Photoluminescence of CdSe Nanoparticles in the Presence of a Hole Acceptor: *n*-Butylamine

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Addition of butylamine to a solution of colloidal CdSe nanoparticles (NPs) caused a decrease in fluorescence intensity, with no effect on the picosecond bleach recovery of the exciton formation or on the luminescence dynamics. The relative fluorescence quantum yield was found to decrease with increasing butylamine concentration and to level off at high concentrations, but the fluorescence lifetimes were not influenced. The nonlinear concentration dependence of the fluorescence quantum yield did not follow the Stern–Volmer equation. This is in agreement with the observation that the CdSe luminescence lifetime was not affected by the addition of butylamine. A mechanism is proposed in which the emission observed in CdSe is assumed to result from the combination of surface-trapped electrons and holes. *n*-Butylamine occupies hole sites, thus blocking the recombination process, which results in decreasing the density of luminescent centers. These results will be discussed in terms of the nature of the binding sites of the amine on the nanoparticle surface.

1. Introduction

Recent years have brought increasing interest in the properties of low-dimensional semiconductor nanoparticles.[1–6] This interest is due to the quantum confinement of electrons that occurs when the size of the particle is near that of the Bohr exciton radius (6 nm in CdSe). At these dimensions, the particle size and shape play an important role in determining the electronic energies of the semiconductor. A decrease in size can cause the band-gap energy to increase and the radiative lifetimes to change dramatically. Many groups have studied II–VI semiconductor nanoparticles (NPs) such as CdSe in order to characterize the relationship between size, shape, and electronic properties.[7–9]

The many reports on the optical dynamics of CdSe NPs reveal that excitation above the band gap energy leads to a bleach in the lowest absorption transition within a few hundred femtoseconds.[10,11] The recovery is multiexponential and occurs over a wide time range from a few picoseconds to a few microseconds.[12] These results suggest that the bleach occurs through band-filling and the bleach decay occurs through a multitude of routes. One possibility is through surface and/or deep trapping routes.[4,13] Additionally, several reports have discussed the possibility that dark exciton states exist in CdSe NPs and contribute either wholly or partially to the observed emission.[14,15] Finally, nonradiative relaxation provides additional routes to electron–hole recombination by processes such as phonon-assisted dissipation, internal conversion, and Auger mechanisms.[16–18]

One way to study the electronic properties in CdSe NPs is to observe changes in their luminescence properties in the presence of electron or hole acceptors. Since NPs by nature have a high surface-to-volume ratio, many of their optoelectronic characteristics are related to the nature of the surface. Many studies have examined the fast electron transfer that occurs when electron acceptors are adsorbed on the NP surface.[19,20] Graetzel developed a photovoltaic device based on a composite of a ruthenium dye and TiO$_2$ NPs.[21] Other investigations have examined the nature and ultrafast dynamics of the electron transfer that occurs between CdSe NPs and methyl viologen cation (MV^{2+}), whereby MV^{2+} accepts a photoexcited electron from the CdSe NP.[22,23]

Some groups have examined the system of CdSe NPs in the presence of electron donors such as amines.[24,25] Dannhauser et al.[24] observed emission enhancement of CdS NPs in the presence of very low concentrations of triethylamine. The authors suggested that this enhancement effect is due to binding of the amine to surface defect sites that otherwise would trap excited electrons and prevent fluorescence. Spanhel et al.[26] presented similar results and analyses for CdS NPs that have been activated by the presence of excess OH$^-$ ions. Cowdery-Corvan et al.[25] noted quenching effects at higher amine concentrations. They proposed that after the initial traps were saturated with amine molecules, the excess amine could quench the radiative emission. In this way, the amine effectively blocks charge recombination and decreases the fluorescence quantum efficiency.

