reduced pressure. The resulting crystals are stored same way as described above. Note that the condensation catalyst also catalyzes the self-polymerization of 4-aminobenzldehyde. The resulting mixture can still be proceeded to the oxidation step and the final product is isolated by flash chromatography using a 50-50 mixture of ethyl acetate and hexanes through a silica column.

The resulting NN radicals are dissolved in DCM and characterized with optical absorption spectroscopy.



Figure 2.5.1. Absorption profiles of APNN, CPNN, NPNN and PNN free radicals dissolved in DCM.

2.6. Optical spectroscopy

UV-vis absorption: UV-vis spectra are measured with an Olis 17 UV/vis/NIR double channel spectrometer. A fixed high voltage of 250 V for the photomultiplier tube (PMT) detector is used and the slit width is then automatically adjusted. With the entire spectrum ranging from 780 to 380 nm (unless otherwise specified), each datum is recorded with an increment of 1 nm and read for 3 times. Samples are prepared either in 1 cm pathlength cuvettes (in most cases) or 1 mm pathlength cuvettes (only used for stock solution of NN radicals).

Steady-state PL: PL QY is measured with Quantaurus integration sphere following its standard operation protocol, with an excitation wavelength of 450 nm unless otherwise specified.

Continuous-wave PL is measured with a home-built spectrometer, consisting of Horiba iHR monochromators and a Horiba Symphony II charge-coupled device (CCD) detector. The excitation light source is a 12 W tungsten lamp, of which the white light is directed and dispersed to monochromatic through an iHR 320 monochromator. For CdSe NCs, excitation wavelength is usually chosen at the 1P_{3/2}1P_e transition unless otherwise specified. The beam is focused at the center of the 1 cm sample cuvette. The emission is collected at 90° angle to the incident beam with CCD camera after an iHR 550 monochromator.

Time-dependent PL: time-dependent PL spectra are measured with a T900 time-correlated single photon counting (TCSPC) instrument with a PMT detector, which is built together with the continuous-wave PL spectrometer. The excitation light source is a 405 nm diode laser from Picoquant (LDH-D-C-405M, CW—80 MHz). The laser beam coincided with the steady-state excitation beam. During the TCSPC measurements the white light is blocked, and vice versa. The laser pulse frequency is set at 125 kHz, as this frequency allows the excited NCs to fully relax (without considering the extremely delayed NCs which is such a small population that is negligible)

while generate reasonably bright PL to practically obtain photon counts with high signal-to-noise ratio (>1000) and avoid photo-degradation of the sample under laser irradiation. 1 MHz frequency has also been used in earlier measurements for NCs with lower PL QY. The laser intensity is adjusted so that the photon emission rate (stop rate) is smaller than 3% of the pulse frequency, to ensure single photon counting within each time window and to minimize multiple excitation. The emission is collected by a PMT detector through the same iHR 550 monochromator. The time window for photon counting is 1 μ s that is divided evenly to 4096 channels. Each channel is approximately equal to the instrument response function (IRF) width (250 ps).

Cryogenic PL: temperature-dependent PL spectra are measured with the same spectrometer setups, but the sample holder is replaced with a cryostat, while the solution sample is sealed in a glass tube. In detail, a 4-mm Pyrex glass tube is filled with solution sample (~ 5 cm in the tube). The sample is then quickly frozen by soaking the bottom of the tube into liquid nitrogen. The tube is then connected to a Schlenk line to pull vacuum. Under vacuum the tube is taken out from liquid nitrogen, and quickly the frozen sample starts to thaw. At this point nitrogen is filled into the tube and the sample is warmed and completely thawed under nitrogen. This freeze-pump-thaw procedure is repeated 3 times in total, and then the sample is kept frozen under vacuum with liquid nitrogen. The glass tube is then flame-sealed and cut with a torch, at ~ 2 cm above the sample level. Note that the solution sample must be kept frozen, otherwise the glass tube cannot be sealed. The resulting sample tube is then taped onto a cold finger with medical tapes, and the cold finger is mounted onto the cryostat. The position of the cryostat/sample tube is adjusted with the spectrometers with the excitation of laser so that the PL signal is maximized. Temperature is controlled with two build-in heaters in the cryostat/cold finger and a flow of liquid nitrogen. Two thermal probes are located at the bottom of the cryostat and at the cold finger. The temperature is adjusted with digital controller and the desired temperature is considered stabilized when the readings from both probes agree with each other (<0.1 °C difference) and hold for at least 5 min. The steady-state and time-dependent PL spectra are collected after the temperature is stabilized.

2.7. PL Quenching Experiments

For a typical PL quenching study, 2.000 mL CdSe NCs suspended in DCM (or toluene, if specified) is added into a 1 cm cuvette with a small magnetic stir bar. The UV-vis absorption, steady-state and time-dependent PL emission spectra are measured. During the steady-state and time-dependent PL measurements the suspension is under continuous stirring to minimize the impact of photo-annealing, photo-degradation and photo-deposition of NCs. Then each time 20.0 μ L quencher (CPNN, CT, AT, etc.) solution is titrated directly into the cuvette with a micropipette. UV-vis absorption, steady-state and time-dependent PL emission are measured after each titration.

2.8. Correction for Inner-Filter Effect in Quenching Experiments

The inner-filter effect describes the reduction of the detected PL emission intensity caused by addition of light absorbing species that absorbs at either excitation or emission wavelength.¹¹ This reduction is not caused by physical quenching mechanism, but rather similar as adding a "filter" to the excitation/emission light beam. Thus, correcting such inner-filter effect is non-trivial for analyzing the underlying photophysics of the PL quenching system yet is often overlooked. The inner-filter effect consists of two components: pre-absorption (of the excitation beam) and re-

absorption (of the PL). The detected intensity is described as follows:

$$I_{obs} = 10^{-A_{ex}} \times I_{inc} \times \Phi \times F \times 10^{-A_{em}} \times D$$
(2.8.1)

where I_{obs} is the measured PL intensity, A_{ex} and A_{em} are the absorbance of light absorbers in the cuvette at excitation and emission wavelength, respectively; I_{inc} is the incident light beam intensity, Φ is the PL QY of the emitter of interest, D is the dilution factor, and F is the instrumental factor related to the acquisition time, beam focus, slit width, detector QY, etc., which is a constant throughout an experiment (if the PL spectrometer set up does not change).

As Φ is the actual quantity of interest, the experimentally recorded I_{obs} is contaminated by the changing D, A_{ex} and A_{em} over the course of addition of quenchers. The correction for dilution D is obvious. Given the alignment of the optics, it is estimated that the focus point of the excitation is at the center of the 1 cm cuvette (0.5 cm to the walls on each side). Assuming the incident (or emission) beam is collimated beam, the pre-absorption and re-absorption can be expressed using Lambert-Beer's law. Note that these two effects actually impact the I_{obs} in sequence, so a total correction on the inner-filter effect can be written as

$$A_{fil} = (0.5 \text{ cm}) \times (\varepsilon_{ex} + \varepsilon_{em})[Q]$$
(2.8.2)

where ε is the molar absorptivity of the quencher at excitation (*ex*) and emission (*em*) wavelengths, and [Q] is its nominal concentration. Note that the NCs themselves also have this inner-filter effect but their contributions are canceled out when taking ratios of I_{obs} , as their nominal concentration remain unchanged after corrected for dilution. REFERENCES

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Chapter 3. Photoinduced Energy Transfer Between CdSe Nanocrystals and Nitronyl Nitroxide Free Radicals: Stern-Volmer Analyses

3.1. Overview

Photoinduced donor-acceptor (D-A) processes provide an excellent platform to investigate complex excited-state dynamics, and conveniently chosen chemical entities (acceptors) can be used to systematically perturb, and thus probe, the excited-state relaxation of NCs. Many DA studies involving NCs have now been reported, with either electron transfer^{1–8} or energy transfer^{9–20} as the dominant mechanism of interaction. Nevertheless, quantitative characterizations of DA processes involving NCs are generally challenging endeavors due the complexity of the intrinsic photophysical behavior of NCs, with the consequence that studies based on steady-state (time-independent) quantities often do not lead to physical pictures that are consistent with those obtained from analyzes of time-dependent data.

In this chapter, photoinduced energy transfer process is described in detail for a hybrid inorganicorganic system involving CdSe NCs and NN free radicals. NN radicals, of which three structures are shown in Figure 3.1.1, are well-known molecular species,^{21–23} and are used here for the first time as molecular acceptors to probe the complex dynamics of CdSe NCs. As demonstrated Section 3.3, an important characteristic exhibited by a specific NN radical (CPNN) is the interesting fact that it binds quite strongly to the NC surface while interacting with CdSe NCs neither too strongly nor too weakly, as measured from simple PL quenching experiments. This intermediate regime of DA interaction allows to capture precisely the nature of the mechanism responsible for the PL quenching, attributed here to efficient dipolar energy transfer and described using a fully-coherent analysis of both steady-state and time-dependent measurements based on independent (Poissonian) DA interactions and a log-normal distribution of intrinsic recombination rate constants for CdSe NCs.



Figure 3.1.1. Structures of (from left to right) PNN, APNN and CPNN free radicals.

3.2. PL Quenching Results

The absorption and PL emission spectra are shown here in Figure 3.2.1(a) for a typical CdSe NCs sample, 3 nm diameter, 1.57 μ M in DCM and with 16.0% PL QY. Figure 3.2.1(b) shows the absorptivity spectrum of the CPNN free radical studied here (structure shown in the inset). This free radical is characterized by a single band in the visible, characteristic of NN radicals with aromatic substituents. Assuming that the whole band corresponds to a single electronic transition (there are in fact two in there),²⁴ a total oscillator strength of ~5×10⁻³ is estimated, consistent with the weakly allowed $n \rightarrow \pi^*$ character of this transition.^{24,25} As will be discussed in further detail in this chapter, the spectral overlap between this absorption feature and the PL transition of the CdSe NCs is conducive to efficient energy transfer from photo-excited CdSe NCs to CPNN.


Figure 3.2.1. (a) UV-vis absorption (blue) and PL emission (red) of a typical CdSe NCs sample (3 nm diameter, 1.57 μ M suspended in DCM, with PL QY of 0.160 ± 0.009). (b) Normalized (to unity area) NC PL emission (red) and the molar absorptivity profile of CPNN radicals (blue).



Figure 3.2.2 (a) PL spectra of NCs upon titration of CPNN, ranging from 0 to 12.8 μ M in DCM, corresponding to [CPNN]/[NC] ratios of 0 to ~9. (b) Decrease of the integrated PL intensity with increasing concentration of CPNN. Each point gives the area-integrated PL intensity relative to that of NCs without quencher (PL intensities corrected for dilution effect, see text for details). The dashed curve is a guide to the eyes. (c) PL decay dynamics (red curves) of the spectra shown in (a), underscoring the highly multi-exponential nature of the excitonic recombination in these samples. (d) Average time of emission (purple diamonds) and time-integrated PL decay curves (red circles) extracted from the data in (c) (each decay curve is also normalized such that I(t=0) = 1, prior to the time-integration). Dashed curves are guides to the eyes.

The experimental procedures are described in Chapter 2. Upon titration of CPNN, the overall PL intensity of the CdSe NCs decreases, as shown in Figure 3.2.2(a). The effect is relatively strong, and micromolar concentrations are sufficient to lead to quantitative PL quenching: with about three radicals added per NC, the PL can be reduced to about half the starting intensity. It is important to note that although the spectral overlap between the CdSe NCs and CPNN radicals could in principle lead to direct absorption of both the excitation beam and the CdSe NC PL and yield an apparent (artificial) quenching of the PL,^{26,27} at the low concentrations used here this "inner-filter" effect is practically negligible, accounting for less than 0.3% of the observed quenching. Nonetheless, both inner-filter and dilution effects have been corrected for based on the CPNN absorption profile and the experimental titration method.

The PL quenching effect can also be directly quantitatively characterized in the time domain, as shown in Figure 3.2.2(c). As typically observed for CdSe NCs,^{28–30} the excitonic recombination is characterized by strong deviations from single-exponential decay dynamics associated with simple first-order relaxation processes, which are signatures of complex underlying inhomogeneities from NC to NC, leading to highly distributed excitonic recombination rate constants.^{29,31–34} Such decays can be fitted empirically with phenomenological models such as multi-exponential functions. Nevertheless, the overall dynamics of complicated decays can be characterized without any specific *a priori* model by using the average time of emission values, which corresponds to the first moment of the experimental decay curve:³¹

$$\langle t \rangle = \frac{\int_0^\infty I(t) t dt}{\int_0^\infty I(t) dt}$$
(3.2.1)

From eq. (3.2.1), the average time of emission of the CdSe NC sample in Figure 3.2.2(c) is found to be 61.2 ns, beyond the reported radiative lifetime of CdSe NCs of that size (20 to 40 ns).^{35–38} It

is important to note that the average time of emission is in general different than the PL lifetime, unless the PL decay is mono-exponential.³¹ Nevertheless, $\langle t \rangle$ drops smoothly with increasing CPNN concentrations, as shown in Figure 3.2.2(d), albeit not at the same rate than the PL intensity reported in Figure 3.2.2(b). A quantitative analysis of the PL quenching is best achieved by plotting the data into the Stern-Volmer formalism, using the ratio I_0/I (or $\langle t_0 \rangle/\langle t \rangle$), where the subscript 0 is used to indicate a quantity measured in the absence of the quencher. The Stern-Volmer analysis of the data in Figure 3.2.2 is presented in Figure 3.2.3 for quencher concentrations between 0 and 12.8 μ M, corresponding to 0 to ~9 quenchers per NC. Both Stern-Volmer ratios (intensity and average time) vary linearly over this concentration range, but with different slopes, which indicates that the average time (eq. (3.2.1)) of the PL decay cannot be used to directly quantify the NC-CPNN interaction, a point which will be further discussed in this chapter. Significantly, Figure 3.2.3 shows clearly that the same Stern-Volmer ratio is obtained by integrating the steadystate PL data over all energies (as shown in Figure 3.2.2(b)):

$$\left(\frac{I_0}{I}\right)_{CW} = \frac{\int I_0(\lambda) d\lambda}{\int I(\lambda) d\lambda}$$
(3.2.2)

or by integrating the normalized intensities of the PL decay over all times (as shown in Figure 3.2.2(d)):

$$\left(\frac{I_0}{I}\right)_{TD} = \frac{\int I_0(t)dt}{\int I(t)dt} \cdot \frac{I(t=0)}{I_0(t=0)}$$
(3.2.3)

indicating the negligible role that ultrafast (shorter than 1 ns here) or very long (longer than 1 μ s here) processes appear to play in the overall PL quenching observed here. In other words, it is clear that the same overall physics is adequately captured by the steady-state and time-dependent data reported in Figures 3.2.2(a) and (c), respectively.



Figure 3.2.3 Stern-Volmer plot of the area-integrated steady-state PL intensity (eq. (3.2.2), solid red circles), of the time-integrated normalized time-dependent PL (eq. (3.2.3), empty red circles), and of the ratio of the average time $\langle t_0 \rangle / \langle t \rangle$ (eq. (3.2.1), empty purple diamonds). The error bars (<1.5%) are smaller than the size of the markers. The red dashed line is a linear fit to eq. (3.2.4) over the 0 to 9 μ M range, with the intercept fixed at 1 and a slope $K_{SV} = (224 \pm 4) \text{ mM}^{-1}$; the black dashed line gives the behavior predicted from the Poisson distribution model of eq. (3.4.4), yielding $\langle k_Q \rangle / \langle k_0 \rangle = 0.417 \pm 0.004$ (see text for details).

Performing a linear fit on the low concentration range (<6 CPNN per NC) of the Stern-Volmer plot in Figure 3.2.3 (PL intensity ratio) yields the so-called Stern-Volmer constant, K_{SV} :

$$\frac{I_0}{I} = 1 + K_{SV}[Q]$$
(3.2.4)

where [Q] is the concentration of the PL quencher (here, Q = CPNN). Stern-Volmer analyses of four NCs samples, including the one shown in Figures 3.2.1 – 3.2.3 here (sample i), are briefly summarized in Table 3.2.1 (the Stern-Volmer data for samples ii – iv is given in Figure S3.1.7 – S3.1.9, respectively); for all samples, K_{SV} varies between $0.1 - 0.3 \mu M^{-1}$. Note that at high concentration range of CPNN the experimental Stern-Volmer plots often deviates from linearity. This is due to the dynamic equilibrium between bound and unbound quenchers as the unbound quencher concentration is no longer negligible (in other words, it can be considered a "saturation" effect of NCs surface, although strictly the NCs surface is far from fully saturated yet). As discussed below, the Stern-Volmer constant conceals valuable information about the fundamental nature and efficiency of the interaction between CPNN and CdSe NCs.

NC sample	Diameter (nm)	$\lambda_{1S}^{a}\left(nm ight)$	[NC] (µM)	Φ_{0} (%)	$\langle t_0 \rangle^{\rm b} ({\rm ns})$	K_{SV}^{c} (mM ⁻¹)
i	2.99 ± 0.30	539	1.6 ± 0.2	16.0 ± 0.9	61.2 ± 2.2	234 ± 4
ii	3.74 ± 0.37	573	0.9 ± 0.1	16.7 ± 0.9	40.4 ± 1.9	290 ± 2
iii	3.68 ± 0.37	571	0.9 ± 0.1	6.7 ± 2.2	44.3 ± 2.3	132 ± 1
iv	4.16 ± 0.42	587	1.5 ± 0.2	11.0 ± 1.4	34.4 ± 1.4	95 ± 1

 Table 3.2.1. CdSe NCs photophysical data.

^a Wavelength of the 1S_e1S_{3/2} peak of the NC sample absorption profile, the uncertainty is ± 1 nm for all samples. ^b Average time of emission in the absence of quencher, obtained from eq. (3.2.1). ^c Stern-Volmer constant, obtained from eq. (3.2.4).

