CHAPTER 3

Modulation of Photophysical Properties of Mercaptopropionic Acid Capped CdTe Quantum Dots upon Exposure to Light

Light-induced modulation of the fluorescence behavior of mercaptopropionic acid (MPA) capped CdTe quantum dots (QDs) in aqueous solution is studied by a combination of fluorescence correlation spectroscopy (FCS) and steady state and time-resolved fluorescence techniques. These investigations reveal a dramatic variation in the fluorescence properties of the QDs under exposure to light. In the FCS measurement, a large decrease in amplitude and change in shape of the correlation curves are observed with increasing excitation power. The change in the shape of the correlation curves, particularly at short lag time, e.g., a faster relaxation at high excitation power, is attributed to the increasing contribution of the off state of the QDs. Interestingly, despite this increasing contribution of the off state, which reduces the effective number of emitters in the observation volume and hence should increase the amplitude of the correlation curve, the latter actually decreases at high excitation power. This apparent contradiction is resolved by considering light-induced transformation of the dark QDs to bright QDs due to surface passivation of the QDs with increasing excitation power. Enhancement of the steady state fluorescence intensity under light irradiation, both in aerated and deaerated environments, supports the mechanism of passivation of the surface trap states by photoadsorption of water molecules. Fluorescence lifetime data is also shown to be consistent with this light-induced surface passivation mechanism.

3.1. Introduction:

Semiconductor quantum dots (QDs) have been receiving increasing attention in recent years because of their interesting size-dependent optical and electronic properties,[1−4] which is due to quantum confinement of both electron and hole (produced because of electronic excitation) in all three dimensions.[1,4−7] Emission covering the entire visible and infrared region can be obtained simply by tuning the size of the QDs.[1,8] As the QDs exhibit broad absorption and narrow emission profile in comparison to organic fluorophores,[9] it is possible to excite multiple QDs at a single excitation wavelength.[10] Furthermore, the narrow emission profile of the QDs provides easy spectral separation,[9] thus making them an efficient system for multicolor imaging of biological samples.[10] QDs also exhibit a higher photostability and superior optical properties compared to conventional organic fluorophores.[9] All these

excellent properties make QDs ideal candidates for applications ranging from biological imaging to lasing to optoelectronics.[3,10−17] Given the huge potential scientific and technological impact of QDs in various applications, the fluorescence response of QDs has remained an intriguing topic of research since its discovery.

The small size of QDs results in a high surface-to-volume ratio of the substances,[1,8] and it has long been believed that the surface of the QD plays an important role in determining its luminescence properties.[5,18−25] Uncoordinated atoms on the surface disrupt the crystalline periodicity and leave behind one or more dangling orbitals on each atom.[1,23] These dangling orbitals form the mid band gap states and reduce the luminescence efficiency of the QDs by providing additional nonradiative deactivation pathways.[1,8,26,27] Surface passivation is a crucial parameter for the preparation of QDs with high fluorescence quantum yield and photostability.[1,8,23,28,29] One of the major obstacles to the progress of the development of highly luminescent and stable QDs is the poorly understood QD surface chemistry and the relation of the surface chemistry to QD photophysical properties[30−32] It is reported that the fluorescence efficiency of the QDs is enhanced under irradiation with light.[22,32−41] This enhancement of emission on exposure to light, which is termed photoactivation, is attributed to photoinduced passivation of the surface trap states. However, no general consensus on the mechanism of photoactivation has yet been reached because of the complicated photophysics and photochemistry of QDs. Suggested mechanisms include elimination of the topological surface defects (i.e., smoothing of the surface during the process of photocorrosion),[26,32,34,42−44] passivation of the surface trap states by photoadsorbed molecules,[22,32,35,38] photoinduced rearrangement of the surface stabilizing agents,[32,33,36,44−47] photoneutralization of the local charged centers inside and outside the QDs, etc.[48] Solvents also have been found to play an important role in the photoactivation of QDs.[32,35,38,48] Photoluminescence enhancement of QDs often strongly depends on the amount of water vapor present in the atmosphere.[35,38,48] This is ascribed to photoadsorption of the water molecules on the QD surface leading to the passivation of the nonradiative surface trap states.[32,35,38,48,49] Polarity of the solvent also affects the photoactivation.[22,32,36] It is observed that addition of methanol to trioctylphosphine oxide (TOPO)-hexane or TOPO-toluene solution shows an accelerated increase of the fluorescence efficiency compared to TOPO-toluene only or TOPO-hexane only QD solutions.[36] Hence, a clear understanding of the

photoactivation mechanism is absolutely essential to understand the role of surface states and surface reaction on the luminescence yields and photostability of QDs. We have studied light-induced changes in the fluorescence behavior of MPA-coated CdTe QDs in water by a combination of FCS, steady-state, and time-resolved spectroscopic techniques. CdTe QDs are chosen as the subject matter of this investigation because the effect of light irradiation on the QD optical properties is not as widely investigated as that on CdSe QDs.