Fluorescence is a useful tool for monitoring electronic changes at the NP surface. Both steady-state and dynamic fluorescence spectroscopy have been used in the past to elucidate the electronic structure of II–VI semiconductor NPs alone and as a function of changing the solvent system or surface adsorbates.[27–30]

The present work reports a detailed study of the effects of *n*-butylamine on the CdSe NP near band-edge fluorescence as well as on the picosecond bleach recovery. A comparison of the steady-state and dynamic fluorescence of fresh and aged NP samples is presented. The different models such as collisional quenching and static quenching due to adsorption of the amine to different binding trap sites (similar to metal binding to enzymes) are proposed and discussed. A multisite binding model is proposed and, with an analysis of the nonradiative relaxation processes, offers insight into the complex electronic structure of the CdSe nanoparticle.

2. Experimental Section

CdSe nanoparticles were prepared by the method developed by Murray et al.[9] with modifications described by Burda et al.[20] The amines and solvents were obtained from Sigma, Aldrich, and Fisher. The only modification is that several size-selective precipitation steps were taken to improve the monodispersity of the samples. This was achieved by first suspending the prepared particles in hexane, after which several milliliters of *tert*-butyl alcohol were added. Methanol was added dropwise until the solution became turbid, indicating that the nonsolvent was causing the TOPO-capped particles to fall out of solution. The samples were centrifuged at 6000 rpm for 15−20 min to collect the particles, and the above steps were repeated until the absorbance spectrum indicated that a desirable level of monodispersity had been achieved. The resulting nanoparticle samples were suspended in toluene, and all analyses were performed with toluene as the solvent. Steady-state absorption spectra show that the primary absorption feature occurred at ∼533 nm, indicating an approximate diameter of 3.2 nm. All measurements were performed on freshly prepared NP samples, except as indicated to compare the differences between fresh samples and those that had been aged.

Stock solutions of the amines were prepared by diluting them with toluene. The appropriate amounts were then added by micropipet to 2 mL aliquots of CdSe particles that had been diluted to a uniform optical density (OD) of ∼0.1 at 533 nm. The samples were mixed and measured immediately after preparation. *n*-Butylamine was the amine of choice for quantifying the changes in emission and kinetics for this experiment. All spectral measurements except for the femtosecond studies were performed with glass fluorescence cuvettes for 90° collection. CdSe samples for use in femtosecond transient absorption experiments were diluted to an OD of 1 over a 2 mm path length at 533 nm.

Steady-state absorption spectra were obtained on a Shimadzu UV-3101PC UV−Vis−NIR scanning spectrophotometer. Steady-state fluorescence spectra were obtained on a PTI Model C60 steady-state spectrofluorometer with a xenon arc lamp source and a photomultiplier detection system. Fluorescence decays were obtained on a PTI Model C-72 fluorescence lifetime spectrometer with a PTI GL-3300 nitrogen laser and a GL-302 tunable dye laser with PLD-366 laser dye, exciting the CdSe sample at 400 nm. Fluorescence decay data were analyzed with a program cowritten by one of the authors.[31] The program performs a Levenberg−Marquardt analysis to determine the multiexponential contributions of the luminescence rise and decay of each component. The emission is detected by a switchable analog/photon counting photomultiplier.