3.3. Nature of PL Quenching Processes

Stern-Volmer analyses are often used in deciphering PL quenching processes. These processes are generally classified within one of two classes, namely the static and dynamic regimes.^{39–41} Static quenching processes involve the pre-association of the quencher (Q) and of the emitter (E). The term static comes from the ideal special case where the associated emitter-quencher complex (E—Q) is non-emissive (QY = 0, or perfect quenching), in which case the remaining PL intensity upon addition of the quencher arises from the fraction of "free" emitters (i.e. those emitters that are not bound to any quencher). As a result, the PL behavior in the time domain remains practically unchanged from that observed from the emitter in the absence of the quencher, aside an "instantaneous" drop in the intensity at t = 0: the ratio τ_0/τ , where τ and τ_0 are the PL decay lifetime with and without quencher respectively, is independent of quencher concentration and equal to unity. Assuming that no more than one quencher can bind to the emitter, the static Stern-Volmer ratio of the PL intensities can be shown to be:

$$\left(\frac{I_0}{I}\right)_{static} = \frac{1 + K_{eq}\left[\mathbf{Q}\right]}{1 + \frac{\Phi_1}{\Phi_0} K_{eq}\left[\mathbf{Q}\right]}$$
(3.3.1)

which is defined by the quencher-emitter binding equilibrium constant:

$$K_{eq} = \frac{\left[\mathrm{E} - \mathrm{Q}\right]}{\left[\mathrm{E}\right]\left[\mathrm{Q}\right]} \tag{3.3.2}$$

and the PL QY constants given by:

$$\Phi_n = \frac{k_r}{k_r + k_{nr} + n_Q \cdot k_Q}$$
(3.3.3)

where k_r , k_{nr} are the radiative/non-radiative rate constants of the emitter, k_Q is the rate constant associated with the quenching process and n_Q is the number of bound quenchers per emitter. In the ideal static scenario outlined above, $k_Q \rightarrow \infty$, $\Phi_1 = 0$, and the ratio I_0/I varies linearly with the quencher concentration if saturation effects are neglected (it is important to note that the quencher concentration, [Q], referred to in eq. (3.3.1) is not the nominal concentration, $[Q]_0$, but the concentration of unbound quencher, although the latter is commonly used in Stern-Volmer analyses as a close approximation when the nominal emitter concentration $[E]_0$ is very small and thus [E-Q] is very small).

A convenient approximation for eq. (3.3.1) is:

$$\left(\frac{I_0}{I}\right)_{static} \cong 1 + \left(1 - \frac{\Phi_1}{\Phi_0}\right) \langle n_Q \rangle \tag{3.3.4}$$

where $\langle n_Q \rangle$ is the average ratio of quencher bound per emitter; eq. (3.3.4) is valid when K_{eq} is large enough, such that

$$\left\langle n_{Q}\right\rangle = \frac{\left[\mathrm{E}-\mathrm{Q}\right]}{\left[\mathrm{E}\right] + \left[\mathrm{E}-\mathrm{Q}\right]} = \frac{\left[\mathrm{E}-\mathrm{Q}\right]}{\left[\mathrm{E}\right]_{0}} \approx \frac{\left[\mathrm{Q}\right]_{0}}{\left[\mathrm{E}\right]_{0}}$$
(3.3.5)

where $[X]_0$ indicates a nominal concentration of all X species, bound and unbound alike. Strictly, eq. (3.3.4) and (3.3.5) are only chemically valid in the limit of small $[Q]_0$ values, more precisely, in the limit where $\langle n_0 \rangle \ll 1$.

The other limiting Stern-Volmer regime is the so-called dynamic limit, where the emitter and quencher remain independent chemical species at all times but interact by colliding with each other. The rate of PL quenching is thus directly linked to the rate constant for the diffusion of the emitter and quencher (k_{diff}), which typically occurs on the same timescale as the PL process itself. The PL intensity in the time-domain then directly reports on the quenching process itself, with the consequence that the ratios τ_0/τ and I_0/I are both equal for the simple case of first-order (mono-exponential) kinetics.

$$\left(\frac{I_0}{I}\right)_{dynamic} = 1 + \frac{k_{diff}}{k_r + k_{nr}} P_Q[Q]_0$$
(3.3.6)

where P_Q expresses the probability that each collision leads to a successful quenching event ($0 \le 1$ $P_Q \leq 1$). From an Arrhenius mechanistic point of view, P_Q can be expressed as an activation barrier term for the quenching process, and for very efficient intrinsic quenching (that is, for $P_Q \sim 1$), the process is said to be under diffusion control (*i.e.* kinetically limited by diffusion, or activationless). In summary, although the two limiting Stern-Volmer scenario, namely the static (associative) and dynamic (collisional) regimes, both lead to linear Stern-Volmer quenching behavior, each can be differentiated from the other by simple comparisons of the time-domain and steady-state PL quenching data. From that perspective, the data shown in Figure 3.2.2 and 3.2.3 seemingly suggests that the PL quenching of CdSe NCs by NN radicals falls into the dynamic Stern-Volmer limit, where each addition of quencher effectively decreases the lifetime of the excited emitters. That being said, it is relatively straightforward to demonstrate that this "dynamic" process cannot arise from a diffusion/collisional mechanism. Indeed, assuming the best-case scenario of activationless regime ($P_Q = 1$) and using the average time of emission of the CdSe NCs (Table 3.2.1) as an estimate for the intrinsic excitonic recombination rate constant ($k_0 = k_r + k_{nr} \approx \langle t \rangle_0^{-1}$), using eq. (3.3.6) and the Stern-Volmer constants in Table 3.5.1 would lead to k_{diff} values that are on the order of $10^{12} - 10^{13}$ M⁻¹s⁻¹, at least 2 orders of magnitude larger than the diffusion-limited rate constants of small molecules, and well beyond any reasonable estimate for diffusional quenching kinetics involving objects as large as the colloidal NCs studied here.⁴² Clearly, the efficient quenching observed at such low quencher/emitter concentrations implies their preassociation, which likely occurs through ligation of the carboxylate group to the NC surface, 43-46 prior to the photo-excitation event. As a control experiment, the PNN radical, a variation of NN radical without the carboxylic acid function group, exhibits PL quenching efficiencies that are lower by several orders of magnitude than CPNN (Figure S3.1.1), suggesting that the binding

group is essential for efficient PL quenching. It is also noted that the PL quenching due to CPNN cannot be assigned to surface modification/destruction, as the control experiment performed with benzoic acid (which possesses a similar binding group) shows no evidence of degradation whatsoever (Figure S3.1.2). Further evidence for the strong affinity of CPNN for the NC surface is obtained from the significant broadening of the EPR spectra of the radical upon addition of CdSe NCs (Figure S3.1.4), indicative of a substantial reduction in motional *g*-factor averaging.^{47,48}

The apparent conflict between the "dynamic" Stern-Volmer signatures implied by the data in Figure 3.2.3 and the "static" (associative) nature of the quenching process simply indicates that the implicit assumption that the pre-associated complex is non-emissive, or $\Phi_1 = 0$, is not valid in this case. That is, the magnitude of k_Q in eq. (3.3.3) is similar to that of $k_r + k_{nr}$. As the quencher to emitter ratio is increased, the average value of n_Q in eq. (3.3.3) increases, which leads to faster and faster PL decay processes. A final important indication of the "static" nature of the PL quenching is obtained from the observation that the Stern-Volmer constant (which relates to the PL quenching efficiency) varies inversely with the concentration of the emitter (Figure S3.1.5), as predicted from eq. (3.3.4); in purely diffusional quenching regimes, varying the concentration of the emitter would not lead to any change in the efficiency of the quenching effect.

In principle, the overall PL quenching could thus be analyzed as arising from a collection of different subgroups of NCs, each subgroup being defined by a specific value of n_Q , the number of quenchers bound per NC. This implies that the PL decays should be analyzed as superpositions of many exponential components (one for each subgroup of NCs), but the intrinsic multi-exponential character of the NC PL complicates tremendously that type of analysis, and other approaches must be sought in order to extract quantitative information from the time-dependent PL data, which will be addressed in Section 3.5. The information that can be extracted from the steady-state data is

considered first.

3.4. Steady-State Analysis

First, consider the quenching efficiency, Φ_Q , which is simply defined as the branching ratio between the intrinsic recombination processes ($k_0 = k_r + k_{nr}$) and the PL quenching process:

$$\Phi_{\mathcal{Q}} = \frac{k_{\mathcal{Q}} \cdot n_{\mathcal{Q}}}{k_0 + k_{\mathcal{Q}} \cdot n_{\mathcal{Q}}} = 1 - \frac{\Phi_n}{\Phi_0}$$
(3.4.1)

There are two main issues with the evaluation of Φ_Q : 1) as indicated above, k_0 is not a uniquely defined quantity for CdSe NCs; 2) n_Q , the number of quenchers bound per NC, is also a distributed quantity. The inhomogeneous character of k_0 can be attributed to ensemble variations in either or both k_r and k_{nr} , and it is first assumed that a properly-chosen average value representing the sum of all radiative and non-radiative processes, $\langle k_0 \rangle$, adequately represents the ensemble, an assumption which will be validated below. The proper way to compute the average quenching efficiency for the whole ensemble then requires the explicit description of the distribution of n_Q , which is assumed following a Poisson distribution, as expected for independent binding events:

$$P_{i,\langle n_Q \rangle} = \frac{e^{-\langle n_Q \rangle} \langle n_Q \rangle^i}{i!}$$
(3.4.2)

where $P_{i,\langle n_Q \rangle}$ is the fraction of NCs with *i* quenchers if the average number of quenchers bound per NC is $\langle n_Q \rangle$. This then leads to the following expression for the ensemble average PL QY of a mixture of CdSe NCs with/without CPNN radicals:

$$\Phi_{\langle n_{Q} \rangle} = \sum_{i} P_{i, \langle n_{Q} \rangle} \frac{k_{r}}{\langle k_{0} \rangle + i \cdot k_{Q}}$$
(3.4.3)

which can then be recast within the Stern-Volmer formalism as:

$$\frac{I_0}{I} = \frac{\Phi_0}{\Phi_{\langle n_Q \rangle}} = \left(\sum_i \frac{P_{i,\langle n_Q \rangle}}{1 + i \cdot \left(k_Q / \langle k_0 \rangle \right)} \right)^{-1}$$
(3.4.4)

with $P_{i,\langle n_{O}\rangle}$ given by eq. (3.4.2). This equation is not reducible to a simpler analytical form and is also not strictly linear as would be expected from simple Stern-Volmer behavior, although the deviation is rather slight for most physical scenarios. Indeed, the experimental Stern-Volmer ratios plotted in Figure 3.2.3 are well fitted with eq. (3.4.4) using a ratio $k_0/\langle k_0 \rangle$ of 0.417 ± 0.007. It is interesting to note that this ratio is close, but not quite exactly the same as would have been obtain by analyzing the Stern-Volmer data by ignoring the Poissonian statistics, but instead using the simplistic approach given by eq. (3.3.4) which is valid only in the lower quencher concentration limit (clearly a bad assumption for the range of $\langle n_O \rangle$ values experimentally probed here). Precisely, the ratio $k_0/\langle k_0 \rangle$ that would be obtained from eq. (3.3.4) is 0.58, about 40% too large compared to the more realistic and physically meaningful value obtained from eq. (3.4.4). It is straightforward to explain: given that the observed behavior in Figure 3.2.3 arises from the simultaneous interaction of multiple quenchers with one emitter, relying directly on eq. (3.3.4)(which is valid in the limit where at most one quencher interacts with each NC) necessarily overestimates the quenching efficiency of a single quencher. A direct corollary of this is that care must be taken when applying the Stern-Volmer formalism to a given dataset, as some of the underlying assumptions that go into the traditional equations do not necessarily apply, as seen here. As demonstrated in the following section, the ratio $k_O/\langle k_0 \rangle$ obtained from the Poisson distribution model is actually identical to that obtained from the rate constant values that are independently extracted from the analysis of the time-dependent data, which validates the extended form of the Stern-Volmer ratio provided by eq. (3.4.4).

3.5. Time-Resolved Analysis

The analysis of the time-dependent PL quenching data shown in Figure 3.2.2 is necessarily complicated by ensemble inhomogeneities of the NC recombination rates (as evidenced from the multi-exponential character of the NC PL decay in Figure 3.2.2) and by the inherently distributed nature of the number of bound quencher per NC which would occur even if each NC is identical among the ensemble. An important limitation imposed by the analysis of the steady-state data is the difficulty in assigning a precise value to the rate constant of the quenching process, k_Q , a key parameter defining the physical interaction between CdSe NCs and CPNN. That is, whereas the steady-state analysis can yield a relatively accurate estimate of the ratio $k_Q/\langle k_0 \rangle$, it cannot independently provide values of either rate constant forming this ratio.

As a first step, the average intrinsic recombination rate constant of the emitter, $\langle k_0 \rangle$, is evaluated; as demonstrated by the Stern-Volmer plot shown in Figure 3.2.3, this quantity is not simply the reciprocal of the average time of emission, that is:

$$\langle k_0 \rangle \neq \frac{1}{\langle t_0 \rangle}$$
 (3.5.1)

or else the Stern-Volmer plots obtained from the average time ratios (purple diamonds), $\langle t_0 \rangle / \langle t \rangle$ would have been identical to those obtained from the steady-state PL quenching data (red circles), I_0/I , which is clearly not the case in Figure 3.2.3. This complication arises from the multiexponential character of the NC excited-state dynamics, as eq. (3.5.1) is formally valid for singleexponential decays, and forms the basis for traditional "dynamic" Stern-Volmer analyses, where the Stern-Volmer constant K_{SV} is identified as k/k_0 or, equivalently for single-exponential decays, as τ_0/τ .³⁹⁻⁴¹

The evaluation of $\langle k_0 \rangle$ for multi-exponential decays requires the determination of the distribution of rate constants responsible for observed photophysical behavior of the NC ensemble. This is obviously a complex challenge given the limited available information on the origin and nature of this distribution, but it is shown here that the specific nature of the chosen distribution does not strongly hinder the determination of the constant k_Q , as long as it reproduces adequately the overall kinetics of the decay. Attention should be paid that once each component of the decay rate constants of the multi-exponential decay is determined, the numerical mean (or weighed average) of all the components is not an adequate expression for $\langle k_0 \rangle$, as rates of multiple pathways are discussed here. Harmonic mean should be used for averaging rates and thus is best suited for this situation.



Figure 3.5.1. Time-dependent PL decays analyses. (a) Experimental PL decay curves (red, same data as Figure 3.2.2(c)) and least-square triple-exponential fits (black lines) using eq. (3.5.2). (b) Average (harmonic mean) rate constant of each triple-exponential function in panel (a). (c) Average rate constants of each fitted decay in panel (a), normalized to the value at $\langle n_Q \rangle = 0$. The slope of the line provides an estimate for the ratio $k_Q/\langle k_0 \rangle = 0.324$. (d) Experimental PL decay curves (red, same data as Figure 3.2.2(c)) and fits (blue lines) of a log-normal distribution of rate constants using eq. (3.5.7). (e) Average rate constant of each log-normal decay function in panel (d). (f) Average rate constants of each fitted decay in panel (d), normalized to the value at $\langle n_Q \rangle = 0$. The slope of the line provides an estimate for the ratio $k_Q/\langle k_0 \rangle = 0.404$.

As a good example of a likely fictitious distribution, the PL decays shown in Figure 3.2.2(c) can be relatively-well represented by a three-member distribution, which would give rise to a triple-exponential decay function:

$$I(t) = \sum_{i=1}^{3} C_i \exp(-k_i t)$$
(3.5.2)

as shown in Figure 3.5.1(a). While it is clear that such a phenomenological (not to say arbitrary) approach to model the excited-state decay cannot be expected to represent faithfully the underlying complex photophysics of the ensemble, the harmonic mean of k_1 , k_2 , and k_3 :

$$\left\langle k \right\rangle = \left(\frac{\sum_{i=1}^{3} C_{i} k_{i}^{-1}}{\sum_{i=1}^{3} C_{i}} \right)^{-1}$$
(3.5.3)

can be used as an adequate average rate constant, as plotted as a function of the quencher/emitter ratio in Figure 3.5.1(b). Interestingly, the average rate constant linearly increases with each equivalent of CPNN added, suggesting that the quenching process can be indeed represented as occurring in parallel to the intrinsic recombination process:

$$\langle k \rangle = \langle k_0 \rangle + \langle n_Q \rangle k_Q \tag{3.5.4}$$

which in turns allows a direct estimate of the ratio $k_Q/\langle k_0 \rangle$ to be obtained, as the slope of the plot of $k_Q/\langle k_0 \rangle$ vs. $\langle n_Q \rangle$:

$$\frac{\langle k \rangle}{\langle k_0 \rangle} = 1 + \frac{k_Q}{\langle k_0 \rangle} \langle n_Q \rangle$$
(3.5.5)

This plot is shown is Figure 3.5.1(c), yielding $k_Q/\langle k_0 \rangle = 0.324 \pm 0.003$, a value roughly in line with the ratio obtained from the empirical Stern-Volmer analyses in the previous section ($k_Q/\langle k_0 \rangle \sim 0.4$, *cf.* Table 3.5.1), suggesting that eq. (3.5.3) describes relatively well the average rate constant of the ensemble, in spite of the overly-simplified distribution model of eq. (3.5.2).

A perhaps more physically meaningful representation for the complex photophysics of the NCs is the log-normal distribution, whose probability density function (PDF) is:^{31,49,50}

$$P_{LN}(k) = \frac{1}{k\sigma\sqrt{2\pi}} \exp\left[-\frac{\left(\ln k - \ln k_{med}\right)^2}{2\sigma^2}\right]$$
(3.5.6)

where k_{med} and σ are the median and the so-called shape parameter of the log-normal distribution, respectively. The temporal decays associated with a given log-normal distribution of rate constants is obtained from:

$$I(t) = C \int_0^{+\infty} P_{LN}(k) \exp(-kt) dk$$
 (3.5.7)

As shown in Figure 3.5.1(d), all PL decay curves are once more fitted to the log-normal model using eq. (3.5.7), yielding for each quencher concentration a set of (k_{med} , σ) values. Again, the ensemble can be well represented using the harmonic mean of the log-normal distribution:

$$\langle k \rangle = k_{med} \cdot \exp\left(-\frac{1}{2}\sigma^2\right)$$
 (3.5.8)

Here also, the average rate constants obtained from the log-normal distribution fits very linearly with each equivalent of added quencher before "saturation" effects occur (Figure 3.5.1(e)), which allows the ratio $k_Q/\langle k_0 \rangle$ to be once more obtained from eq. (3.5.5), as given by the analysis in Figure 3.5.1(f), yielding now a value of $k_Q/\langle k_0 \rangle = 0.404 \pm 0.003$, practically identical to the value extracted from the empirical Stern-Volmer analyses (Table 3.5.1). This excellent correspondence obtained from two completely independent sets of analyses (one from the steady-state PL quenching data, the other from the analysis of the PL decay curves) not only validates the log-normal distribution as a realistic model for the complex photophysics of CdSe NCs, but also simultaneously validates the Poisson-distributed nature of the quencher binding interaction. This in turns suggests that the

values of $\langle k_0 \rangle$ obtained from the log-normal analysis and listed in Table 3.5.1 likely provide an excellent estimate of the average recombination rate constant, allowing the estimation of the quenching rate constant to be obtained, as also given in Table 3.5.1. Having these values, the discussion is proceeded to the precise physical mechanism responsible for the PL quenching of the CdSe NCs by CPNN radicals.