It is known that FCS is a highly sensitive and powerful technique in which the fluorescence fluctuations arising from a small observation volume (on the order of a femtoliter) is correlated to obtain the temporal evolution of the system about its equilibrium state.[50] This technique has been successfully applied to study the fluorescence blinking dynamics and the kinetics of bimolecular reactions, binding of ligands to a protein, protein-protein interaction, DNA hybridization, and conformational fluctuation and translational diffusion of the fluorescent probes in polymer, lipid vesicles, micelles, ionic liquids etc.[51−61] Considering that QDs are superior fluorescent probes compared to organic fluorophores, the FCS technique has been used for the characterization of QDs; specifically, it has been used to determine their hydrodynamic radius, concentration, monodispersity, and aggregation tendency.[12,37,62−68] Interestingly, only a handful of FCS studies on QDs photophysics have been made despite the potential of this technique to determine the blinking kinetics at faster time scales.[51,52,69−74] Widely distributed kinetics of fluorescence blinking[75] of QDs limited its study using the FCS technique.[70,71,73] The blinking kinetics of QDs complicates the analysis of the FCS data as it distorts the shape of the correlation curve, especially at shorter correlation times,[73] thus making it difficult to model QD blinking dynamics. Doose et al. attempted to simulate the anomalous shape of the correlation curve by employing Monte Carlo calculations of the diffusing and blinking dots.[73] However, no unique set of blinking parameters for a given data set could be found. As the amplitude of the correlation curve, G(0), provides information on the number of emitters in the observation volume, a comparison of the G(0) value as a function of the laser power is expected to provide a comprehensive understanding of the light-induced changes in QDs. Larson et al. observed a decrease in the G(0) value with increasing excitation power by two photon excitation FCS and attributed this to the broadening of the observation volume on excitation saturation.[12] Doose et al. compared the photophysical and colloidal properties of some biocompatible QDs

using FCS.[73] They examined the G(0) values at different excitation power and compared them with those obtained for the fluorescence beads and rhodamine 6G. The decrease of the G(0) value for the QDs is found to be much higher than that of the beads and rhodamine 6G and is attributed to excitation saturation and change in the blinking statistics at high excitation power, which increases the concentration of the emitters in the observation volume. However, they could not model the blinking statistics of the QDs as a function of the excitation power. Miyasaka and coworkers could fit the blinking dynamics of water-soluble CdTe QDs by introducing a stretched exponential term in the correlation function.[52] This stretched exponential term takes care of the widely distributed kinetics of the blinking of QDs. These authors also observed a decrease in the G(0) value and a faster decay of the autocorrelation with increasing excitation power. They agreed to the point that excitation saturation alone could not explain the changes in the shape and amplitude of the correlation curves and ascribed the observation to a faster relaxation from the dark state at higher excitation power. These authors, however, did not compare the fraction of the dark state as a function of the excitation power, which would have provided more information on the changes in the shape of the correlation curves. Dong et al. attributed the decrease of G(0) value with irradiation times to the photoactivation of the QDs.[37] According to them, photoactivation occurred because of laser-induced aggregation of the QDs and consequent modification of the QD surface structure, which turns the permanently dark QDs to bright QDs.[37] It is therefore evident that no single mechanism can explain light-induced variation of the luminescence efficiency of the QDs and determination of the mechanism of photoactivation requires a thorough and detailed investigation. This explains the motivation for the present study. We have also carried out steady state and time-resolved conventional emission studies to supplement the results of the FCS measurements and also to obtain a clear understanding of the mechanism of this light-induced change in the luminescence properties of the QDs. To the best of our knowledge, this is the first study in which the origin of decreasing amplitude of the correlation curve with increasing excitation power is explained clearly. We have also successfully monitored the evolution of the blinking parameters as a function of the excitation power to provide support for the mechanism involved in the photoactivation process.