Femtosecond transient measurements were obtained with an amplified Ti-sapphire laser system (Clark MXR CPA 1000) pumped by a Nd:YVO ring loss (Verdi 5W) Coherent laser. This produced laser pulses of 100 fs duration (fwhm) and an energy of 1 mJ at 790 nm. The repetition rate was 1 kHz. A small part (4%) of the fundamental was used to generate a white light continuum in a 1 mm sapphire plate. The excitation wavelengths in the visible range were produced by second-harmonic generation (395 nm) and sum-frequency generation (490−550 nm) of the signal wave. The excitation beam was modulated by an optical chopper (HMS 221) with a frequency of 500 Hz. The probe light was split into a reference and a signal beam. After passing the monochromator (Acton Research), both beams were detected by two photodiodes (Thorlab). The kinetic traces were obtained by use of a sample-and-hold unit and a lock-in amplifier (Stanford Research Systems).
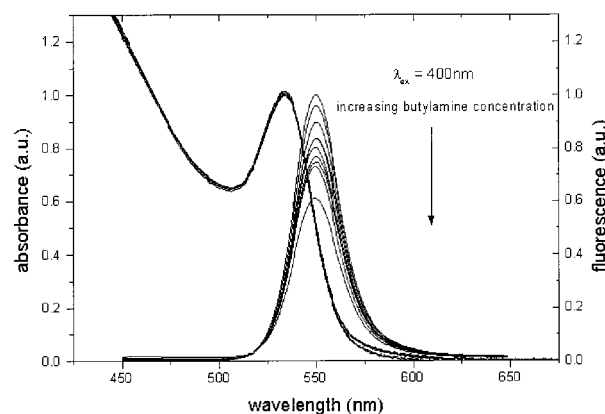
Figure 1. Absorption ($\lambda_{max} = 533$ nm) and steady-state fluorescence spectra ($\lambda_{ex} = 400$ nm, $\lambda_{obs-max} = 550$ nm) of CdSe NPs in toluene, having an optical density at 533 nm of ∼0.1, with increasing concentrations of *n*-butylamine. Butylamine decreases the CdSe fluorescence yield.

The typical measured optical density (OD) changes were in the range of 50 mOD.

3. Results

The steady-state luminescence and absorption spectra indicate a domination of near-band-gap phenomena, with a primary absorption at ∼533 nm and emission at 550 nm when excited at 400 nm, as can be seen in Figure 1. When *n*-butylamine is added, the NP absorption spectrum does not change, but the emission intensity is decreased nonlinearly as the amount of butylamine that has been added to the sample increases. Figure 1 illustrates this effect.

In Figure 2, the quenching efficiency, ϕ_0/ϕ, is shown as a function of the butylamine concentration, [Q]. ϕ_0/ϕ is the ratio of the quantum yield of the CdSe NP luminescence in the absence of butylamine to that in the presence of butylamine, calculated in this case as the ratio of intensities, (I_0/I), because of the uniformity of emission. There exists a saturation effect in the quenching efficiency at higher amine concentrations.

In standard Stern−Volmer quenching, quenching of the steady-state luminescence is accompanied by a corresponding quenching of the excited-state lifetimes.[32,33] Neither the ultrafast dynamics of the bleach recovery in CdSe NPs nor the fluorescence lifetimes exhibit a change in lifetime in the presence of *n*-butylamine.

The bleach decay dynamics of CdSe NPs alone and in the presence of 0.01 M butylamine, excited at 400 nm and monitored at 550 nm, are shown in Figure 3. This figure illustrates that in this time regime, the bleach recovery is exponential and ∼60% of the decay has occurred within 7 ps. Previous studies have suggested that the bleach occurs through band filling and the recovery is due to fast trapping by densely packed shallow traps. Figure 3 also indicates that the decrease in the luminescence that occurs in the presence of butylamine does not affect the 7 ps bleach decay. Thus, butylamine does not seem to alter the ultrafast trapping mechanism whereby the excited electrons are removed from the conduction band and shuttled to shallow trap sites.

Figure 4 illustrates the normalized fluorescence decay dynamics of the CdSe NPs alone and in the presence of different concentrations of butylamine. Analysis of the decay data yields a biexponential rise and decay of the fluorescence. The decay times of the two emitting states are 3 (± 2) ns and 30 (± 5) ns. The inset of Figure 4 shows a delayed rise in luminescence that is consistent with the population of traps. These results