NC sample	Steady-state $k_Q/\langle k_0 \rangle^{a}$	Time-dependent $k_Q/\langle k_0 \rangle^{b}$	$\langle k_0 \rangle^{c} (\mu s^{-1})$	$k \varrho^{\mathrm{d}} (\mathrm{\mu s}^{-1})$
i	0.417 ± 0.007	0.404 ± 0.003	50.4 ± 0.2	20.3 ± 0.2
ii	0.255 ± 0.021	0.252 ± 0.006	57.4 ± 0.3	14.5 ± 0.4
iii	0.117 ± 0.005	0.132 ± 0.002	83.3 ± 0.2	11.0 ± 0.2
iv	0.140 ± 0.007	0.145 ± 0.003	84.6 ± 0.2	12.2 ± 0.3

Table 3.5.1. Analysis of the steady-state and time-dependent PL quenching of CdSe NCs due to interaction with CPNN.

^a From a fit of the data in Figure 3.2.3, using eq. (3.4.4).

^b From a fit of the data in Figure 3.5.1(d), using the log-normal distribution model, eqs. (3.5.5) - (3.5.8).

^c Obtained from the NC-only PL decay fit, using the log-normal distribution model.

^d Obtained from the product of the entries in the third and fourth columns here.

3.6. Energy Transfer Scheme

In general, PL quenching effects either result from direct energy (excitonic) transfer or from redox (oxidative or reductive) processes arising from the excited state of the emitter.^{39–41} Energy transfer processes broadly fall into two different classes, namely electronic multipole D-A interactions (with the dipole-dipole mechanism due to Förster and often designated under the acronym FRET as the main representative),^{51,52} and exchange-based processes, also often designated as Dexter processes.⁵³ The theory of electron transfer processes is a rich field often described within the framework of Marcus theory.⁵⁴ Since free radicals often possess both low-lying electronic excited states and easily accessible redox states, both energy transfer and electron transfer mechanisms can reasonably be invoked as working hypotheses, and only further insight into the underlying photophysics can differentiate these alternative processes. Dexter energy transfer process has an efficiency decreasing exponentially against the D-A distance, and usually considered a short-range process (inefficient beyond 1 nm distance).⁵³ Considering the diameter of the NCs already exceeds 1 nm, and the length of the bridging 4-carboxyphenyl group, it is argued that Dexter process is unlikely to be dominant. FRET process, however, remains a promising hypothesis. On one hand, the spectral overlap between the emission of CdSe NCs and the absorption of CPNN, shown in Figure 3.2.1(b), is significant enough to facilitate FRET process. On the other hand, there is further indirect evidence against the electron transfer mechanism is the absence of any noticeable activation barrier in low-temperature PL quenching data (which are expected for electron transfer processes), as shown in Figure S3.1.6. It is shown here that the FRET mechanism is very likely responsible for the observed PL quenching due to CPNN radicals.

The general expression for the rate constant of the FRET process depends on the distance between the donor and the acceptor, r_{DA} , and is given by:

$$k_{FRET} = \left\langle k_0 \right\rangle \left(\frac{R_0}{r_{DA}}\right)^6 \tag{3.6.1}$$

where the so-called Förster radius, R_0 , represents the D-A distance corresponding to 50% FRET efficiency (that is, $I_0/I = 2$ in a Stern-Volmer experiment designed at probing this process). The efficiency of the FRET mechanism is given by:

$$\Phi_{FRET} = \frac{k_{FRET}}{\langle k_0 \rangle + k_{FRET}} = \frac{1}{1 + (r_{DA}/R_0)^6}$$
(3.6.2)

The Förster radius effectively contains all the physics of the dipolar interaction (i.e. the strength of the dipole-dipole interaction):

$$R_0 = 6 \sqrt{\frac{9\ln 10}{128\pi^5 N_A}} \frac{\kappa^2 \Phi_0}{n^4} J_{DA}$$
(3.6.3)

where Φ_0 is the empirical PL QY of the donor in the absence of acceptor, *n* is the refractive index of the solvent (1.4244 for DCM),⁵⁵ N_A is Avogadro constant, and κ^2 is the orientation factor between the transition dipole moments of the donor and acceptor.⁵⁶ Whereas the CdSe NCs studied here are close to spherical, NN radicals are anisotropic species and likely to lead to strong variations in the orientation factors. That being said, if that each NN is bound to the surface in the same fashion is assumed, it is then likely that a constant value of the orientation can be used for all D-A interactions, which is taken here as being equal to the isotropic value, $\kappa^2 = 2/3$. Details about the orientation factor and its value range is discussed in Appendix C. The discussion that follows does not rely on a precise determination of R_0 , but it is easy to show that this value of κ^2 at most leads to an error of about 30% in the value of R_0 . It is also noted that the validity of the point charge approximation for NCs has been discussed previously.^{13,15,17,19,57} Finally, the quantity J_{DA} is the spectral overlap integral between the donor (here, CdSe NCs) PL and the acceptor (CPNN) absorption spectra. In wavelength scale, the spectral overlap is obtained from:

$$J_{DA} = \int \overline{I}_D(\lambda) \varepsilon_A(\lambda) \lambda^4 d\lambda \tag{3.6.4}$$

where \overline{I}_D is the normalized (to unity area) donor PL intensity and ε_A is the acceptor absorption profile, in molar absorptivity units. Spectral overlaps between the NCs and CPNN radical studied here (see Figure 3.1.1(b)) are given in Table 3.6.1 and correspond to values of R_0 that vary between 1.8 and 2.1 nm. These Förster radius values are similar, or shorter, than the D-A distances estimated by adding the NC radii (1.5 – 2.1 nm) and the CPNN bridging group length (about 0.7 nm).

QD	$J_{DA} (imes 10^{13}$	R_0	r_{DA} ^a	Φb	
sample	$nm^4 M^{-1} cm^{-1}$)	(nm)	(nm)	Ψ FRET	KSV[INC]
i	2.21 ± 0.05	1.92 ± 0.02	2.14 ± 0.12	0.34 ± 0.11	0.36 ± 0.04
ii	3.27 ± 0.07	2.07 ± 0.02	2.52 ± 0.14	0.24 ± 0.08	0.25 ± 0.03
iii	3.29 ± 0.06	1.78 ± 0.10	2.49 ± 0.14	0.12 ± 0.06	0.11 ± 0.01
iv	3.77 ± 0.07	1.97 ± 0.04	2.73 ± 0.15	0.12 ± 0.05	0.14 ± 0.02

Table 3.6.1. FRET analysis of CdSe NCs (donor) and CPNN radicals (acceptor).

^a The D-A distance r_{DA} is obtained from the sum of the NC radius and the length of CPNN bridging group (0.70 ± 0.05 nm). ^b Values obtained from eq. (3.6.2). ^c Using K_{SV} values listed in Table 3.5.1.

Assuming that the contribution of each quencher is additive (that is, each quencher acts independently of each other and all binding sites are equivalent), the Stern-Volmer representation of the FRET-based quenching, in the limit where $\langle n_0 \rangle \ll 1$, can be shown to be:

$$\frac{I_0}{I} = 1 + \Phi_{FRET} \left\langle n_Q \right\rangle = 1 + \Phi_{FRET} \frac{[Q]}{[E]}$$
(3.6.5)

which allows to make the following equivalence from eq. (3.2.4):

$$\Phi_{FRET} = K_{SV}[NC] \tag{3.6.6}$$

This expression is consistent with the observation that the Stern-Volmer slopes K_{SV} are inversely proportional to [NC] (cf. Figure S3.1.5) if the FRET efficiency is taken as independent of the concentration of the emitter (as expected). The Stern-Volmer slopes obtained from the FRET analysis are reported in Table 3.6.1. Within the limit of precision of this analysis, these calculated values are in excellent agreement with the experimental values given in Table 3.5.1. It is important to realize here that whereas the values are derived from spectroscopic data of the donor (CdSe NCs) and acceptor (CPNN radical) in isolation of each other, the K_{SV} values are directly extracted from the observed PL quenching data from mixtures of the CdSe NC donors and CPNN acceptors. The excellent agreement between the values predicted by these two completely independent experimental datasets and analyses thus strongly supports the assignment of FRET as the dominant interaction mechanism between CdSe NCs and CPNN radicals.



Figure 3.6.1. Validity of the FRET mechanism between CdSe NCs and CPNN radicals. $k_Q/\langle k_0 \rangle$ ratios obtained from analyses of the time-dependent PL decays in Figure 3.5.1 (Table 3.5.1) and normalized to the 6th power of the FRET radius R_0 (Table 3.6.1) are plotted here as a function of the D-A distance r_{DA} (Table 3.6.1). The dashed red curve shows the theoretical FRET behavior (not a fit) from eq. (3.6.1).

Another clear demonstration of the validity of the FRET mechanism can be obtained from the time-dependent data. As discussed in Section 3.4, the CdSe NCs average intrinsic recombination rate constant, $\langle k_0 \rangle$, and the effective PL quenching rate constant, k_Q , can each be obtained from the time-dependent PL decay data under the assumption that the intrinsic recombination rate constant is a log-normally-distributed quantity. In Figure 3.6.1, the ratios $k_Q/\langle k_0 \rangle$ obtained from this analysis and normalized to the 6th power of the Förster radius, have been plotted against the D-A distance, r_{DA} . The assignment of FRET as the dominant mechanism of the PL quenching implies $k_Q = k_{FRET}$ in eq. (3.6.1), which then force (i.e. there are no further adjustable parameters) the quantity $(k_Q/\langle k_0 \rangle) \cdot R_0^{-6}$ to decrease as r_{DA}^{-6} , as shown by the red dashed line in Figure 3.6.1. Within the uncertainty of the analysis and data, an excellent agreement is observed, strengthening both the validity of the FRET hypothesis and of the PL quenching analysis presented here.

APPENDICES



APPENDIX A: Supplementary Data for NCs-CPNN System

Figure S3.1.1. Control experiments of **(a)** steady-state PL quenching, **(b)** Stern-Volmer plot extracted from (a) and **(c)** TCSPC measured PL decay of 3.0 nm CdSe NCs (sample i) with varying concentration of PNN (radical without carboxy-phenyl binding group) in DCM.



Figure S3.1.2. Control experiments of (a) Stern-Volmer plot extracted from: (b) TCSPC measured PL decay of 3.0 nm CdSe NCs (sample i) with varying concentration of benzoic acid (binding group without radical). With large concentration of either PNN or benzoic acid, no significant steady-state PL quenching is observed, and the lifetime change is negligible. The overall decrease in PL intensities is due to less important factor such as dilution from the titration and introduction of surface trap states (which is negligible in CPNN analogs due to much lower quencher concentration).



Figure S3.1.3. The TCSPC IRF measured at the laser wavelength (405 nm). DCM in 1 cm cuvette is used as scattering sample.



Figure S3.1.4. EPR spectrum line broadening of CPNN with the presence of 3.7 nm CdSe NCs (red solid, sample ii), comparing to CPNN signal without CdSe NCs (blue dotted). Both CPNN and NCs (if present) are made 15 μ M in toluene in order to obtain satisfying EPR spectra. Oxygen is removed by standard freeze-pump-thaw process prior to the EPR experiment.



Figure S3.1.5. Stern-Volmer ratio plotted against (a) concentration of CPNN and (b) average number of CPNN per NC. The PL quenching experiment is performed similarly as described above. Same concentration of CPNN is titrated against 3.0 nm NCs (starting at 11.3% PL QY) of different concentrations: 0.47 μ M (red) and 0.23 μ M (blue). It is obvious that the Stern-Volmer slope obtained by plotting against [CPNN]/[NC] ratio is more universally useful on determining the PL quenching efficiency. Slight deviation from linearity at higher [CPNN]/[NC] ratio, due to binding-dissociation equilibrium, are observed for all the PL quenching experiments and are not surprising.



Figure S3.1.6. Cryogenic steady-state PL measurements. PL of NCs only (green dots, sample ii) and NCs with CPNN (black circles) at decreased temperature are measured and normalized to the PL intensity of pristine NCs at room temperature (298 K) according to the PL quenching experiment. The quenching behavior continues and becomes more efficient at low temperature, indicating that the mechanism is a barrierless energy transfer process.



Figure S3.1.7. Summary of PL quenching experiment of of NCs sample **ii**, including **(a)** the steady-state PL spectra, and **(b)** the Stern-Volmer plot of steady-state (red dots) and normalized integrated time-dependent (red circles) PL. The red dashed line is a linear fit to eq. (3.2.4) and the black dashed line gives the behavior predicted from the Poisson distribution model of eq. (3.4.4). Time-dependent PL with **(c)** triple-exponential fits and **(e)** log-normal fits are shown, with their rate constant ratio plotted in **(d)** and **(f)**, respectively. Parameters obtained from each fit are shown in corresponding colors.


Figure S3.1.8. Summary of PL quenching experiment of of NCs sample **iii**, including **(a)** the steady-state PL spectra, and **(b)** the Stern-Volmer plot of steady-state (red dots) and normalized integrated time-dependent (red circles) PL. The red dashed line is a linear fit to eq. (3.2.4) and the black dashed line gives the behavior predicted from the Poisson distribution model of eq. (3.4.4). Time-dependent PL with **(c)** triple-exponential fits and **(e)** log-normal fits are shown, with their rate constant ratio plotted in **(d)** and **(f)**, respectively. Parameters obtained from each fit are shown in corresponding colors.



Figure S3.1.9. Summary of PL quenching experiment of of NCs sample **iv**, including **(a)** the steady-state PL spectra, and **(b)** the Stern-Volmer plot of steady-state (red dots) and normalized integrated time-dependent (red circles) PL. The red dashed line is a linear fit to eq. (3.2.4) and the black dashed line gives the behavior predicted from the Poisson distribution model of eq. (3.4.4). Time-dependent PL with **(c)** triple-exponential fits and **(e)** log-normal fits are shown, with their rate constant ratio plotted in **(d)** and **(f)**, respectively. Parameters obtained from each fit are shown in corresponding colors.



Figure S3.1.10. Degradation of CPNN. (a) Change in the absorption spectra of CPNN DCM solutions with time, with CdSe NCs (sample ii) and kept in dark (black), with CdSe NCs and kept under continuous laser irradiation (red), and without CdSe NCs and kept under laser irradiation (blue). (b) Normalized change in absorbance of each sample at 380 nm (peak of CPNN absorption) to the absorbance of each solution at 405 nm (laser wavelength) against exposure time to laser (or in dark). Dashed lines are exponential fittings, assuming the degradation is a first-order reaction. With CdSe NCs, the absolute change in absorbance of CPNN is large, while the normalized degradation efficiency is less than that of pure CPNN. CdSe NCs may act as a sensitizer as well as a filter to the degradation of CPNN.

APPENDIX B: Equation Derivations

Below demonstrates the derivation of eq. (3.3.4).

Starting from the general static Stern-Volmer form given by eq. (3.3.1):

$$\left(\frac{I_0}{I}\right)_{static} = \frac{1 + K_{eq}[Q]}{1 + \frac{\Phi_1}{\Phi_0} K_{eq}[Q]}$$
(3.3.1)

and from the general form of the equilibrium constant:

$$K_{\rm eq}[Q] = \frac{[E-Q]}{[E]} = \frac{[E-Q]}{[E]_0 - [E-Q]}$$
(S3.2.1)

where [X]₀ indicates the total concentration of a given species, bound and unbound alike.

If making the assumptions that:

- 1) K_{eq} is large enough such that $[E-Q] \approx [Q]_0$ (i.e., all quencher is bound to the emitter);
- 2) $[Q]_0$ is small enough that $[E-Q] \ll [E]$;

then eq. (S3.2.1) becomes:

$$K_{\rm eq}\left[\mathbf{Q}\right] \approx \frac{\left[\mathbf{Q}\right]_0}{\left[\mathbf{E}\right]_0} = \left\langle n_{\mathbf{Q}} \right\rangle \tag{S3.2.2}$$

Inserting this into eq. (3.3.1) leads to:

$$\left(\frac{I_0}{I}\right)_{static} = \frac{1 + \langle n_{\rm Q} \rangle}{1 + \frac{\Phi_1}{\Phi_0} \langle n_{\rm Q} \rangle}$$
(S3.2.3)

Since this equation is only valid in the limit $\langle n_Q \rangle \ll 1$ (see assumption 2) above), the first term of its Taylor expansion can be taken to yield eq (3.3.4):

$$\left(\frac{I_0}{I}\right)_{static} = 1 + \left(1 - \frac{\Phi_1}{\Phi_0}\right) \langle n_Q \rangle$$
(3.3.4)

Below demonstrates how $k_Q/\langle k_0 \rangle$ ratio is obtained from eq. (3.3.4).

Starting by relating eq 8 to the experiment Stern-Volmer equation (eq. (3.2.4)):

$$1 + K_{\rm SV} \left[\mathbf{Q} \right]_0 = 1 + \left(1 - \frac{\Phi_1}{\Phi_0} \right) \left\langle n_{\mathbf{Q}} \right\rangle \tag{S3.2.4}$$

Since $\langle n_{\rm Q} \rangle = \frac{[{\rm Q}]_0}{[{\rm E}]_0}$, it is straightforward that:

$$K_{\rm sv} \left[{\rm E} \right]_0 = 1 - \frac{\Phi_1}{\Phi_0}$$
 (S3.2.5)

The right-side term can be recast as:

$$1 - \frac{\Phi_1}{\Phi_0} = \left(\frac{\langle k_0 \rangle}{k_0} + 1\right)^{-1}$$
(S3.2.6)

Which rearranges to:

$$\frac{k_{\rm Q}}{\langle k_0 \rangle} = \frac{1}{\frac{1}{K_{\rm SV} \left[{\rm E} \right]_0} - 1}$$
(S3.2.7)

Here, $[E]_0 \equiv [NC]_0$ which are listed in Table 3.5.1 of the main text, alongside the experimental Stern-Volmer constants K_{SV} ; using these values, the ratio $k_Q/\langle k_0 \rangle = 0.55 \pm 0.07$ is obtained for sample **i**, which is about 32% larger than the value extracted from the Poissonian model, which is not limited to the assumption that only one quencher can bind to the emitter.