3.2. FCS study of CdTe/MPA QDs in aqueous solution:

Figure 3.1 shows the FCS curves of the 55 nM CdTe QDs in water (size of the QD estimated from TEM measurement is 4.7 nm and emission peak is at 635 nm) and G(0) values at different excitation power. The correlation curves could be best fitted (as determined by the residuals) to a stretched exponential with a 1-component diffusion model (Equation 2.7). The quality of the fits to other models is provided in Figure 3.2. This stretched exponential fit is in accordance with the distributed kinetics of fluorescence blinking of the QDs, as reported in the literature.[52,70,75] It is important to note that the amplitude of the correlation curve decreases sharply with increasing excitation power (Figure 3.1). The G(0) value decreases from 0.98 ± 0.13 at 6 μW to 0.30 ± 0.12 at 186 μW. A further increase in power, however, slightly increases the G(0) value (0.45 ± 0.12 at 392 μW). This decrease in G(0) value with increasing excitation power for CdTe/MPA is much larger than that for R123 in water (Figure 3.3). Figure 3.4 shows the normalized correlation curves and the dependence of the diffusion time on increasing excitation power. The shape of the correlation curves is strongly dependent on the excitation power especially at short correlation times.[73] Figure 3.5 shows the dependence of the off-state fraction (T) and the blinking time (τ_t) on increasing excitation power. T increases and τ_t decreases with increasing excitation power and attains a saturation value at around 186 μW.

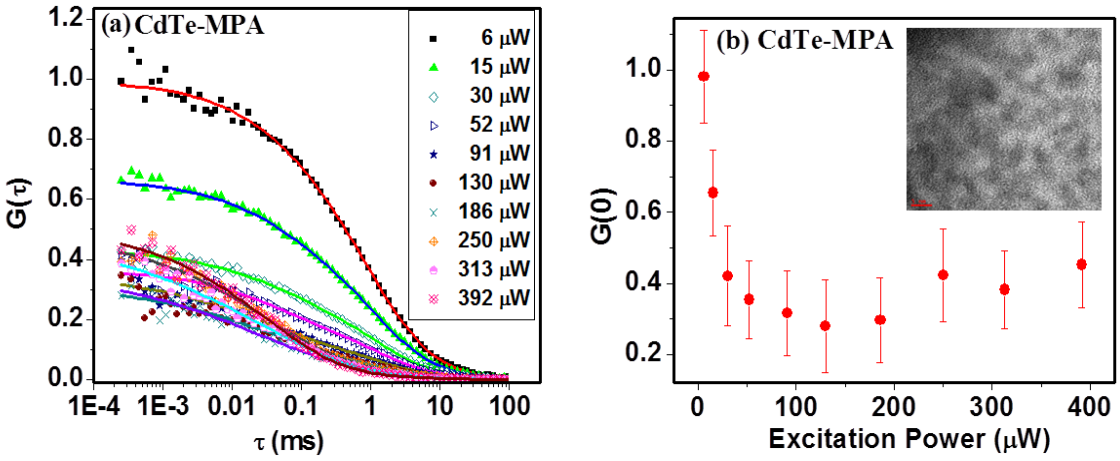

Figure 3.1. (a) Correlation curves of the 55 nM CdTe/MPA QDs in aqueous media at different excitation power. Points are the data and lines represent fit to Equation 2.7 and (b) change of the G(0) value with excitation power (inset shows the TEM images of the QDs). Excitation wavelength is 485 nm.