Photoluminescence of CdSe Nanoparticles

J. Phys. Chem. B, Vol. 105, No. 15, 2001 **2983**
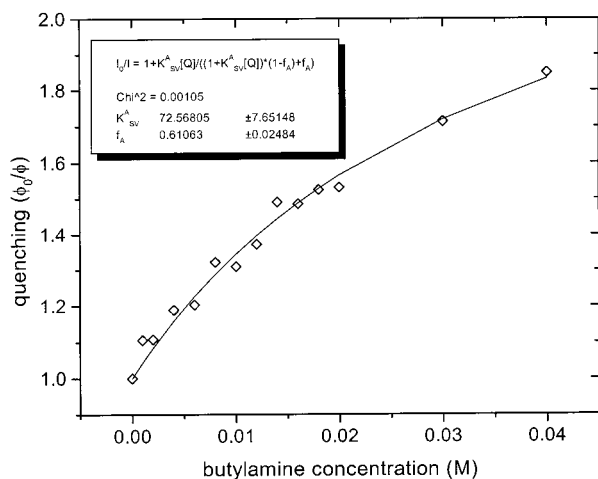

Figure 2. Quenching efficiency, ϕ_0/ϕ, as a function of butylamine concentration, where ϕ_0 and ϕ represent the quantum yields of the CdSe particles in the absence and in the presence of quencher, respectively. The quenching does not follow a linear Stern−Volmer plot, as predicted by eq 2. The standard Stern−Volmer model requires a single mode of operation for the quenching mechanism, as well as an infinitely available source of quenching sites. With the use of a modification in the Stern−Volmer equation as described by eq 4, the quenching can be expressed in terms of the contributions of different emitting states. In this case, the fluorescence can be expressed as the contribution from two emitting states, one of which does not suffer significantly from butylamine quenching. Thus, the quenching is observed to saturate at a critical concentration of amine, indicating the suppression of all of the available emitting states. The parameters from the nonlinear fit, K^A_{SV} and f_A, correspond to the Stern−Volmer constant and the fraction of total emission from the Ath component, respectively. The points represent the averaged data, and the curve is a nonlinear fit to the modified Stern−Volmer equation in eq 4.
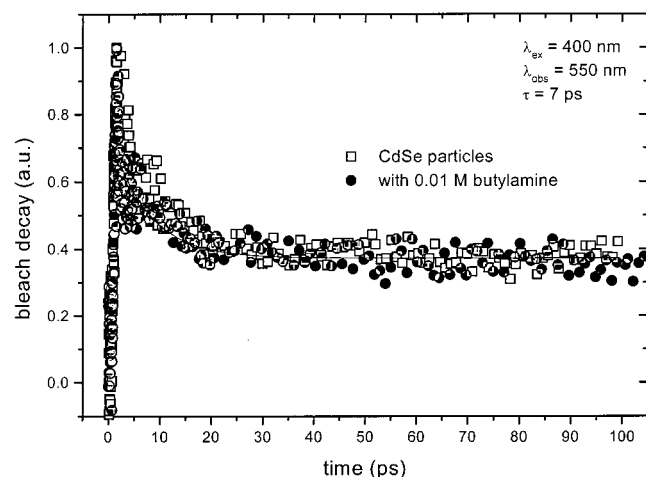

Figure 3. Bleach decay as a function of time (picoseconds) for a CdSe sample with and without butylamine. The monoexponential bleach decay occurred with a decay time of 7 ps and was unaffected by the presence of butylamine. The bleach recovery is assumed to occur by efficient trapping, and butylamine is not involved in this step. The initial trapping step is thought to be followed by further trapping to radiative and nonradiative states, which can be affected by butylamine.

support the contention that the luminescence occurs from traps instead of from exciton emission and that there are at least two distinct types of emitting traps. The lifetimes clearly do not change as the butylamine concentration increases, as would be predicted by a collisional quenching model.

Experiments that deduce the relationship between butylamine and the NP surface quality were performed. All of the previous experiments were performed on NP solutions that had been exposed to air. To compare the effect of air exposure on the
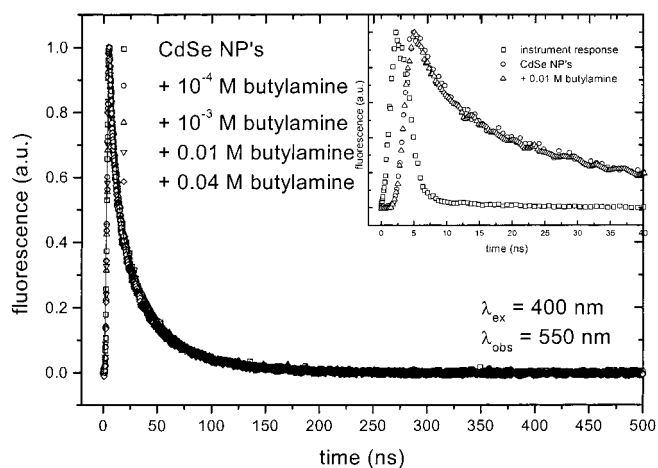