APPENDIX C: Orientation Factor for FRET

The orientation factor, κ^2 , in the FRET radius R_0 expression in eq. (3.6.3), is assumed to be 2/3. This value corresponds to a pair of D-A dipoles that are both isotropic. Here the detail of obtaining this result is demonstrated. For a pair of D—A dipoles with a fixed direction, the orientation factor can be calculated using:

$$\kappa^{2} = \left(\sin\theta_{D}\sin\theta_{A}\cos\varphi - 2\cos\theta_{D}\cos\theta_{A}\right)^{2}$$
(S3.3.1)

where $\theta_D(\theta_A)$ is the angle between donor(acceptor) dipole $\vec{\mathbf{d}}(\vec{\mathbf{a}})$ and the D—A axis, $\vec{\mathbf{r}}_{DA}$, and φ is the angle between the planes of $\vec{\mathbf{d}} - \vec{\mathbf{r}}_{DA}$ and $\vec{\mathbf{a}} - \vec{\mathbf{r}}_{DA}$. It is easy to see that when the two dipoles are parallel and both perpendicular to the D—A axis ($\theta_D = \theta_A = 90^\circ$ and $\varphi = 0$), $\kappa^2 = 1$; when the two dipoles are colinear ($\theta_D = \theta_A = \varphi = 0$), $\kappa^2 = 4$; and when the two dipoles are perpendicular to each other ($\theta_D = \theta_A = 90^\circ$, $\varphi = 90^\circ$), $\kappa^2 = 0$. In the isotropic (or spherical) scenario, one will integrate over all possible combination of angles to obtain an average orientation factor, $\langle \kappa^2 \rangle = 2/3$. This result can also be obtained with a simper method. Given that each of the dipole vectors can be decomposed to 3 components in Cartesian coordinates (x, y, z, where z is the D—A axis), the overall probability $p_x = p_y = p_z = 1/3$ can be considered for isotropic dipoles. The combination of D—A dipoles both along x (or y) direction contributes 1 towards $\langle \kappa^2 \rangle$, the combination along z direction contributes 4, while all other combinations contributes 0. Thus the $\langle \kappa^2 \rangle$ is the weighted average by the probabilities of all the combinations:

$$\langle \kappa^2 \rangle = \frac{1}{3} \times \frac{1}{3} \times 1 + \frac{1}{3} \times \frac{1}{3} \times 1 + \frac{1}{3} \times \frac{1}{3} \times 4 = 2/3$$
 (S3.3.2)

the three terms denotates the combination of x-x, y-y and z-z, respectively.

While the isotropic dipole is a good approximation for the donor CdSe NCs, knowing their spherical shape and the nature of their exciton wave function, the acceptor CPNN apparently has anisotropic dipole on the radical center (the conjugated O-N-C-N-O structure). It is worth noted that the radical center is not conjugated with the phenyl ring (another reason to exclude Dexter process in the discussion), which leads free rotation of the radical center with respect to the C-C bond between the phenyl ring and the radical center (see Figure 3.1.1 for the molecular structure of NNs). This angle, together with the binding modes (monodentate or bidentate from carboxy group to NC surface Cd atom), complicates the analysis of the acceptor dipole angle θ_A . Nevertheless, the radical center can be considered freely rotating along an axis. Set the angle between this rotation axis and the z direction as θ_T . To obtain a range of $\langle \kappa^2 \rangle$, extreme scenarios such $\theta_T = 0^\circ$ and $\theta_T = 90^\circ$ are considered separately and the actual scenario has to fall in between of these two extremes.

When $\theta_T = 0^\circ$, the acceptor dipole average can be decomposed to x and y components, each has 50% probability. In this case,

$$\langle \kappa^2 \rangle = \frac{1}{3} \times \frac{1}{2} \times 1 + \frac{1}{3} \times \frac{1}{2} \times 1 = 1/3$$
 (S3.3.3)

When $\theta_T = 90^\circ$, the acceptor dipole average can be decomposed to x (or y, or anywhere in between which does not affect the result) and z components, each has 50% probability. In this case,

$$\langle \kappa^2 \rangle = \frac{1}{3} \times \frac{1}{2} \times 1 + \frac{1}{3} \times \frac{1}{2} \times 4 = 5/6$$
 (S3.3.4)

The actual $\langle \kappa^2 \rangle$ value should then fall in the range of (1/3, 5/6). Compared to the average value used in FRET analysis in Section 3.6, it can cause a maximum of 30% deviation on R_0 .





Figure S3.4.1. (a) (d) Absorption, **(b) (e)** steady-state PL quenching and **(c) (f)** TCSPC decays of CdSe NCs (synthesized by hot-injection, 3.2 nm diameter, 1.2 μ M) suspended in hexane (red, top, PL QY = 0.206) and toluene (blue, bottom, PL QY = 0.237) with varying concentration of PNN (dissolved in toluene) of 0 – 1.9 mM.



Figure S3.4.2. (a) Steady-state and **(b)** time-dependent PL spectra of CdSe NCs (4 nm diameter, PL QY = 0.2, 1.0 μ M) in hexane with addition of APNN dissolved in DCM with varying concentration from 0 to 2.9 mM. **(c)** Stern-Volmer plot of the quenching experiment extracted from (a) and (b).



Figure S3.4.3. (a) Steady-state and **(b)** time-dependent PL spectra of CdSe NCs (4 nm diameter, PL QY = 0.2, 1.0 μ M) in hexane with addition of PNN dissolved in DCM with varying concentration from 0 to 2.6 mM. **(c)** Stern-Volmer plot of the quenching experiment extracted from (a) and (b).



Figure S3.4.4. Comparison of Stern-Volmer ratio (quenching efficiency) between PNN (red) and APNN (blue) for PL quenching of CdSe NCs (4 nm diameter, PL QY = 0.2, 1.0 μ M) in hexane. Both steady-state (solid dots) and time-dependent (open circles) PL quenching efficiencies are shown.



Figure S3.4.5. Stern-Volmer plot of PL quenching of two similar CdSe NCs (with different diameters) with PNN radical. The quenching efficiency is low and about the same for both samples, which suggests that such a quenching behavior may not be due to energy transfer from NCs to surface bound quenchers (unlike CPNN).



Figure S3.4.6. (a) Steady-state and (b) time-dependent PL quenching of CdSe NCs (3 nm diameter, 1.6 μ M) in hexane with varying concentration of NPNN from 0 to 3.4 mM. (c) Stern-Volmer plot of the steady-state (red dots) and time-dependent (blue circles) PL quenching extracted from (a) and (b). The TCSPC counts become too low to be measured with high concentration of NPNN added.

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Chapter 4. Analyses and Modeling on the Multi-Exponential Excited-State Dynamics of

Colloidal CdSe Nanocrystals

4.1. Overview

To probe excited state CdSe NCs photophysics, the hybrid FRET system involving NCs and CPNN free radicals are designed to measure the PL quenching of the NCs. The nature of the PL quenching effect have been extensively discussed in Chapter 3.¹ Temporally, the deactivation of the NC emissive state due to CPNN occurs mostly on the nanosecond timescale. The strength of this well-characterized energy-transfer process is ideally suited to investigate in detail the nature of the complex dynamical behavior of the emissive state of CdSe NCs: indeed, the quenching interaction is strong enough to effectively impact the recombination dynamics, but not so strong that it would instantly deactivate excited NCs, thereby preempting further insights into their excited-state dynamics to be gained. This "Goldilocks" quenching strength – neither too strong nor too weak – thus offers an attractive approach to probe the complex, multiexponential excitonic dynamics of CdSe NCs by intercepting the recombination process at various time points along the excited-state lifetime.

In this chapter, the PL formalism is briefly reviewed with a classical 2-states emitter and compared to the complex PL decay of NCs. The phenomenological log-normal model, invoked in previous chapter to fit the multi-exponential PL decays of NCs, is discussed in further detail. The fitting results reveal physical insights about the serial kinetic processes in excited-state dynamics of NCs. Carrier trapping and "storage" mechanism is introduced, and a kinetic model is proposed to explain the observed PL quenching dynamics. This kinetic model is then further simplified to a thermal equilibrium model. The identity of trapped carriers that are mainly responsible for such a "storage" mechanism is examined with a combination of up-conversion PL (uPL) and TA spectroscopies and is found to be holes.² In addition, such a thermal "storage" model combined with the existence of charge-intercepting acceptor reveals information about bright/dark distribution of the NCs that can

lead to the "blinking" behavior with ensemble experiments, which previously has only been able to be probed through single NC experiments.^{3–7} Such ensemble method provides a way to characterize the NCs bright/dark distribution in a more statistically significant fashion.

4.2. Log-normal Distribution Models

In chapter 3, the dynamics of photoexcited NCs is briefly analyzed as shown in Figure 3.5.1. In order to better understand the nature of the problem offered by multiexponential dynamics, a statistical model is provided based on the log-normal probability distribution function can capture the essence of the multiexponential character of the CdSe NCs PL decays. Although such a phenomenological approach cannot provide direct physical information on the nature of the photophysical processes at play here, a few strict yet general properties can nevertheless be established. These properties of the intrinsic decays provide a set of conditions that any physical model must necessarily possess in order to properly describe the multiexponential character of the excited-state dynamics of CdSe NCs.



Figure 4.2.1. (a) Time-dependent PL decays with fits (blue) using a log-normal model, eq. (4.2.1), for NCs with an average of 0 - 9 CPNN. (b) Normalized probability distribution functions, $P_{LN}(k)/P_{LN}(k_m)$, plotted against rate constants k on a logarithm scale. The arrows show the direction of change upon addition of CPNN. (c) and (d) show the fitting parameters k_m and σ_{LN} against the average number of quenchers, respectively. The orange dotted lines are guides to the eyes.

Figure 4.2.1(a) shows the time-dependent CdSe NCs PL decays, measured with and without CPNN. As discussed previously,¹ such decays can be fitted using a variety of mathematical models that each treat the underlying distribution of the intrinsic recombination rate constant differently. A particularly useful approach though is the one relying on the log-normal model, which occasionally has been used in analyzing NCs PL decay.^{8–11} The observed emitted photon rate (intensity) at time *t* can be given by:

$$I(t) = A \int_{0}^{+\infty} P_{LN}(k_{obs}) \exp(-k_{obs} \cdot t) dk_{obs}$$
(4.2.1)

where A is a pre-exponential factor determined by I(t = 0). The observed rate constant k_{obs} that defines the recombination is not a unique quantity, but a distributed variable over the entire ensemble of emitters. The probability P_{LN} that a given emitter recombines at a specific rate constant k_{obs} is given by the log-normal PDF:

$$P_{LN}(k_{obs}) = \frac{1}{\sqrt{2\pi}\sigma_{LN}k} \exp\left(-\frac{(\ln k_{obs} - \ln k_m)}{2\sigma_{LN}^2}\right)$$
(4.2.2)

where k_m is the ensemble's median rate constant and the shape parameter σ_{LN} determines the width of the PDF. As shown in Figure 4.2.1(a), eq. (4.2.1) fits the experimental PL decay curves very well, providing a way to follow the photophysical behavior of the ensemble of emitters. Although these results do not imply that the log-normal model necessarily represent the actual underlying distribution of rate constants (as a matter of fact, other phenomenological models, some as simple as three-members distributions, often describe nearly as-well the time-dependent PL of CdSe NC ensembles),¹ it is shown below that the log-normal model nevertheless offers deeper insights than simpler models would.

The log-normal PDF (P_{LN} , eq. (4.2.2)) obtained from fitting each PL decay curve are plotted in Figure 4.2.1(b) on a logarithmic rate constant scale. As anticipated from the accelerated decays

reported in Figure 4.2.1(a), increasing amounts of CPNN shift the PDFs toward larger rate constant values; quantitatively, this effect is reported in Figure 4.2.1(c), where the median rate constant of each PDF is reported in a Stern-Volmer style against the average number of CPNN radicals per NC, $\langle n_Q \rangle$:

$$k_m = k_{m,0} + k_{\mathcal{Q},eff} \cdot \left\langle n_{\mathcal{Q}} \right\rangle \tag{4.2.3}$$

where $k_{m,0}$ is the median (observed) rate constant of the NC-only (no quencher) decay curve and $k_{Q,eff}$ is an effective quenching rate constant, per quencher added per NC. From Figure 4.2.1(c), $k_{Q,eff} = 0.046 \pm 0.01 \text{ ns}^{-1}$

A somewhat more surprising feature of the collection of PDFs in Figure 4.2.1(b) is the fact that the shape factors σ_{LN} (visually, the apparent "width" of each PDF) do not vary substantially with quencher concentration: the shape factors of each PDF shown in Figure 4.2.1(b) are plotted in Figure 4.2.1(d), indicating that $\sigma_{LN} = 1.16 \pm 0.01$ across the whole range of CPNN concentrations studied here. The invariable "width" of the log-normal PDFs reveals an important characteristic of the PL quenching process, as it indicates that the overall PL rate constant cannot be described as the sum of independent ("parallel") recombination pathways:

$$k_{obs,i} \neq k_{0,i} + k_{\mathcal{Q},eff} \cdot \left\langle n_{\mathcal{Q}} \right\rangle \tag{4.2.4}$$

where $k_{0,i}$ is the intrinsic (no quencher) PL rate constant of the *i*-th member of the ensemble and the other quantities retain the same meaning as above. Indeed, if the quenching process were to occur as one of two parallel branches of the overall excited-state recombination process (the other being the intrinsic recombination process itself), then those emitters in the distribution that recombine slowly (left-side of the distributions in Figure 4.2.1(b)) would be much more sensitive to the addition of quenchers (*i.e.* experience a larger rate-constant shift), whereas those members of the ensemble that have large intrinsic rate constants (right-side of the distributions in Figure 4.2.1(b)) would be much less likely to be quenched (*i.e.* experience a smaller rate-constant shift). In other words, the quantum efficiency of PL quenching vis-à-vis the intrinsic recombination process one would vary widely across the distribution, which would lead to a strong reduction of the shape factor (if anything, the shape factor somewhat increases slightly with addition of the quenchers, which is definitely irreconcilable with a parallel model of quenching). It is important to note here that the inequality in eq. (4.2.4) should not be read as implying that a linear quenching relationship cannot be established for individual members of the distribution – indeed, this is precisely how the median rate constant of the distribution (k_m) does behave, see eq. (4.2.3). Rather, what the inequality in eq. (4.2.4) implies is that it is impossible to define a unique quenching constant $k_{Q.eff}$ that uniformly applies to the whole ensemble while also following the linear behavior of the right-hand side.

The proper way of interpreting the invariant "width" of each log-normal distribution as quenchers are added is that the overall rate constant must be directly proportional to the intrinsic recombination rate constant ($k_{Q,i} \propto k_{0,i}$): the faster the intrinsic recombination is for a given member of the ensemble of emitters, the faster the quenching process must be for that same emitter. This somewhat surprising statement arises directly from the behavior of logarithmically-scaled quantities:

$$P_{LN}\left(\log k_{obs,i}\right) = P_{LN}\left(\delta + \log k_{0,i}\right) \tag{4.2.5}$$

where δ is the logarithmic displacement of the PDFs, a quantity which varies with the concentration of CPNN ($\delta \ge 0$). From eqs. (4.2.3) and (4.2.5), it is straightforward to show that (see Appendix C for derivation):

$$k_{obs,i} = k_{0,i} + \frac{k_{Q,eff}}{k_{m,0}} \cdot k_{0,i} \cdot \left\langle n_Q \right\rangle$$
(4.2.6)

that is, each member of the distribution is characterized by an effective quenching rate constant, $k_{Q,i}$, given by:

$$k_{Q,i} = \frac{k_{Q,eff}}{k_{m,0}} k_{0,i}$$
(4.2.7)

directly showing that fixed-width log-normal distributions indeed imply that the quenching rate constant of each member of the distribution must be directly proportional to their intrinsic recombination rate constants, as stated above.

Kinetically, the behavior of eq. (4.2.7) is a telltale mark of processes occurring sequentially ("in series"). Such a sequence of processes requires that both quenching (energy-transfer to CPNN) and intrinsic recombination first be preceded by a slower process. In the following section, the question of the origin of the heterogeneity of the serial kinetics is addressed specifically.

4.3. Origin of the Serial Process & Nature of the Trapped Carrier

In order to better understand the physical nature of the problem offered by multiexponential dynamics, the excited-state decay of CdSe NCs alone (i.e., without CPNN) is discussed first, and the observed data is compared to the behavior of an idealized (single-exponential decay) emitter. Figure 4.3.1(a) offers a closer look at the multiexponential PL decay dynamics of CdSe NCs, which contrasts starkly with the behavior that would be expected from a simple two-state radiative process, whose dynamics would be described with a mono-exponential function, g(t):

$$g(t) = k_r \exp\{-(k_r + k_{nr})t\}$$
(4.3.1)

where k_r and k_{nr} are the radiative and non-radiative recombination rate constants of the emitter, respectively. The decay function of eq. (4.3.1) is normalized such that its integration over all times following excitation (t = 0 to infinity) yields the total PL QY, Φ , of the emitter:

$$\int_{0}^{\infty} g(t) dt = \frac{k_{r}}{k_{r} + k_{nr}} = \Phi$$
(4.3.2)



Figure 4.3.1. (a) Normalized (to PL QY) experimental PL decay, I(t), of unquenched NCs (red, $\Phi_0 = 0.16$) and simulated decay, g(t), of a purely radiative process (grey shaded area, $\Phi = 1$) with the same $k_r = 0.0417$ ns⁻¹ as NCs. (b) A zoom-in of panel (a) between 0 – 1 ns time window, appended with uPL (red solid dots) decay and relative TA bleach recovery of the $1S_{3/2}1S_e$ transition (blue solid curve). The uPL decay is scaled with TCSPC data in the 0 – 1 ns window(see text). TA bleach recovery is normalized at t = 0.