Figure 4. Fluorescence decay as a function of time (nanoseconds) for a CdSe sample alone and with different concentrations of butylamine. The decay in this time domain is dominated by two emission components, with corresponding lifetimes of 3 ($\pm$ 2) ns and 30 ($\pm$ 5) ns, consistent with a photoluminescence model that includes multiple emission pathways. The addition of butylamine to the sample does not affect the fluorescence lifetimes appreciably. These results suggest that collisional quenching is an inappropriate model, because such a model requires the emission lifetimes to change in accordance with the luminescence intensity. Instead, the authors propose that the butylamine binds to specific emissive sites and eliminates them from the electron relaxation pathway. The inset shows an expansion of the 0−40 ns region, where it is clear that the fluorescence exhibits a delay of ∼1−2 ns in the luminescence rise, suggesting that emission does not occur directly from the band-edge.
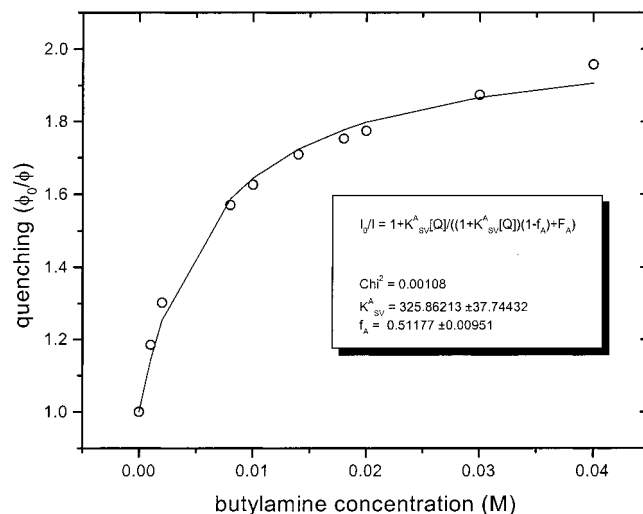

Figure 5. ϕ_0/ϕ vs amine concentration for NP samples that were purged with argon for 20 min. A comparison with the data shown in Figure 2 shows that butylamine has a greater effect on the radiative efficiency when excess air has been removed from the sample.

NP surface, the steady-state fluorescence experiment was repeated on samples that had been purged with argon for 20 min. When ϕ_0/ϕ vs [Q] is plotted for these degassed samples (shown in Figure 5), the efficiency of butylamine at reducing the fluorescence intensity is improved at lower concentrations. When a sample has been purged with argon, the amine can more effectively reduce the fluorescence yield. The corresponding fluorescence decay experiments did not indicate a change in the decay lifetimes of samples that had been purged with argon.

Other groups have reported changes in the fluorescence of II−VI semiconductor NPs over time and have associated these changes with interaction of surface defect sites with oxygen that occur as the NP solution is aged.[9,34] The steady-state and
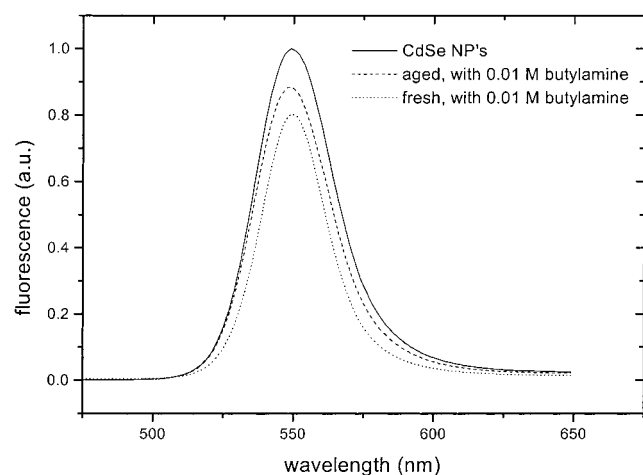
Figure 6. Steady-state fluorescence of fresh and aged NP samples in the absence and presence of 0.01 M butylamine. Note the greater effect of butylamine on decreasing the NP fluorescence on fresh samples as compared to aged samples.
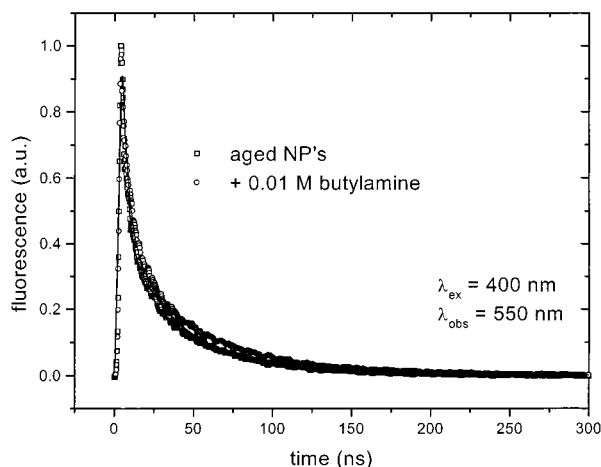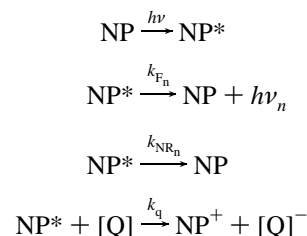

Figure 7. Fluorescence decays of aged NPs alone and in the presence of 0.01 M butylamine. When the analysis of the decays are compared with those presented in Figure 4, one can determine that the aged NP sample has a lower fluorescence contribution from the ~30 ns component. In fresh samples, this component contributes ~30% to the overall emission, but its contribution is reduced to ~17% in the aged samples shown here. It is a reasonable assumption, then, that if this site is not as involved in the fluorescence of aged samples, then the fluorescence dynamics of this site will not be affected by the presence of butylamine.

dynamic fluorescence of CdSe NPs in the presence of butylamine were studied in NP solutions that had been stored for ~5 months, to compare the results with those obtained from fresh samples. Figure 6 illustrates the steady-state fluorescence of aged NPs alone and in the presence of 0.01 M butylamine. Although butylamine still reduces the fluorescence intensity of these aged NPs somewhat, it does so with much lower efficiency than with fresh samples. Figure 7 shows the fluorescence decays of aged NPs alone and in the presence of butylamine. These results illustrate clearly that butylamine does not affect the decay dynamics in any quantifiable manner. Perhaps more importantly, however, these results show a change in the contribution of the 30 ns component to the overall fluorescence. Whereas in fresh NP samples this component represents approximately 30% of the overall emission, as was shown in Figure 4, in aged samples, with or without butylamine, this longer-lived component contributes only ~17% to the observed decay. These results indicate that the 30 ns fluorescence component is more susceptible to gradual changes in the NP surface that occur as

the particles are stored over long periods of time. One such change is the formation of selenium–oxygen complexes at surface defects characterized by Cd vacancies.[9,34]

4. Discussion

If the decrease in CdSe emission in the presence of butylamine is due to collisional quenching, the following model would describe the interaction. A photoexcited CdSe particle that has multiple relaxation pathways can be expected to undergo luminescence, radiationless decay, or quenching as described by[32]

$$NP \xrightarrow{h\nu} NP^*$$

$$NP^* \xrightarrow{k_{F_n}} NP + h\nu_n$$

$$NP^* \xrightarrow{k_{NR_n}} NP$$

$$NP^* + [Q] \xrightarrow{k_q} NP^+ + [Q]^-$$

where k_{F_n} represents the fluorescence decay constant for the nth emitting site, k_{NR_n} represents the nonradiative decay constant for the nth nonradiative pathway, $[Q]$ is the concentration of quencher, and k_q is the quenching constant. The observed quantum yield of fluorescence, Φ_F, will be