Although ensemble NCs are generally far from ideal emitters, the observed PL decays of NCs, I(t), can always be described as a sum of single exponential decays with their specific weight and rate constant:

$$I(t) = \sum_{i} A_{i}k_{r} \exp\{(k_{r} + k_{nr,i})t\}$$
(4.3.3)

where A_i and $k_{nr,i}$ are the weighing and non-radiative rate constant of *i*-th member of the distribution, and k_r is the radiative rate constant that is assumed to be universal for a specific ensemble of NCs. Although in principle, k_r is also distributed along with the size/shape variation of the NCs,^{8,12–15} such uncertainty is far from causing the multi-exponential feature shown in Figure 4.3.1(a) and is negligible compared to that of k_{nr} . Under this assumption eq. (4.3.3) is written as a normalized formalism that satisfies:

$$\int_{0}^{\infty} I(t)dt = \sum_{i} A_{i} \left(\frac{k_{r}}{k_{r} + k_{nr,i}} \right) = \Phi_{0}$$
(4.3.4)

where the fraction terms denote the PL QY of each member and Φ_0 represents the ensemble PL QY. Such normalized I(t) is shown in Figure 4.3.1(a) for the NC-alone PL decay. For comparison, an ideal purely radiative ($k_{nr} = 0$) decay, g(t), with the radiative rate constant typically attributed to CdSe NCs of this size, ^{13,16} is plotted on the same graph. The comparison of both observed and simulated decays immediately highlights the multiexponential character of the NCs PL decay, but also emphasizes a critical feature of the excited-state dynamics of CdSe NCs: the experimental data has a much lower intensity at t = 0 compared to the ideal decay curve. This disparity indicates that ultrafast photodynamics (which are not resolved in the measurement shown in Figure 4.3.1(a)) rapidly depopulate the emissive state of CdSe NCs.

To further explore the nature of the processes responsible for the initial drop in PL intensity, TA and uPL measurements have been conducted in the sub-nanosecond time range. Figure 4.3.1(b)

summarizes the excitonic dynamics extracted from both spectroscopic tools. As expected, the uPL intensity rapidly drops from its maximal t = 0 value on a timescale of about 40 ps. Interestingly, normalizing the integrated uPL intensity within the first nanosecond to the integrated intensity measured by TCSPC (data in Figure 4.3.1(a)) within the same timescale allows to overlay both PL decays on top of each other, not only validating the argument presented above, but indicating that the whole decay is captured by the uPL measurement (*i.e.*, there are no processes depopulating the emitting state on a timescale faster than ~500 fs time-resolution of the uPL measurement). Per eq. (4.3.3), the intensity at t = 0 of the composed PL decay reveals the radiative rate constant $k_r = 0.0417 \text{ ns}^{-1}$ for our NCs sample. This value falls perfectly in line with the literature reported value^{13,16} and is used for our further analyses.

Comparatively, following a small drop perhaps associated with the same ultrafast process measured in uPL, the $1S_e1S_{3/2}$ excitonic TA bleach occurs on a much slower timescale overall (with a time constant of ~1 ns). As the $1S_e1S_{3/2}$ TA bleach recovery is almost entirely sensitive to the population of conduction band edge,¹⁷ the large discrepancy between the TA and uPL data in Figure 4.3.1(b) allows to conclude that the ultrafast process that rapidly depopulates the excitonic state must be due to hole trapping to the surface.

The ultrafast dynamics of uPL could be construed as implying that a fraction of the ensemble NCs are afflicted by such ultrafast hole trapping and thus behave as "dark" NCs and the observed PL emission are purely from the "bright" NCs (with a certain PL QY Φ_B). Such a "bi-modal" behavior of NCs is well-known.^{3–5,18–21}

Yet the hole trapping process is not necessarily yielding "dark" NCs (whereas the energy of the exciton would be lost) but can also store the charge carrier to later repopulate the emissive bandedge state to yield "bright" NCs. In fact, this latter perspective, to some extent, also allows to simply explain a second important puzzling feature of Figure 4.3.1(a), where a substantial fraction (~10%) of the observed decay are seen to occurs on a much slower timescale than the purely radiative simulated process. Since the purely radiative process is theoretically the longest one that can occur in a simple two-state picture, this observation was recognized early on as necessarily implying the existence of at least one long-lived resting state, where the energy can be stored, before being reinjected in the emissive excitonic state. Such three-state models have been invoked relatively often in the past, with the resting state assigned to long-lived (optically dark) surface trap states.^{22–28} The three-state model would also explain the sequential behavior revealed by lognormal analyses: both quenching and intrinsic recombination of excitonic state are preceded by energy detrapping from a surface trap state:

Step 1)
$$NC^{\text{Trap}} \xrightarrow{\text{slow re-population}} NC^{\text{ES}}$$

Step 2*a*) $NC^{\text{ES}} \xrightarrow{k_{\overline{i}}=k_r+k_{nr}} NC^{\text{GS}}$
(4.3.5)
Step 2*b*) $NC^{\text{ES}} \xrightarrow{k_{Q} \cdot \langle n \rangle} NC^{\text{GS}}$

where NC^{GS}, NC^{ES} and NC^{Trap} represent "bright" NCs in the ground, excitonic, and surface-trap states, respectively. The "dark" NCs, on the contrary, is assumed not observable in the ns-timescale PL decay. An interesting feature of three-states models is that the multiexponential character can easily be attributed to the existence of a variety of trap states, each with more-or-less long resting time; a particularly notable and insightful series of studies that has built on such a perspective is due to Jones, Scholes et al.^{27–29}

Due to the possible dual-origin of such ultrafast dynamics in Figure 4.3.1(b), the exact fraction of "dark" and "bright" NCs remain unknown, yet two extreme scenarios can still be concluded based on the uPL data. As shown in Figure 4.3.2, to one extreme, the whole NC ensemble behaves homogenously ($f_{Bright} = 1$ and no "dark" NCs) with a PL QY of the "bright" NCs, Φ_B , being

uniformly 16%; to the other extreme, 73% of all NCs are completely "dark" while the remaining $f_{Bright} = 0.27$ of "bright" NCs emit with PL QY of $\Phi_B = 59\%$. In the former extreme the excited NCs rapidly reaching pseudo-thermal excited-state equilibrium between the emitting excitonic and the hole-trap states within ~100 ps. In the latter extreme, all the ultrafast dynamics observed on uPL is attributed to non-emissive "dark" NCs – meaning that this fraction of NCs are completely irrelevant in long time-resolution measurements such as steady-state PL and TCSPC and do not participate in PL quenching. Even at this extreme, "bright" NCs cannot be 100% emissive, or the ensemble PL QY would exceed the experimentally measured value of $\Phi_0 = 16\%$.



Figure 4.3.2. "Bright" fractions and respective PLQY of NCs in "bi-modal" distribution. The red squares are specific points tested in fitting the TCSPC decay curves (see next section) and the dashed line represents the relationship between Φ_B and f_{Bright} . The arrow points at the fraction parameter used in thermal model analyses (see text below). Based on the uPL data in Figure 4.3.1(b), f_{Bright} below 0.27 (the erased part) is impossible to reach.

4.4. Excited-State Kinetics & Nature of the Trap-State Distribution

It has only been reported that the "bright"/"dark" fraction is determined from single NC measurements.^{3–7,20,21} The ensemble PL decay, on the other hand, is unavoidably plagued by multiexponential feature that originates from other distributions within the "bright" fraction of the NCs. To analyze such data, the distributed nature of the overall rate constant must be assigned to the first step in eq. (4.3.3): the location of a given NC within the distribution of excited-state recombination rate constant is essentially defined by the kinetics of the trapping/detrapping process. The distribution of trapping/detrapping rates can be explained by invoking one of two types of statistically-distributed quantities: i) energetic variations of the trap states, with deeper traps associated with longer overall storage periods ("thermodynamic heterogeneity"); ii) variations in the height/width of energy barriers separating trap and excitonic states ("kinetic heterogeneity"). Although not mutually exclusive, the kinetic heterogeneity hypothesis necessarily implies non-thermalized excited-state conditions, which is not trivial (but by no means impossible) to reconcile with the ultrafast timescale of the trapping process and the comparatively long lifetime of the NC excited state. Consequently, the discussion here is focused on exploring the consequences of thermodynamic heterogeneity which, as shown below, can readily explain the observed ensemble excited-state dynamics of the "bright" NCs. A simple picture of this scenario is shown in Scheme 4.4.1, with a normal (Gaussian) distribution of the trap state energy, which effectively serve as excitonic energy storage states.


Scheme 4.4.1. 3-States model of NCs with a distribution of trap energies.

Following photoexcitation (assumed here to lead directly to population of the lowest-energy excitonic state), NCs can either recombine to the ground state (with rate constant $k_r + k_{nr}$) or transfer the energy to one of the trap states (with k_{trap}). Once in a trap state, NCs can either return to the excitonic state (with k_{dtrap}), or return directly to the ground state (with k_{leak} , see discussion below); for simplicity, the possibility of trap-to-trap energy transfer is ignored here which would not introduce observable effects from an ensemble point-of-view. The presence of quenchers opens an additional relaxation pathway (with k_Q per quencher), which is only active from the excitonic state (see discussion below).

The kinetic scheme given in eq. (4.3.5) and Scheme 4.4.1 is associated with the following set of coupled differential equations:

$$\frac{d\left[\mathrm{NC}^{\mathrm{ES}}\right]}{dt} = k_{dtrap} \left[\mathrm{NC}^{\mathrm{Trap}}\right] - (k_r + k_{nr} + n_Q \cdot k_Q + k_{trap}) \left[\mathrm{NC}^{\mathrm{ES}}\right]$$
(4.4.1)

$$\frac{d\left[\mathrm{NC}^{\mathrm{Trap}}\right]}{dt} = k_{trap} \left[\mathrm{NC}^{\mathrm{ES}}\right] - (k_{dtrap} + k_{leak}) \left[\mathrm{NC}^{\mathrm{Trap}}\right]$$
(4.4.2)

When $k_{leak} = 0$, the totality of the exciton energy stored in trap states is ultimately recovered, over a timescale that can largely exceed the intrinsic lifetime of the exciton itself (k_r ⁻¹). Processes that increase the value of k_{leak} can then be thought of as losses, or "leaks". Although not straightforward to directly characterize, "leak" rate constants k_{leak} values are likely very small, as otherwise this would a dominant loss channel due to the long-lived NC^{Trap} states, eliminating the possibility of excitonic PL on timescales slower than k_r .

This set of equations can readily be used to fit the experimental PL decay curves by assuming that the fractional population of NCs in the excitonic state:

$$f_{\rm NC^{\rm ES}}(t) = \frac{\left[\rm NC^{\rm ES}\right]}{\left[\rm NC^{0}\right] + \left[\rm NC^{\rm ES}\right] + \left[\rm NC^{\rm Trap}\right]}$$
(4.4.3)

is equal to f_{Bright} immediately after excitation event (at t = 0, $f_{NC^{ES}}(0) = f_{Bright}$). At any given time following photoexcitation, the number of photons emitted per unit time is proportional to the excitonic-state population, which not only varies with time, but is also a distributed quantity in the ensemble of NCs depending on the depth of the trap, ΔE (and the actual number of bound quenchers, n_Q , for quenched NCs). Mathematically, the (normalized) PL intensity of a particular member of the ensemble can thus be expressed by:

$$I_{n_Q,\Delta E}(t) = k_r \cdot f_{\rm NC^{\rm ES}}(n_Q,\Delta E,t)$$
(4.4.4)

The overall PL intensity is then simply a properly weighted average of the signal from all members of the distribution, i.e. over all possible values that the trap state energy (ΔE) and number of quenchers per NC (n_Q) can take. The probability that a given NC has a trap state at energy ΔE from the excitonic state is assumed to follow a normal distribution:

$$P_{N}(\Delta E) = \frac{1}{\sqrt{2\pi}\sigma_{\Delta E}} \exp\left[-\frac{\Delta E - \langle \Delta E \rangle}{2\sigma_{\Delta E}^{2}}\right]$$
(4.4.5)

where $\langle \Delta E \rangle$ and $\sigma_{\Delta E}$ are the mean and standard deviation of the trap energies. The probability of a given NC to have n_Q quenchers bound to its surface, if the average of the number of quenchers per NC is $\langle n_Q \rangle$, is assumed to follow a Poisson distribution:

$$P_{P}(n_{Q}) = \frac{e^{-\langle n_{Q} \rangle} \langle n_{Q} \rangle^{n_{Q}}}{n_{Q}!}$$
(4.4.6)

The total ensemble PL intensity is then given by the kinetic model:

$$I(t) = k_r \sum_{n_Q} P_P(n_Q) \int_{-\infty}^{\infty} P_N(\Delta E) f_{\rm NC^{ES}}(n_Q, \Delta E, t) d\Delta E$$
(4.4.7)

The experimental PL decay curves can be directly fitted to eq. (4.4.7) by solving the differential excited-state rate laws, eqs. (4.4.1) and (4.4.2). In practice, the summation/integral in eq. (4.4.7)

are cut when either P_P or P_N are smaller than 0.001, which introduces overall errors of no more than 0.3%.

Closer inspection of the kinetic analysis presented above reveals that the excited-state manifold reaches thermal equilibrium within a fraction of a nanosecond. This effectively allows the excitonic population to be reduced to a simple Boltzmann expression:

$$f_{\rm NC^{ES}}\left(\Delta E, t\right) = P_B\left(\Delta E\right) \exp\left(-k_{n_Q,\Delta E} \cdot t\right)$$
(4.4.8)

where $P_B(\Delta E)$ is the Boltzmann fraction of the excitonic state, i.e.:

$$P_B(\Delta E) = \left(1 + \exp\left(\frac{\Delta E}{k_B T}\right)\right)^{-1}$$
(4.4.9)

and $k_{n_0,\Delta E}$ is an effective excited-state rate constant given by:

$$k_{n_{\mathcal{Q}},\Delta E} = P_B\left(\Delta E\right) \cdot \left(k_r + k_{nr} + n_{\mathcal{Q}} \cdot k_{\mathcal{Q}}\right)$$
(4.4.10)

Combining eqs. (4.4.7) and (4.4.8) yields the thermal model. The effective rate constants $k_{n_Q,\Delta E}$ are directly comparable to the observed overall PL rate constants (k_{obs}) extracted from the lognormal analyses of the experimental PL decay curves in Figure 4.2.1. Fundamentally, both quantities are intimate encryptions of the distributed character of the excited-state dynamics of CdSe NCs, each from a different perspective: phenomenologically from the observed decay (k_{obs}), or physically from a simulation of the 3-states model in Scheme 4.4.1 ($k_{n_Q,\Delta E}$). The direct comparison is given in Figure 4.4.1(e), establishing clearly that both methods lead to homologous representations and that these are indeed substantially meaningful descriptors of the underlying distributions that dictate the ensemble photophysics of CdSe NCs. There is however one notable difference between the two approaches: whereas the log-normal distribution extends to infinity with non-zero probability, the kinetic-model distribution is characterized by a maximum rate constant value. This end points originates from the excitonic Boltzmann population term (eq. (4.4.9)), which reaches unity as the energy of trap is taken to be much higher than the excitonic states ($\Delta E \rightarrow -\infty$). From eq. (4.4.10), the maximum value that the observed rate constant can thus take is:

$$k_{\max}\left(n_{Q}\right) = k_{r} + k_{nr} + n_{Q} \cdot k_{Q} \tag{4.4.11}$$

Physically, it is readily obvious that rate constants cannot assume arbitrarily large values and, as such, phenomenological models such as the log-normal analysis described in Section 4.2 can only at best approximate the real underlying distribution of rate constants and ultimately fail at providing physical insights into the underlying machinery responsible for the complex ensemble dynamics. Consequently, although phenomenological analyses are often powerful at describing and systematizing data, care must be taken to keep track of their inherent limitations: parameters extracted from phenomenological models often have no direct connection to actual physical processes. A particularly striking illustration of this is given here by the value of the phenomenological quenching rate constant extracted from the Stern-Volmer analysis of the PL quenching data (Figure 4.2.1(c)), which is about five times smaller than the value extracted from the kinetic analysis ($k_{Q,eff} = 0.04 \text{ ns}^{-1} vs. k_Q = 0.19 \text{ ns}^{-1}$). Whereas the constant k_Q provides a direct physically-meaningful estimate of the strength of the coupling interaction between CPNN and the excitonic state (*i.e.* the probability per unit time that energy is transferred to CPNN when the NC is in the lowest excitonic state), the effective quenching rate constant only provides a measure of the probability per unit time for energy transfer onto CPNN once the NC is in any of all possible excited (excitonic or surface trap) states. Given that most photoexcited NCs spend much more of their overall lifetime into trap states, where direct energy-transfer is not operative, the apparent rate at which energy is being transferred onto CPNN is much smaller than if the excitonic state

was continuously populated until either of the intrinsic recombination or quenching processes occur, and thus $k_{Q,eff} < k_Q$.



Figure 4.4.1. TCSPC traces of (a) unquenched (NCs only) and (b) maximum quenched (NCs with ~9 equivalent CPNN) and fitting curves with thermal equilibrium model from eq. (4.4.7) under different assumptions of bright/dark fractions (see discussion below): 1. maximum f_{Bright} (uniformly "bright", black dotted curve); 2. minimum f_{Bright} (extreme "bi-modal", blue dot-line curve); 3. mathematical best fit for NCs only trace (orange solid curve). (c) Best global fit (black dashed curve) for all quenched and unquenched PL decay traces (red). (d) Trap energy distribution (black) extracted from global fitting, with respect to the excitonic energy (red). (e) Observed rate constant distribution extracted from global fitting (black solid) plotted on logarithmic scale, compared to that of log-normal fitting (blue dotted) from Figure 4.2.1(b), for NC only PL decay trace.

Table 4.4.1. Kinetic model fitting parameters of the PL decay curves shown in Figure 4.4.1

Fixed Parameters		Best-Fit Parameters	
k_r^1	0.042 ns ⁻¹	k_Q	$0.12 \pm 0.01 \text{ ns}^{-1}$
k_{nr}^2	0.19 ns ⁻¹	kleak	0 ns ⁻¹
k_{trap}^{3}	25 ns ⁻¹	$\langle \Delta E \rangle$	$47.4\pm0.2\ meV$
k_{dtrap}^4	variable	$\sigma_{\Delta E}$	$38.0\pm0.2\;meV$

¹ Obtained from literature values.^{14,15}

² k_{nr} is fixed by the PL QY of the bright fraction: $k_{nr} = k_r (\Phi_B^{-1} - 1)$, which is valid in the limit where $k_{leak} \approx 0$, as it is here.

 ${}^{3}k_{trap}$ is fixed to the PL decay rate constant measured by uPL (Figure 4.3.1(b)); practically, the overall fit (*i.e.* the values obtained for the best-fit parameters) depends little on the value used for k_{trap} , as long as it is larger than ~2 ns⁻¹.

⁴ For a given trap depth, k_{dtrap} is fixed in our model by Arrhenius relationship: $k_{dtrap} = k_{trap} \exp(\Delta E/k_B T)$.

4.5. "Bright"/"Dark" Distribution in the NCs Ensemble

The analysis above is within the limit of the "bright" fraction of NCs. If the ensemble NCs would be homogeneous, that is, every NC emits with the same probability given by the ensemble PL QY ($\Phi_B = \Phi_0$), the modeling above provides enough insights to explain entirely the multiexponential behavior of the excited state NCs dynamics, while no probing process such as PL quenching is necessary. However, as shown in Figure 4.4.1(a), within the range of possible f_{Bright} pre-determined with the uPL measurement as shown in Figure 4.3.2, such a thermal model can always make a fit that represents the NCs only (without CPNN) decay curve reasonably well, due to the flexibility of the three parameters (ΔE), k_{nr} and f_{Bright} , which are coupled together. Such flexibility is also reflected in the criteria of the goodness of fitting, as shown in Figure 4.5.1: for NCs-only sample, the reduced χ^2 value remains at low level with f_{Bright} varying through the entire possible range.

As previously stated, such "bright"/"dark" distribution of NCs has only been reported by single NC measurements.^{3–7} Due to the its limitation in the number of representative samples, single NC measurements can potentially suffer statistical insignificance compared to ensemble measurements. To study the "bright"/"dark" fraction of an ensemble, a PL quencher is employed as a probe to perturb the excited state of NCs. It is assumed that the chemical binding properties is similar between "bright" and "dark" NCs towards CPNN but the as-measured nanosecond dynamics (with TCSPC) is dominated by only "bright" fraction of the NCs (i.e. the excitons of "dark" NCs recombine at sub-nanosecond timescale and contributes partly to the observed ultrafast decay in uPL spectrum but not observed by TCSPC). The comparison between Figure 4.4.1(a) and (b) clearly shows that only certain range of f_{Bright} value can satisfy the thermal model fitting of both quenched and unquenched NCs PL decay curves: the assumed "uniform" distribution ($f_{Bright} = 1$) apparently fits better than assumed extreme "bi-modal" ($f_{Bright} = 0.31$). It is interesting that even

the best-fit parameter for NCs-only fails to simulate the maximum quenched PL decay compared to a simple "uniform" assumption, which clearly shows the limitation of studying the ensemble sample without perturbation.

It is known that CdSe NCs studied here undergo FRET when coupled with CPNN,¹ the series of quenching PL spectra introduces two more fitting parameters ($\langle n_Q \rangle$ and k_Q), of which the former can be directly obtained from the experimental procedure after considering the Poisson distribution (eq. (4.4.6)) nature of the bound quenchers, and the latter can be obtained from FRET analysis ($k_Q = k_{FRET}$).¹ The master equation for thermal model is provided here:

$$I(t) = \sum_{n} P_{P}(n_{Q}) \int_{-\infty}^{+\infty} \frac{\Phi_{0}}{\Phi_{B}(\Delta E)} P_{N}(\Delta E) P_{B}(\Delta E) k_{r} \exp\left(-P_{B}(\Delta E) \left(\frac{k_{r}}{\Phi_{B}(\Delta E)} + n_{Q}k_{Q}\right)t\right) d\Delta E \qquad (4.5.1)$$

where I(t) is the normalized (to PL QY) PL intensity in nanosecond timescale (measured with TCSPC) as a function of time *t* after photoexcitation, n_Q is the actual nubmer of quencher for each NC, ΔE is the trap state energy (difference from exciton level), P_P is the Poisson distribution (eq. (4.4.6)) of n_Q , Φ_0 is the ensemble PL QY, Φ_B is the PL QY of the "bright" fraction of NCs (when $k_{leak} = 0$, Φ_B is no longer a function of and has a simple relation ship with Φ_0 as $\Phi_0 = f_{Bright}\Phi_B$), P_N is the normal distribution PDF of ΔE (eq. (4.4.5)), P_B is the Boltzmann population factor (eq. (4.4.9)) for each ΔE , k_r is the radiative recombination rate constant of the NCs, k_Q is the physical quenching rate constant (here $k_Q = k_{FRET}$). To fit a decay curve, the following parameters are estimated/fixed and then fit with eq. (4.5.1): fixed: Φ_0 , k_r , k_Q , (ΔE), T (temperature); varying: (ΔE) (mathematical mean of ΔE), $\sigma_{\Delta E}$ (standard deviation of ΔE), k_{nr} , k_{leak} (this term is fixed to 0 if the best-fit value is smaller than 10^{-5} ns⁻¹ or negative).

Although each quenched PL decay should in principle yield the same information about the NCs ensemble, the analysis is much strengthened with fitting all obtained PL decay curves

simultaneously (global fitting) and find the global minimum of the χ^2 value. As shown in Figure 4.5.1, the global fitting suggests a much narrower range at which the fits are considered good (below the criteria χ^2 value) and the best fitting parameter (the valley) locates at $f_{Bright} = 0.899$. This work for the first time provided a tool to probe such "bright"/"dark" distribution with statistically significant ensemble NCs sample with a simple thermal model.



Figure 4.5.1. Reduced chi-square values obtained from the thermal equilibrium model fits with selected f_{Bright} values, for NCs only (blue) and whole quenching data (global fitting, black).

Of course, as for most scientific models, the physical picture proposed here is unlikely to fully capture all aspects of the complex excited-state manifold of CdSe NCs. It does nevertheless offer a simple yet flexible way to describe the ensemble excited-state dynamics and also has some predictive potential. For instance, temperature-dependent PL decays for the same sample studied here are given in Figure 4.5.2. Although the effect of temperature generally leads to complicated and hard to control effects on the overall PL QY of NCs that are still not well understood,^{26,30–32} here it is shown that the same thermal model presented above, using the observed temperature-dependence of the PL QY to directly modify the value of k_{nr} at each temperature (see Appendix A) but otherwise using the exact same parameters that were obtained from fitting the room-temperature decay data (Table 4.4.1 and Figure 4.4.1), successfully predicts well the excited-state dynamics all the way down to 177 K, the freezing point of the DCM suspension used here. The excellent agreement further strengthens the value of the simple physical model presented here.



Figure 4.5.2. PL decays of 3.0 nm CdSe NCs measured between 298 K and 177 K, along with kinetic simulations (eq. (4.5.1). The room temperature simulation is the same best-fit curve shown in Figure 4.4.1. (parameters given in Table 4.4.1); all other simulations are obtained by keeping the same parameters as for the 298 K one, except for k_{nr} , which is adjusted to the observed PLQY value (see Figure S4.1.2).

APPENDICES

APPENDIX A: Supplementary Data



Figure S4.1.1. (a) Time-dependent up conversion PL spectra, selectively shown to represent the ultra-fast PL decay. (b) TA bleach recovery spectra.



Figure S4.1.2. Temperature dependent PL QY of 3.0 nm CdSe NCs as shown in Figure 4.5.2.



Figure S4.1.3. Fit residuals of temperature dependent PL data in Figure 4.5.2. The as-measured PL decays have signal-to-noise ratios >1000, and the residuals are shown in actual number of photon counts. Traces are offset on the vertical axis for clarity.



Figure S4.1.4. PL decays of Figure 4.4.1 selectively (at 298 K and 177 K) replotted here and normalized to t = 0 to emphasize the temperature dependence.



Figure S4.1.5. Exciton and trap emission of 3.0 nm CdSe NCs at 77 K measured by TCSPC, at 550 and 730 nm, respectively. The acquisition time of trap emission is 5 times longer than that of the exciton emission to yield good signal-to-noise ratio. The black trace is a single-exponential fit on the tail of the trap emission decay and yield a rate constant (used for k_{leak}) of $1.4 \pm 0.1 \times 10^{-3}$ ns⁻¹.



Figure S4.1.6. Start-rate dependent PL decay of CdSe NCs. While there is obviously not enough time for the entire ensemble to relax when the start-rate of TCSPC is set at 1 MHz (the fraction of NCs that does not get enough time to relax shows up as an elevated baseline), 125 kHz start-rate is slow enough to ensure that this fraction is negligible.



Figure S4.1.7. Whole vision (a) and power-law fit (b) of extremely delayed PL emission. The data is collected with 31.25 kHz start-rate until the photon counts reaches maximum allowed by the instrument (integrated for 11 h). The power-law fit starts from 256 ns, where radiative decay (0.0417 ns^{-1}) transitions to this power-law decay (the intensities of two decays are equal at this point).

APPENDIX B: Impact of Poisson distribution



Figure S4.2.1. Graphic demonstration of importance of adapting Poisson distribution of surface bound quenchers in the model. PL decay curves are simulated using our thermal-equilibrated model, with a set of parameters fixed as follows: $k_r = 0.05$ ns, PL QY = 0.16, $\langle \Delta E \rangle = 0.05$ eV, $\sigma_{\Delta E}$ = 0.03 eV, $k_0 = 0.2$ ns⁻¹, and with quencher to emitter ratio $\langle n_0 \rangle = [Q]/[NC] = 0 \sim 9$ that follows (a) Poisson distribution or (d) uniform distribution. As the "pristine NCs" decay curves in (a) and (d) are identical, there is distinct deviation between the "quenched NCs" decay curves (the curves with shortest average lifetime exhibits the most pronounced difference, as expected). The simulated decays are then fit with log-normal function (eq. (4.2.1) in the main text). The fitting parameters A is fixed at 1 and the median k_m is plotted against $\langle n_O \rangle$ in (b) and (e) while the shape factor σ_{LN} is plotted in (c) and (f), respectively. It is noticable that with uniform distribution, the k_m in panel (e) increases perfectly linearly with $\langle n_O \rangle$, while σ_{LN} in panel (f) has only a slight increase at low [Q] then plateaus. On the contrary, when Poisson distribution is applied, k_m in panel (b) starts to deviate from linearity at high [Q], suggesting that the log-normal model starts to fail. More interestingly, at low [Q], a much more significant increase of σ_{LN} is observed in panel (c). The log-normal fits behavior on Poisson adapted simulations is in a surprisingly well agreement with the fits applied on experimental data in Figure 4.2.1(c) and (d) in the main text.

APPENDIX C: Equation Derivations

Derivation of eq. (4.2.6) :

It is immediately obvious from eq. (4.2.5) that:

$$\log k_i = \log k_{0,i} + \delta \tag{S4.3.1}$$

which is equivalently expressed as:

$$k_i = k_{0,i} \cdot 10^{\delta}$$
 (S4.3.2)

or:

$$k_i = k_{0,i} + (10^{\delta} - 1)k_{0,i}$$
(S4.3.3)

We recall here that k_i represents the *i*-th member of the ensemble; the median of that distribution is directly given by:

$$k_m = k_{m,0} + (10^{\delta} - 1)k_{m,0}$$
(S4.3.4)

Comparing this equation with eq. in the main text allows the following equivalence to be made:

$$(10^{\delta} - 1)k_{m,0} = k_{\mathcal{Q},eff} \cdot \langle n_{\mathcal{Q}} \rangle$$
(S4.3.5)

which directly rearranges to:

$$\left(10^{\delta} - 1\right) = \frac{k_{\mathcal{Q},eff}}{k_{m,0}} \left\langle n_{\mathcal{Q}} \right\rangle \tag{S4.3.6}$$

Substituting this equation for $(10^{\delta}-1)$ yields eq. (4.2.6) of the main text:

$$k_{i} = k_{0,i} + \frac{k_{\mathcal{Q},eff}}{k_{m,0}} \cdot k_{0,i} \cdot \left\langle n_{\mathcal{Q}} \right\rangle$$

$$(4.2.6)$$

Synchronous change of k_{trap} and k_{dtrap} , with assuming simple Arrhenius process:

$$\frac{k_{trap}}{k_{dtrap}} = \frac{k_a \exp\left(\frac{-E_{trap}^{\ddagger}}{k_B T}\right)}{k_a \exp\left(\frac{-E_{dtrap}^{\ddagger}}{k_B T}\right)} = \frac{k_a \exp\left(\frac{-E_{trap}^{\ddagger}}{k_B T}\right)}{k_a \exp\left(\frac{-(E_{trap}^{\ddagger} + \Delta E)}{k_B T}\right)} = \exp\left(\frac{\Delta E}{k_B T}\right)$$
(S4.3.7)

where k_a is a rate constant for the situation of barrierless trapping, and E^{\ddagger} represents the activation barrier.

Derivation of eq. (4.4.9):

$$P_{B}(\Delta E) = \frac{[\mathrm{NC}^{\mathrm{ES}}]}{[\mathrm{NC}^{\mathrm{ES}}] + [\mathrm{NC}^{\mathrm{Trap}}]} = \left(1 + \frac{[\mathrm{NC}^{\mathrm{Trap}}]}{[\mathrm{NC}^{\mathrm{ES}}]}\right)^{-1}$$
$$= \left(1 + \frac{\exp\left(\frac{-(E^{*} - \Delta E)}{k_{B}T}\right)}{1 + \frac{\exp\left(\frac{-E^{*}}{k_{B}T}\right)}{\exp\left(\frac{-E^{*}}{k_{B}T}\right)}}\right)^{-1} = \left(1 + \exp\left(\frac{\Delta E}{k_{B}T}\right)\right)^{-1}$$
(S4.3.8)

where E^* is the energy of the exciton of NCs.

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REFERENCES

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Chapter 5. Ultrafast Hole Extraction from Photoexcited Colloidal CdSe Nanocrystals

Coupled to TEMPO Derivatives

5.1. Overview

Charge transfer processes are ubiquitous in nature and technology.¹⁻⁴ A primary topic of interest is the ability of NCs to participate in interfacial electron transfer processes, which can occur between NCs,⁵⁻¹⁰ between NCs and bulk semiconductors,⁹⁻¹¹ and between NCs and molecular species.^{8–10,12–20} The latter is particularly attractive with regards to photophysical schemes such as those based on the dye-sensitized solar cell (DSSC) framework^{11,21-23} or for photocatalytic applications,^{19,24–30} where photoinduced electron transfer is often the first of a series of steps that ultimately lead to useful chemical or physical energy transformation. Whereas a large number of studies have been devoted to reductive electrochemical work - extracting electrons from the conduction band level of NCs - comparatively little work has been done on the oxidative counterpart processes – extracting holes from NCs.^{16,17,31–35} This is due to challenges associated with typically sluggish hole-extraction kinetics^{31,32,35,36} along with the relative instability of oxidized NCs,^{37,38} two problems that are usually addressed by the use of high concentrations of sacrificial reducing species with large electron-transfer driving forces, allowing to kinetically bypass the detrimental processes associated with photoexcited holes in NCs. The identification of efficient (i.e., rapid and energy-economical) molecular hole extractors thus remains an important challenge in the development of efficient opto-electronic and photo-conversion devices based on colloidal NCs.



Scheme 5.1.1. Ultrafast hole transfer from CdSe NC to surface bound AT molecule.

Among the many molecular species that have so far been coupled to NCs, nitroxide free radicals are fascinating electro-active systems as they are stable molecules that can undergo facile, reversible one-electron transfer processes in either oxidative or reductive directions, allowing them to be used as redox shuttles in $DSSCs^{39-43}$ and as molecular memory elements.⁴⁴ Nitroxides related to the archetypical TEMPO have been shown to efficiently quench the PL of CdSe and CdTe NCs through a process that can only be assigned to electron transfer between the photoexcited NC and the nitroxide species (Scheme 5.1.1).⁴⁵⁻⁴⁸ That being said, further details on the photophysical mechanism responsible for this quenching process, starting with the simplest question of the direction of the photoinduced charge transfer (*i.e.*, valence-band hole *vs.* conduction-band electron transfer), are yet unknown.

In this chapter, a combination of time-dependent spectroscopic methods shows that free nitroxides related to TEMPO act as efficient hole acceptors for photoexcited chalcogenide NCs with transfer rate constants exceeding 10^{12} s⁻¹ (i.e., sub-picosecond timescale), which is the direct cause for the well-established PL quenching of NCs coupled to nitroxide radicals. Such large transfer rate constants are uncommon for simple NC-molecule dyads and underline the great potential that organic radicals can play in the development of NC-based opto-electronic applications.

5.2. PL Quenching of CdSe NCs with AT

Figure 5.2.1 shows the absorption and steady-state PL spectra of a 3.7 nm CdSe NC sample, before and after the addition of AT (Figure 5.2.1 inset), illustrating the PL quenching activity of that species. From Figure 5.2.1 it can be concluded that ~3,000 equivalents of AT per NC reduce the PL intensity by about an order of magnitude. it is previously shown that the relatively low PL quenching efficiency of AT arises from poor NC-binding competition against native ligands, rather than to an intrinsically slow quenching process;⁴⁸ this observation is further confirmed here by the ultrafast spectroscopic data presented below.



Figure 5.2.1. Steady-state absorption (solid lines) and PL (dashed lines) spectra of a suspension of 3.7 nm CdSe QDs (0.9 μ M in toluene), with 3.3 mM (blue) and without (black) AT, whose molecular structure is shown here.
Although the PL quenching of AT might not be huge on a per-quencher-per-emitter basis (for reference, AT is about a thousand times less efficient a PL quencher than CPNN),⁴⁹ its activity is not negligible either: for comparison, Figure 5.2.2 shows that the impact of aniline – another CdSe NC PL quencher that has received some attention previously⁵⁰ – is two orders of magnitude lower than that of AT, as measured from the Stern-Volmer quenching constant, K_Q :

$$\frac{I_0}{I} = 1 + K_{Q}[Q]$$
(5.2.1)

where I and I_0 are the PL intensities with and without the quencher Q.



Figure 5.2.2. (a) Impact of the addition of four molecular species (TEMPO, cyclohexylamine, aniline, and 4-amino-TEMPO) on the total integrated PL intensity of CdSe NCs; the lines are Stern-Volmer best fits curves, eq. 1 in the main text. **(b)** PL quenching efficiency of each molecular species (structure shown below); the horizontal dashed line denotes the scale change of the vertical axis.

Although it is not strictly possible to revert the addition of AT on NCs, at least not in a way that would not impact the photophysical properties of the ensemble, it is highly unlikely that the PL quenching effect reported in Figure 5.2.1 is due to irreversible modification of the core structure of the NCs. First, as shown in Figure 5.2.1, the absorption spectrum of the CdSe NCs does not noticeably change upon addition of AT, indicating that no evidence of substantial etching or reconstruction effects on the NCs. As further control experiments, the addition of different molecular species that each are chemically and sterically similar to AT is tested. The addition of TEMPO, the nitroxide equivalent to AT, but without the amino group, has no measurable impact on the PL of CdSe NCs, even on the mole-per-liter scale (Figure 5.2.2). Clearly, the free nitroxide functionality itself is not enough to induce the observed PL quenching effect. The addition of cyclohexylamine, an amine that has about the same dimensions and basicity as the amino group of AT, also does not lead to PL quenching of the order of magnitude observed for AT: although some reduction of the overall PL intensity of CdSe NCs is observed upon addition of cyclohexylamine, the impact is only about 1/200 that of AT. It is speculated that the origin of the quenching from cyclohexylamine is due to poorer surface passivation following native ligand displacement; no matter what, there is no reason to believe that the impact of the amino group of AT is more important than that of cyclohexylamine, which suggest that the impact of the amino group alone in the millimolar range (i.e., same as Figure 5.2.1) would be at best a 0.5% reduction of the initial PL intensity – clearly much less than observed here.