$$\Phi_F = \frac{\sum_1^n k_{F_n}}{\sum_1^n k_{F_n, NR_n, q_n}} \quad (1)$$

A comparison of unquenched quantum yield Φ^0_F versus quenched quantum yield Φ_F yields the following linear Stern–Volmer equation:[32,33]

$$\frac{\Phi^0_F}{\Phi_F} = 1 + K_{SV}[Q] = \frac{\tau_0}{\tau} \quad (2)$$

In cases of dynamic quenching, a plot of I_0/I vs $[Q]$ yields a linear plot that shares the same slope as a plot of τ_0/τ, corresponding to the Stern–Volmer constant, K_{SV}.

A Stern–Volmer plot that exhibits downward curvature is an indication that there are multiple fluorescence pathways, some of which are more/less susceptible to quenching.[32,33,36,37] The Stern–Volmer plot of CdSe fluorescence quenching by butylamine exhibits such downward curvature, as shown in Figure 2. The nonlinear quenching observed in Figure 2 and the multiexponential fluorescence decay of CdSe NPs shown in Figure 3 support such a multiple path fluorescence model.

Several papers have discussed fluorescence quenching in systems where there are multiple emitting states and not all are quenched equally.[36,37] The simplest model for multistate emission quenching is one in which there are two emitting states, each of which has a different affinity for the quencher. In this case, Φ^0_F/Φ_F is given by

$$\frac{\Phi^0_F}{\Phi_F} = \frac{1}{\dfrac{f_1}{(1 + K_{SV1}[Q])} + \dfrac{f_2}{(1 + K_{SV2}[Q])}} \quad (3)$$

Here, f_i is the relative fractional contribution to the observed

Photoluminescence of CdSe Nanoparticles

J. Phys. Chem. B, Vol. 105, No. 15, 2001 **2985**

fluorescence from the ith emitting state in the absence of quencher, and K_{SVi} is the Stern–Volmer constant for the ith component. A reasonable simplification is to assume that one component has a much greater probability of being quenched by the added quencher. This reduces eq 3 to

$$\frac{\Phi_F^0}{\Phi_F} = \frac{1 + K_{SV1}}{(1 + K_{SV1})(1 - f_1) + f_1} \qquad (4)$$

Using eq 4, a nonlinear regression analysis was performed on the quenching data shown in Figure 2. This yielded values for f_1 and K_{SV1} of 0.61 and 72.5 M^{-1}, respectively. The solid line in Figure 2 is the fitted curve, which closely matches the quenching data.

Description of the dynamic effects of the multistate quenching described by eqs 3 and 4 requires the use of weighted lifetimes, as in[33]

$$T_m = \frac{\sum \alpha_i \tau_i}{\sum \alpha_i} \qquad (5)$$

where α_i is the preexponential factor for each decay component. Thus, a plot of T_m^0/T_m should yield a similar relationship as a plot of Φ_F^0/Φ_F. However, T_m^0/T_m does not change significantly for the observed fluorescence decays shown in Figure 3. That the weighted fluorescence decay lifetimes do not change is an indication that collisional quenching is not the appropriate model for the decrease in CdSe NP fluorescence intensity that is observed when butylamine is present.

An alternative model is needed that can explain the change in the fluorescence intensity without requiring a change in lifetime. This model is suggested by the results of the experiments performed on samples purged with argon and on aged samples. It is that of preferential binding of the amine to NP surface emitting sites. The path of excited electrons in CdSe NPs in the presence of butylamine is as follows.

Step 1 involves the band-edge excitation corresponding to the absorption feature centered at 533 nm in Figure 1. Norris and Bawendi[38] have assigned this transition to the creation of the $1S_e1S_{3/2}$ exciton. Both the hole and electron are in the $n = 1$ or spherically symmetric S-like function, where parity, total hole angular momentum, and total electron angular momentum contribute to splitting of energy levels in the band structure at this size domain.