5.3. Time-Dependent Spectroscopies Revealing Ultrafast Hole Extraction

The time-dependence of the PL decay with varying amounts of added AT, as measured by TCSPC, is shown in Figure 5.3.1(a) and (b). As is often the case for CdSe NCs, the PL decay is multiexponential when observed over the full time scale of the emission, which occurs over the microsecond range (or longer).^{51–53} Although the same is observed here, within the first 50 ns or so, the CdSe NC PL is described well by a single-exponential decay with a time constant of 12.6 ns. As AT is added to the NC sample, two changes occur. First, the PL intensity at t = 0 drops as more AT is added, as more clearly seen in Figure 5.3.1(b); this effect is designated here as the "instantaneous" component of the PL quenching. The second effect appears as a change of the decay at longer times, referred to here as the "slow" component of the PL decay. The slow dynamic quenching component is readily assigned to diffusion-based processes due to the large fraction of unbound AT in the sample, whereas the instantaneous component arises from AT species that are bound to NCs at the photo-excitation event.⁴⁸

Due to the very small oscillator strength of AT, it is previously concluded that a purely dipoledipole ("Förster") energy transfer mechanism could not account for the observed PL quenching by AT.⁴⁸ The instantaneous drop in the PL intensity reported here for the first time strongly corroborates that conclusion, as the DA distances required to yield sub-nanosecond dipole-dipole couplings are estimated to be on the order of a few angstroms,⁴⁸ i.e., at least an order of magnitude smaller than the radius of the NCs studied here – clearly an unphysical scenario. Two important mechanisms for the PL quenching thus remain: exchange-based ("Dexter") energy-transfer and electron-transfer processes between CdSe NCs and AT. These two scenarios can be directly distinguished by the fact that energy transfer involves the synchronous displacement of both carriers (electron *and* hole) from the donor to the acceptor, whereas electron transfer processes relocate only one of the two carriers (electron *or* hole) to the acceptor. Pump-probe TA spectroscopy provides a direct approach to differentiate between those two mechanisms.



Figure 5.3.1. (a) TCSPC PL decay of 3.7 nm CdSe NCs (0.9 μ M in toluene) with varying amounts of AT; (b) Zoomed-in view of the data in (a); (c) TA spectra (CdSe NCs, no AT) measured at different times after excitation at 400 nm (5, 90, 250, 420, 600, and 850 ps, respectively); (d) Time-dependence of the bleach recovery of the $1S_{3/2}1S_e$ excitonic transition at 570 nm, with varying amounts of AT. The color legend for AT concentrations is given in the inset.

TA spectra from the same 3.7 nm CdSe NCs are shown in Figure 5.3.1(c). Because of the extremely low absorptivity of AT, no direct signatures of that species are observed in the TA data of AT/NC mixed solutions. The TA spectra are characterized by a strong bleach (negative differential absorption) signal at the lowest excitonic transition (1S_{3/2}1S_e excitonic transition, designated in the rest of the text as the "1S" transition), around 570 nm for the CdSe NC sample studied here, and the next excitonic transition (2S_{3/2}1S_e, the "2S" transition) around 530 nm. Importantly, whereas very strong PL effects are observed instantaneously at t = 0 (within TCSPC) time resolution, ~ 0.25 ns), Figure 5.3.1(b), the bleach recovery of the 1S transition in Figure 5.3.1(d) and the 2S transition is comparatively unaffected by the addition of AT, with practically no changes observed instantaneously. Clearly, the PL quenching process is not correlated with the processes that TA spectroscopy is probing. This striking difference between the temporal decay in the PL and the TA experiments unambiguously rules out an energy-transfer mechanism as the origin of the PL quenching process observed in Figure 5.3.1(a) and (b), leaving charge transfer as the only possible mechanism for PL quenching due to AT. It is noted that previous control experiments using a variety of other ligands with similar steric volumes and binding affinities as AT showed that the PL quenching of CdSe NCs by AT is directly due to the action of the free radical species itself, and not to some indirect effect such as surface re-functionalization or the creation of surface trap sites.⁴⁸ The extraction of charge carriers from a NC affects the dynamics of the TA spectrum, and for CdSe NCs, the specifics of the electronic structure are such that only the population of the conduction band states contributes to the bleach of the 1S transition: the presence or absence of valence band holes is largely inconsequential for the 1S exciton bleach signal.54-58

Using this important photophysical characteristic of CdSe NCs to interpret the difference between the TA and PL data in Figure 5.3.1 unambiguously demonstrates that the PL quenching is due to the transfer of the valence band hole to AT: if the extraction of conduction band electrons was the direct cause of the instantaneous PL quenching, then the TA data would necessarily show an equivalently fast bleach recovery, which is not observed here. The same process can be alternatively described as an electron injection from AT into the photoinduced valence-band hole of excited CdSe NCs, *i.e.*, a reductive PL quenching mechanism from the luminophore's point of view.

The most consequential feature of the hole-transfer process is its ultrafast character. Whereas the time resolution of the TCSPC data shown in Figure 5.3.1 is limited by a ~250 ps IRF, uPL measurements with 0.5 ps time resolution show the same instantaneous PL quenching as a function of added AT (Figure 5.3.2(a)), suggesting an intrinsic hole-transfer rate constant larger than $k_0 \sim$ 10¹² s⁻¹. Such a large rate constant is atypical for hole-transfer processes:^{31,32,35} although subpicosecond hole extraction has been recently reported for phenyldithiocarbamate-linked acceptors,^{16,17} here ultrafast hole transfer from colloidal NCs is achieved in the absence of strong hole delocalization effects, suggesting that ultrafast hole extraction processes from NCs-molecule DA dyads can be achieved in the weak coupling regime. Overall, the degree of quenching induced by AT measured in the uPL measurements is in good agreement with the TCSPC experiments, as characterized by the Stern-Volmer ratios shown in Figure 5.3.2(b). These ratios I_0/I represent the ratio of PL intensities of the CdSe NCs alone (I_0) and of the CdSe NC + AT sample (I). The TCSPC Stern-Volmer ratios are obtained from the instantaneous, t = 0 ns, PL intensities, whereas the uPL ratios are obtained from the integration of the uPL decay between t = 0 and t = 250 ps, that is, the nominal time-resolution of the TCSPC measurements. The excellent agreement between the two time-dependent PL measurements indicates that both methods are probing the same photophysical quenching process. The slope of the Stern-Volmer data shown in Figure 5.3.2(b) is similar to that reported previously for the static component of the total quenching of CdSe NCs due to AT,⁴⁸ which underlines that the ultrafast quenching process is also associated with a rather weak surface binding interaction. Together, the fast quenching and weak surface binding result in the observed rapid but incomplete quenching despite the large excess of AT.



Figure 5.3.2. (a) Excitonic uPL decays of 3.7 nm CdSe NCs (0.9 μ M in toluene; black symbols) and of the same sample mixed with 0.45 mM (red) and 0.89 mM (blue) AT. The arrows on the left indicate the uPL intensity at t = 0 ps. (b) Stern-Volmer quenching ratios obtained from the instantaneous TCSPC PL intensities (blue diamonds) and from the uPL signal integrated between t = 0 and 250 ps. The Stern-Volmer slope obtained from a global fit of both data sets is $K_{SV} = 1.34 \pm 0.6 \text{ mM}^{-1}$, as represented by the black dashed line here.

In Figure 5.3.2(a), the PL decay of CdSe NCs alone is characterized by a relatively fast component (about 30 ps). From comparison with the TA data of the same sample in Figure 5.3.1 (which does not show a significant short-lived decay) and to previous photophysical studies on CdSe NCs,⁵⁹ this picosecond component is directly assigned to hole-trapping, likely to surface states. Although the overall uPL decay curves for CdSe NCs with and without AT appear similar to each other (aside from the instantaneous PL intensity drop at t = 0), closer inspection indicates that there are slower dynamics also at play here that perhaps indicate the role of slower hole-transfer contributions occurring in the ~10 ps timescale.

It is finally noted that the subsequent electron transfer from the conduction band to the oxidized AT (the "regeneration" step) is not directly observed here. It is awared that a distribution of rate constants varying over the time window of the TA experiment (1 ns) is observed in Figure 5.3.1d. In principle, this might reflect a complex (non-unique and/or non-uniform across the NC-AT moiety ensemble) recombination mechanism; whereas such complex behavior is often observed in semiconductor/molecular acceptor interfacial recombination dynamics,^{60–62} the possibility that this is associated with carrier traps cannot be ruled out. In any case, these faster effects could only apparently account for a very small fraction of the regeneration of all photo-reduced NCs, as evidenced by the contrast in the amplitude of the effects due to hole transfer (Figure 5.3.1b) and electron recombination (Figure 5.3.1d). This suggests that the electron recombination process occurs on a relatively long (> 1 ns) timescale, longer than that is extracted from the data shown here.

The results presented here suggest that nitroxide radicals can extract photoexcited holes from CdSe NCs very efficiently, as long as direct binding to the nanoparticle surface, as bestowed by the amino anchoring group of AT, is provided. Evidently, such large rate constants for hole transfer

entail significant DA electronic coupling, although the specific extent to which driving force and reorganization energies favorably contribute to the overall transfer process is yet unknown. Studies to further characterize such effects as well as the complexity of the recombination process that follows the oxidation of AT after the photoexcitation of CdSe NCs are currently underway.

APPENDICES

APPENDIX A: Supplementary Data



Figure S5.1.1. Steady-state absorption (solid lines) and PL spectra from a suspension of 5.0 nm CdSe QDs (1.2 μ M in toluene), without (black) and with (green) 0.9 mM AT.



Figure S5.1.2. TCSPC data from a suspension of 5.0 nm CdSe QDs (1.2 μ M in toluene), without (black) and with (red) 0.9 mM AT.



Figure S5.1.3. 1S bleach recovery of TA (squares) of a suspension of 5.0 nm CdSe QDs (1.2 μ M in toluene; blue squares) and of the same sample mixed with 0.9 mM AT (green squares) and excitonic uPL decays (circles) from the same QDs without (black circles) and with (red circles) 0.9 mM AT.



Figure S5.1.4. Steady-state absorption (solid lines) and PL (dashed lines) spectra from a suspension of 3.0 nm CdSe QDs (1.6μ M in toluene), without (black) and with (blue) 4.0 mM AT



Figure S5.1.5. TCSPC data from a suspension of 3.0 nm CdSe QDs (1.6 μ M in toluene), without (black) and with (colors) AT.



Figure S5.1.6. 1S bleach recovery of TA (squares) of a suspension of 3.0 nm CdSe QDs (1.6 μ M in toluene; blue squares) and of the same sample mixed with 4.0 mM AT (green squares) and uPL decays (circles) of the same QDs without (black circles) and with (red circles) 4.0 mM AT.

APPENDIX B: Carboxy TEMPO Analog



Figure S5.2.1. (a) Steady-state and (b) time-dependent PL quenching of CdSe NCs (4.5 nm diameter, PL QY = 0.1, 1.53 μ M) in DCM with varying concentration of CT from 0 to 1.1 mM. (c) Stern-Volmer plots of steady-state (red dots), time-dependent (blue circles) and their ratio (instantaneous quenching, black triangle).



Figure S5.2.2. (a) Absorption spectra (red to black), (b) steady-state and (c) time-dependent PL quenching of CdSe NCs (see sample i in Chapter 3. 3.0 nm diameter, PL QY = 0.16, 1.54 μ M) in DCM with varying concentration of CT from 0 to 1.1 mM. (d) Stern-Volmer plots of steady-state (red dots), time-dependent (blue circles) and their ratio (instantaneous quenching, black triangle).



Figure S5.2.3. (a) Absorption spectrum of CdSe NCs (see sample ii in Chapter 3: 3.7 nm diameter, PL QY = 0.17, 0.87 μ M) in DCM. (b) Steady-state PL quenching of the NCs with varying concentration of CT from 0 to 1.1 mM. (c) Time-resolved PL quenching spectra and (d) zoom-in of the first 50 ns. (e) Stern-Volmer plots of steady-state (red dots), time-dependent (blue circles) and their ratio (instantaneous quenching, black triangle).



Figure S5.2.4. (a) TCSPC measured time-resolved PL quenching spectra of CdSe NCs with varying concentration of CT, which reproduces Figure S5.2.3(c). All panels share the same color legend. (b) Normalized time-resolved PL quenching spectra zoomed-in for the first 200 ns and first 2-orders of magnitude drop in intensity. (c) Transient-absorption measured bleach-recovery of the 1S peak (573 nm). The sample spectra are examined to show no obvious shift. (d) Normalized bleach-recovery decay plotted at the same scale of panel (b) for comparison. The bleach-recovery is slower than PL decay which suggests that valence band holes is depleted in a faster rate than conduction band electrons of the NCs even without CT. The change in PL decay rate upon addition of CT is not followed by the bleach recovery, suggesting that the PL quenching of NCs by CT cannot be due to electron transfer from photoexcited NCs to CT.

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6.1. Average Arrival Time of PL Decay

Equation (3.2.1):
$$\langle t \rangle = \frac{\int_0^{+\infty} I(t) t dt}{\int_0^{+\infty} I(t) dt}$$
.

Code:

#pragma rtGlobals=3

// Use modern global access method and strict wave access.

Function TAvg(tns,It,[EndPnt,BL])

//This function returns average time of wave I(t) as a function of tns, which is defined as the first momentum: $\langle t \rangle = {Integral[I(t)tdt]}/{Integral[I(t)dt]}.$

Wave tns,It as a function of time

//tns:time wave in the x-axis; It: I(t) PL intensity

Variable EndPnt,BL integral; BL: baseline //EndPnt: the end point of x-axis of the

Variable n,i,m,k,t0,tav photon emission

//t0: time-zero; tav: average time of

n=NumPnts(tns)

if (EndPnt==0)

EndPnt=n-1

endif

make/O/D/N=(n) tt,Itt,IntT,IntTT integral of I(t); IntTT: integral of I(t)*t

//tt: dummy wave for tns; Itt: I(t)*t; IntT:

//to find time-zero (maximum point of the PL decay).	
k=It[0]	
tt = tns	
m=0	
for (i=0;i <n;i+=1)< td=""><td></td></n;i+=1)<>	
If (It[i]>k)	
k=It[i]	
m=i	
Endif	
Endfor	
t0=tt[m]	
tt-=t0	//correct for time-zero
It-=BL	//correct for baseline

Itt=It*tt

Integrate/METH=1 It/X=tt/D=IntT

Integrate/METH=1 Itt/X=tt/D=InttT

tav = (InttT[EndPnt]-InttT[m])/(IntT[EndPnt]-IntT[m])

Print "<t>= ",tav

killwaves tt,Itt,IntT,InttT

It+=BL

//recover the original data

Return tav

End

Example:



Figure 6.1.1. Example time-dependent PL decay of NCs.

Command: Tavg(tns,n0)

Result: <t>= 61.1866

Command: Tavg(tns,n0,EndPnt=2000)

Result: <t> = 48.0945

6.2. Creating Poisson Distribution Probability Mass Function

Equation (3.4.2):
$$P(\langle n \rangle, i) = \frac{e^{-\langle n \rangle} \langle n \rangle^{i}}{i!}$$

Code:

#pragma TextEncoding = "Windows-1252"

#pragma rtGlobals=3

// Use modern global access method and strict wave access.

Function/wave Poisson(xw,avg,pmf)

wave xw,pmf

variable avg

variable n,i

//set the dimension of x-wave and the PMF wave, that the minimum dimension is 6 and the maximum is 60, to minimize the run time (for other functions calling this one) while ensuring the integrated PMF is close enough to 1.

```
n = round(avg + 6)
if (n>60)
n = 60
```

endif

redimension/N=(n) xw,pmf

//initialize x-wave and PMF wave

 $\mathbf{x}\mathbf{w} = \mathbf{0}$

pmf = 0

xw[0] = round(avg-n/2)

if (xw[0]<0)

xw[0] = 0

endif

xw[i] = xw[0] + i

endfor

End
Example:

Create double-precision real number waves "w0" and "w1" regardless their dimensions (this function will re-dimension them)

With average value of 0.5:

Command: Poisson(w0,0.5,w1)

Result: w0 = $\{0, 1, 2, 3, 4, 5, 6\}$

 $w1 = \{0.606531, 0.303265, 0.0758163, 0.0126361, 0.00157951, 0.000157951, 1.31626e-05\}$

With average value of 5:

Command: Poisson(w0,5,w1)

Result: w0= {0,1,2,3,4,5,6,7,8,9,10}

w1= {0.00673795,0.0336897,0.0842243,0.140374,0.175467,0.175467,0.146223,0.104445,0.065278,0 .0362656,0.0181328}

6.3. FRET Analysis

Equation (3.6.3):
$$R_0 = \sqrt[6]{\frac{9\ln 10}{128\pi^5 N_A}} \frac{\kappa^2 \Phi_0}{n^4} J_{DA}$$

Code:

#pragma TextEncoding = "UTF-8"

#pragma rtGlobals=3 // Use modern global access method and strict wave access.

//Given the donor emission spectra and absorber absorption profile, calculate the FRET integral J and radius R0 in nm.

 $//R0 = 9\ln 10 * ksq * QY / (128pi^5 * NA * n^4) * J$ where ksq is the orientation factor kappa^2, n is the solvent refractive index.

 $//J = integrate|FD(w)*epsilonA(w)*w^4|dw/(integrate|FD(w)|dw)$ where w is the wavelength, FD is the donor fluoresence emission spectrum, epsilonA is the acceptor molar absorptivity.

//Format:

FRET(FL_Donor,w_FL,Epsilon_Acceptor,w_Epsilon,FLQY,w_left_cutoff,w_right_cutoff,[RfId x=refractive index,ksq=kappa^2])

//Default: DCM solvent, spherical dipoles assumption.