Step 2 involves two types of relaxations. One is observed as the 7 ps bleach decay (Figure 2), and this constitutes ~60% of excited electrons and holes. The remaining excited electrons and holes relax in a time longer than 100 ps, the time scale of the ultrafast experiment whose results are shown in Figure 2. The difference between the mechanism of these two types of relaxations is not yet known. It is possible that the fast relaxation is a result of an Auger-type relaxation due to energy transfer of the excited electron to the dense hole states of the NP, as proposed by Klimov and McBranch.[17] The long relaxation process could result from trapping by sites bound to TOPO and thus involve its vibrational motion as the sink.

Of course, it could be that the two mechanisms are reversed since we have no calculation regarding electron–phonon relaxation in surface trapping sites bound to capping material. From Figure 2 it can be seen that neither the decay time nor the relative amplitudes of these two types of recovery mechanisms change upon addition of butylamine. Because the emission intensity, but not the lifetime, changes, one reaches the
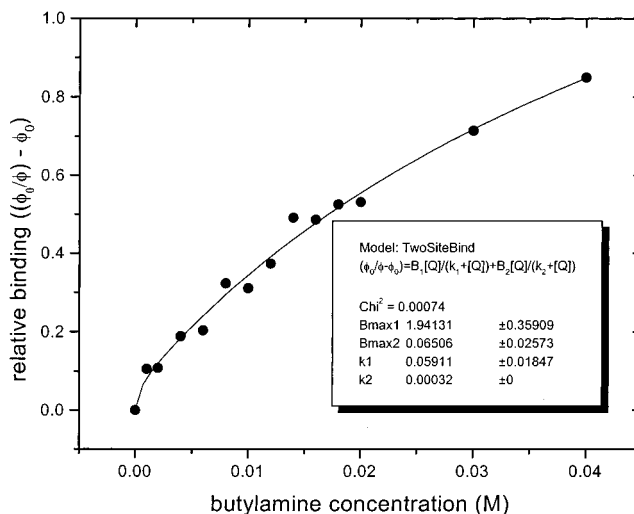
Figure 8. ϕ_0/ϕ vs amine concentration data shown in Figure 2 but fit to the two-site binding model described by eq 6. The calculated k_1 and k_2 values support the contention that the amine binds preferentially to one type of site.

conclusion that the emitting sites (the electron and hole recombination sites) are not the original trapping sites. Thus, electron and/or hole diffusion must occur to new trapping sites on the surface in order for radiative recombination to transpire. If butylamine molecules block these radiative trapping sites, the emission intensity, but not the lifetime, should decrease.

It is suggested that butylamine can bind selectively to the CdSe NP surface. Binding models similar to those presented here are routinely used in biology to describe the enzyme/ligand system.[35,39,40] In cases where there are multiple types of binding sites with different affinities for the ligand, an appropriate description is the two-site binding model, which when applied to our system gives the following equation:

$$\frac{\Phi_F^0}{\Phi_F} - \Phi_F^0 = \frac{B_1[Q]}{k_1 + [Q]} + \frac{B_2[Q]}{k_2 + [Q]} \qquad (6)$$

where B_i is the relative number of each type of binding site and k_i is the binding constant for the quencher at each site. A plot of the observed steady-state fluorescence of CdSe in the presence of butylamine fit to eq 6 is shown in Figure 8. The calculation of k_1 and k_2 values of 0.06 and 0.0003 M, respectively, supports the conclusion that the amine has a much greater affinity for one site over another.

Thus, the authors suggest that the selective binding model described above provides a possible explanation for the steady-state and dynamic fluorescence effects of CdSe NPs in the presence of butylamine. The fit to the observed data in Figure 8 strongly supports our conclusion that the decrease in the CdSe NP fluorescence observed with concentration is not a result of excited-state collisional quenching but rather of eliminating the fluorescence site by binding of the hole acceptor to the hole trapping emitting sites.

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