Function FRET(FD,wF,eA,wA,QY,Startw,Endw,[RfIdx,ksq])

wave FD,wF,eA,wA //FD: fluorescence spectrum of the donor; wF: wavelength of fluorescence in nm; eA: molar absorptivity (epsilon) of the acceptor; wA: wavelength of absorption in nm

variable Startw,Endw,QY,RFIdx,ksq //Startw & Endw: starting and ending wavelength of the integral; QY: PL QY; RFIdx: refractive index of the solvent; ksq: orientation factor kappa square

variable nD,nA,dw,n

variable reversecheckD=0

variable reversecheckA=0

nD = NumPnts(wF)

nA = NumPnts(wA)

if (wF[0]>wF[nD-1])
reversed way

//check if the donor wave is plotted in a

```
reverse wF,FD
```

reversecheckD=1

endif

if (wA[0]>wA[nA-1]) a reversed way //check if the acceptor wave is plotted in

reverse wA,eA

reversecheckA=1

endif

//create dummy waves

duplicate/O FD,fl

duplicate/O wF,wfl

duplicate/O eA,eabs

duplicate/O wA,wabs

dw = min((Abs(wF[nD-1]-wF[0])/nD),(Abs(wA[nA-1]-wA[0])/nA))
//derivative of the wavelength dw

//check the ranges of the spectra

if (Startw<max(wF[0],wA[0]))

```
Startw=max(wF[0],wA[0])
```

endif

```
if (Endw>min(wF[nD-1],wA[nA-1]))
```

```
Endw=min(wF[nD-1],wA[nA-1])
```

endif

```
n=Round((Endw-Startw)/dw+1)
```

variable i,j,flnorm

//flnorm: normalized fluorescence spectrum to its integral

//trim the spectra

i=0

do

i += 1

while (wF[i]<Startw)

DeletePoints 0,(i),wfl

DeletePoints 0,(i),fl

j=nD-i+1

do

j-=1

while (wF[j+i-1]>Endw)

DeletePoints (j),(nD-i-j),wfl

DeletePoints (j),(nD-i-j),fl

InsertPoints (j),1,wfl

wfl[j]=Endw

InsertPoints (j),1,fl

fl[j]=fl[j-1]

//normalize fluorescence spectrum. Called the function "IntPL"

flnorm=IntPL(0,j,wfl,fl)

fl=fl/flnorm

killwaves/Z wfl_integral,intfl

InsertPoints 0,1,wfl

wfl[0]=Startw

InsertPoints 0,1,fl

fl[0]=fl[1]

i=0

do

i+=1

```
while (wA[i]<Startw)
```

DeletePoints 0,(i),wabs

DeletePoints 0,(i),eabs

j=nA-i+1

do

j-=1

while (wA[j+i-1]>Endw)

DeletePoints (j),(nA-i-j),wabs

DeletePoints (j),(nA-i-j),eabs

InsertPoints (j),1,wabs

wabs[j]=Endw

InsertPoints (j),1,eabs

eabs[j]=eabs[j-1]

InsertPoints 0,1,wabs

wabs[0]=Startw

InsertPoints 0,1,eabs

eabs[0]=eabs[1]

make/D/O/N=(n) wlmd,Flmd,elmd,Jintegrand,Jintegral //create these waves: wlmd: wavelength lamda; Flmd: fluorescence; elmd: molar absorptivity

interpolate2/T=1/N=(n)/X=wlmd/Y=Flmd wfl,fl

interpolate2/T=1/N=(n)/X=wlmd/Y=elmd wabs,eabs

Jintegrand = $Flmd*elmd*wlmd^4$

variable Jcorr,R0

variable NAv=6.022e23

//Avogadro's number

Jcorr=(1E24/1E7)*(Jintegral[n-1]-Jintegral[0])

//correct for the unit

 $R0 = (9*\ln(10)*ksq*QY/(128*pi^5*NAv*RfIdx^4)*Jcorr)^{(1/6)}$

Print "J =",Jcorr,"nm^6/mol"

Print "R0 =",**R0**,"nm"

//display the normalized donor fluorescence and acceptor molar absorptivity

Display Flmd vs wlmd

AppendtoGraph/R elmd vs wlmd

Label left "Norm. PL Intensity (\Enm\\S-1\\M)"

Label right "Molar Absorptivity (\EL·mol\\S-1\\Mcm\\S-1\\M)"

Label bottom "Wavelength (nm)"

SetAxis/A/N=1/E=1 left

SetAxis/A/N=1/E=1 right

ModifyGraph standoff=0,btLen=4,mirror(bottom)=2,lblMargin(bottom)=2

ModifyGraph rgb(elmd)=(0,0,65535)

ModifyGraph width=216,height={Aspect,0.618},gfSize=10

ModifyGraph expand=2

killwaves/Z fl,wfl,eabs,wabs,Jintegrand,Jintegral

//sort the waves if they are reversely plotted

if (reversecheckD)

reverse FD,wF

endif

if (reversecheckA)

reverse eA,wA

endif

Return R0

End

Example:



Figure 6.3.1. Original plots of the PL of CdSe QDs (PL QY = 0.16) wave i0 vs. wPL, and absorptivity spectra of CPNN wave eCPNN vs. wCPNN

Command: FRET(i0,wPL,eCPNN,wCPNN,0.16,400,700)

Result: 1.11867e+06

 $J = 2.26889e+30 \text{ nm}^6/\text{mol}$

R0 = 1.9298 nm

Result figure:



Figure 6.3.2. Resulting figure after running command "FRET". Two new waves are created displaying the range of spectral overlap.

6.4. NCs Sizing Curves

Code:

#pragma rtGlobals=3 // Use modern global access method and strict wave access.

Function CdSe(w1s,ap,hwhm)

//This function returns the diameter of CdSe QDs based on Mulvaney's paper JPCC 2009.

//wave A,wA

variable w1s,ap,hwhm //w1s: wavelength of 1s peak in nm; ap: absorbance of the peak; hwhm: half-width half maximum of 1s peak in nm

variable d,epsilon,conc,E1s,dE1s

variable h = 6.626196E-34

variable c = 3E8

//speed of light

//planck's constant

variable e = 1.6E-19 //electron charge

//w1s = wA[FirstPeakP(A,wA)]

//ap = A[FirstPeakP(A,wA)]

//hwhm = HWHMW(A,wA)

d = 59.60816 - 0.54736*w1s + 1.8873E-3*w1s^2 - 2.85743E-6*w1s^3 + 1.62974E-9*w1s^4

$$E1s = h*c/(w1s*1E-9)/e$$

$$dE1s = E1s - h*c/((w1s+hwhm)*1E-9)/e$$

epsilon = 155507 + 6.67054E13*exp(-(E1s/0.10551))

conc = ap/epsilon*dE1s/0.06

print "CdSe Diameter = ",d,"nm";

print "CdSe Concentration = ",conc,"M";

print "CdSe Epsilon = ",epsilon,"/M/cm";

Return d;

End

Function CdTe(w1s,ap,hwhm)

//This function returns the diameter of CdTe QDs based on Peng's paper Chem Mater 2003.

//wave A,wA

variable w1s,ap,hwhm //w1s: wavelength of 1s peak in nm; ap: absorbance of the peak; hwhm: half-width half maximum of 1s peak in nm

variable d,epsilon,conc

//w1s = wA[FirstPeakP(A,wA)]

//ap = A[FirstPeakP(A,wA)]

//hwhm = HWHMW(A,wA)

 $d = 9.8127E - 7*w1s^3 - 1.7147E - 3*w1s^2 + 1.0064*w1s - 194.84$

epsilon = 10043*d^2.12

conc = ap/epsilon*hwhm/18

print "CdSe Diameter = ",d,"nm";

print "CdSe Concentration = ",conc,"M";

print "CdSe Epsilon = ",epsilon,"/M/cm";

Return d;

End

Function CdS(w1s,ap,hwhm)

//This function returns the diameter of CdS QDs based on Peng's paper Chem Mater 2003.

//wave A,wA

variable w1s,ap,hwhm //w1s: wavelength of 1s peak in nm; ap: absorbance of the peak; hwhm: half-width half maximum of 1s peak in nm

variable d,epsilon,conc

//w1s = wA[FirstPeakP(A,wA)]

//ap = A[FirstPeakP(A,wA)]

//hwhm = HWHMW(A,wA)

 $d = -6.6521E - 8*w1s^3 + 1.9557E - 4*w1s^2 - 9.2352E - 2*w1s + 13.29$

epsilon = 21536*d^2.3

conc = ap/epsilon*hwhm/11

print "CdSe Diameter = ",d,"nm";

print "CdSe Concentration = ",conc,"M";

print "CdSe Epsilon = ",epsilon,"/M/cm";

Return d;

End

Function ZnO(lamda)

//Function that calculates ZnO QDs radius

variable lamda

//onset wavelength

variable a,b,c

a = 3.301

c = -294.0 //constant b in the paper

b = -1.09 // constant c in the paper

variable k

k = 1240/lamda - a

variable solp, soln

 $solp = (-b+sqrt(b^2-4*k*c))/(2*k)$

 $soln = (-b-sqrt(b^2-4*k*c))/(2*k)$

print "radius:", solp/2,"A"

print "the other solution:", soln/2

return solp/2

End

Example:

Command: CdSe(500,0.1,13)

Result: CdSe Diameter = 2.43316 nm

CdSe Concentration = 6.58165e-07 M

CdSe Epsilon = 159454 /M/cm

6.5. Fitting Function: Thermal Equilibrium Model

Equation (4.5.1):

$$I(t) = \sum_{i} P_{P}(i) \int_{-\infty}^{+\infty} \frac{\Phi_{s}}{\Phi_{b}(\Delta E)} P_{N}(\Delta E) f_{B}(\Delta E) k_{r} \exp\left(-f_{B}(\Delta E) \left(\frac{k_{r}}{\Phi_{b}(\Delta E)} + ik_{q}\right)t\right) d\Delta E$$

This function is to fit TCSPC measured PL decay curves and has 12 parameters, of which t0, y0, Int_c0, k_r, k_Q, QY_S, $\langle n_Q \rangle$, T are usually measured independently and thus have fixed values.

Code:

#pragma TextEncoding = "UTF-8"

#pragma rtGlobals=3 // Use modern global access method and strict wave access.

Function ThermalEquilibriumModel(pw, yw, xw) : FitFunc

WAVE pw, yw, xw

//pw[0] = t0

//pw[1] = y0, baseline

//pw[2] = Int c0, integral of the decay

 $//pw[3] = dE_m$, center of the trap-to-* defference

//pw[4] = sigma of dE

 $//pw[5] = k_r$

 $//pw[6] = k_Q$

//pw[7] = QY_S, ensemble PLQY

//pw[8] = <n_Q>
//pw[9] = T
//pw[10] = knr
//pw[11] = k_leak

//Make a wave containing all the values of the rate constants

Variable nYpnts = numpnts(yw) Variable A Variable n = 400 variable trapmin = -1 variable ddE = 0.01 variable kBT

kBT = 8.617E-5*pw[9]

A = pw[2]/pw[7]

Make/D/O/N=(nYpnts) Iw

Make/D/O/N=(n) dE, pdE, fB, QY_B

Make/D/O PSx,PPS

Poisson(PSx,pw[8],PPS)

SetScale/P x (trapmin),(ddE),"", dE

dE=x

 $//pdE = 1/(sqrt(2*pi)*pw[4])*exp(-((dE-pw[3])^2)/(2*pw[4]^2))$

PMF_Normal(dE,pw[3],pw[4],pdE) //PMF of dE: normal distribution

fB = 1/(1+exp(dE/kBT)) //Boltzmann Fraction: this is to ignore the fine structure of QDs to obtain a phenomenological result of k_int

 $QY_B = pw[5]/(pw[5]+pw[10]+pw[11]*fB)$

Variable i,j,k,t

k = NumPnts(PPS)

yw = 0

Iw = 0

For (i=0;i<k;i+=1)

For (j=0;j<n;j+=1)

For (t=0;t<nYpnts;t+=1)</pre>

 $Iw[t] (pw[7]/QY_B[j])*PPS[i]*pdE[j]*fB[j]*pw[5]*exp(-fB[j]*(pw[5]/QY_B[j]+i*pw[6])*(xw[t]-pw[0]))$

=

Endfor

 $\mathbf{y}\mathbf{w} = \mathbf{y}\mathbf{w} + \mathbf{I}\mathbf{w}$

Endfor

Endfor

yw = A*yw+pw[1]

End

Function/wave PMF_Normal(xw,med,sigma,pmf)

wave xw,pmf

variable med, sigma

duplicate/O xw,pmf

variable n = NumPnts(xw)

 $pmf = 1/(sigma*sqrt(2*pi))*exp(-(xw-med)^2/(2*sigma^2))*(xw[n-1]-xw[0])/(n-1)$

End



Figure 6.5.1. Example time-dependent PL decay of CdSe NCs (by command "display c0 vs tns", both waves have 4096 points) and its fit curve (3899 points).

Parameterwave:Par(12points,withinitialguess)= $\{0,0,58053.8,0.05,0.03,0.0417,0,0.16,0,298,0.4,0\}$ Command:FuncFit/L=3899/H="111001111111"ThermalEquilibriumModelPar

c0[pcsr(A),pcsr(B)] /X=tns /W=c0w /I=1 /D

FitProgressDialog allocating a dialogFitFunction instance

Fit converged properly

Curve fit with data subrange:

c0[197,4095]

Duplicate/O fit_c0,WMCF_TempAutoXWave

ThermalEquilibriumModel(Par,fit_c0,WMCF_TempAutoXWave)

KillWaves/Z WMCF TempAutoXWave

Par={0,0,58054,0.04712,0.034381,0.0417,0,0.16,0,298,0.1926,0}

V_chisq= 3841.38;V_npnts= 3570;V_numNaNs= 0;V_numINFs= 0;

V_startRow= 197;V_endRow= 4095;

W_sigma={0,0,0,0.00011,0.00014,0,0,0,0,0,0,0}

Coefficient values \pm one standard deviation

$$pw_0 = 0 \pm 0$$

$$pw_1 = 0 \pm 0$$

$$pw_2 = 58054 \pm 0$$

$$pw_3 = 0.04712 \pm 0.00011$$

$$pw_4 = 0.034381 \pm 0.00014$$

$$pw_5 = 0.0417 \pm 0$$

$$pw_6 = 0 \pm 0$$

$$pw_7 = 0.16 \pm 0$$

$$pw_8 = 0 \pm 0$$

$$pw_9 = 298 \pm 0$$

$$pw_{10} = 0.1926 \pm 0$$

$$pw_{11} = 0 \pm 0$$

Chapter 7. Conclusion and Outlook

7.1. Conclusion

The D-A system of CdSe NCs with surface bound CPNN free radicals is well-adapted to allow insightful analyses of the complex excited photophysics of NCs to be done. The CPNN radicals are efficient CdSe NCs PL quenchers, but act in a time-regime which is commensurate with the multi-exponential components of the intrinsic recombination of the CdSe NCs. The non-unity quenching efficiency combined with the Poisson nature of NCs surface coverage is well-modeled with a non-traditional general Stern-Volmer formalism. Importantly, the analyses presented in Chapter 3 shows that the complex dynamics of CdSe NCs can be directly analyzed in a way which is fully consistent with steady-state ensemble measurements if the underlying distribution that defines the multiexponential character of the CdSe NCs excited-state relaxation is taken to follow a log-normal form. This agreement between steady-state and time-dependent perspectives is an obvious, yet important, *a priori* requirement for any physical model that aims at describing the photophysics of CdSe NCs.

A closer look into the successful fits of log-normal model towards CdSe NCs PL decay reveals that the FRET process involves a serial, or multi-step, mechanism. Comparison between the complex multi-exponential decays with proper PL formalism of an ideal emitter shows a mismatch at t = 0 intensity and a "delayed" PL much slower than the radiative recombination. Such mismatch indicates an ultrafast depletion followed by a re-population of the excitonic states of NCs, which can be explained by hole trapping and "storage". The multi-exponential feature also necessarily indicates a distribution of the trap states. A physical model is built by assembling the rate laws of the excitonic state and the trap states. With only 2 degrees of freedom (same as the log-normal model) in the fitting parameters, the NCs PL decay curve can be perfectly fit. Then with fixed parameters all the quenched PL decay curves can also be fit and yield same quenching rate constants, in the experimental range of CPNN concentrations. The re-population of excitonic state is interpreted as a thermal process, and then the temperature dependent PL decays are also successfully predicted by the thermal model. So far, this thermal model is able to explain all observed, despite complex, NCs photodynamics. This knowledge is contradictory to common thoughts of "traps are bad" in NCs and calls for rethinking about possibly different identities and distinct behaviors of trap states.

A similar NC-radical system involving photoinduced charge transfer is also studied with the power of ultrafast spectroscopies. The results suggest that TEMPO derivatives can extract photoexcited holes from CdSe NCs very efficiently, as long as direct binding to the nanoparticle surface, as bestowed by the amino anchoring group of AT, is provided. Evidently, a rate constant larger than 10^{12} s⁻¹ for hole transfer entail significant D-A electronic coupling, although the specific extent to which driving force and reorganization energies favorably contribute to the overall transfer process is yet unknown. Such an efficient hole extracting molecular species carries the great potential of solving the problem of sluggish hole transport in NCs sensitized solar cells.

7.2. Outlook

In the NCs-CPNN system, a proposed normal distribution of trap energetics successfully explains all the observed photodynamics of NCs. A full understanding of the identities of these trap states and the reason for such a normal-distribution like energy-distribution is desired. Surface ligand stripping with amines provides an interesting tool as it can correlate absorption, PL emission and surface ligand NMR signals altogether. Temporal EPR spectroscopy is another powerful tool as the surface bound radicals give rise to a change in the g-factor or line-shape in EPR spectra when accepting energy from NCs. Monitoring the acceptor side would yield a full picture of the photophysics of NCs, starting from excitation and ending at completely relaxation to ground state (for both NCs and acceptors). Having this full physical picture at hand, it is possible to design spintronics with such NC-radical system, and it would be interesting to probe their magnetic coupling using magnetic circular dichroism spectroscopy.

Origin of non-radiative recombination of excited NCs is another challenging problem. The trap states proposed in Chapter 4 are only responsible for "storage" of exciton energy. However, evidence shows that non-radiative recombination rate is largely related to the number of trap states – perhaps of a different type. Identifying these trap states would reveal the real targets to fix in order to "cure" the PL QY of NCs. Trap emission is also known in NCs such as CdS. Interesting questions remain such as what affects the brightness of a trap state, whether CdS and CdSe have drastically "leakage" rate constants, etc.