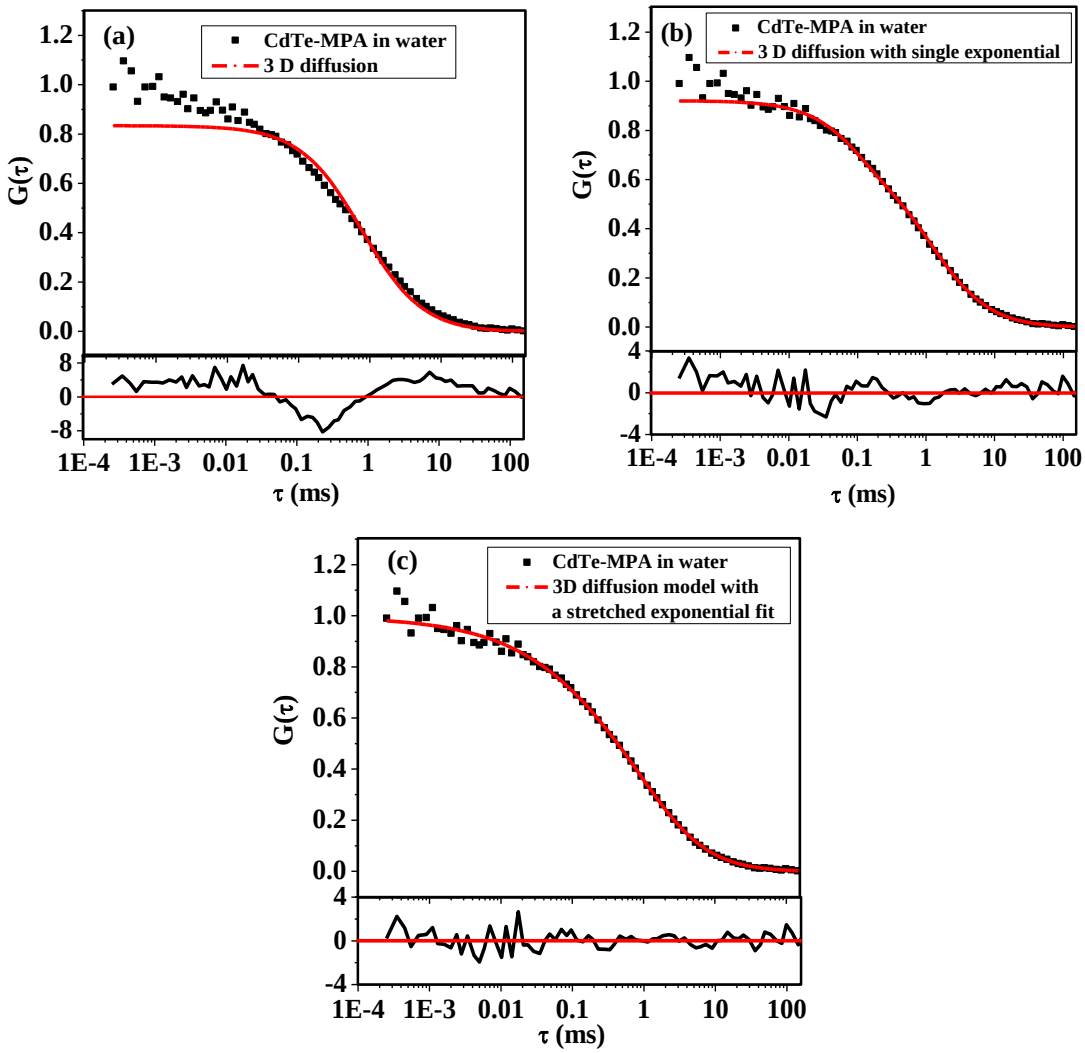

Figure 3.2. Fit of the correlation curves of a 55 nM aqueous solution of CdTe-MPA at 6 μW excitation power into (a) simple 3 D diffusion model, (b) 3 D diffusion model with single exponential term and (c) 3D diffusion model with a stretched exponential term. Here black points are the data and red line represents the fit. The residuals depicting the quality of the fits are shown in the lower part of each panel.

These results suggest that the blinking kinetics becomes faster and dominant with increasing excitation power. At high excitation power blinking kinetics dominates the entire correlation curve. This is why the correlation curves are shifted to shorter correlation time with increasing excitation power. As the amplitude of the correlation curve depends on the number of fluorescent molecules in the observation volume, $G(0) = 1/N(1-T)$,[50] where, N is the average number of molecules in the observation volume undergoing reversible transition

between fluorescent on and off state, an increase in T implies a decrease in the number of fluorescent molecules N(1−T) in the confocal volume. Hence, the amplitude of the correlation curves should increase with increasing excitation power. However, a completely opposite observation is made in the experiment. A decrease in the G(0) value is commonly rationalized considering the broadening of the observation volume due to excitation saturation that increases N.[12,70,73]

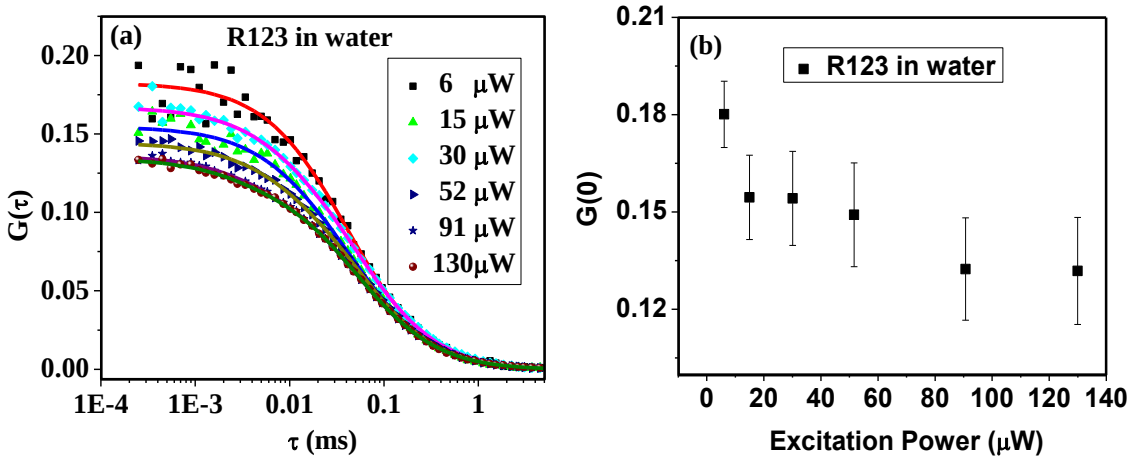

Figure 3.3. Plot of (a) correlation curves of R123 at different excitation power, (b) G(0) value versus excitation power.

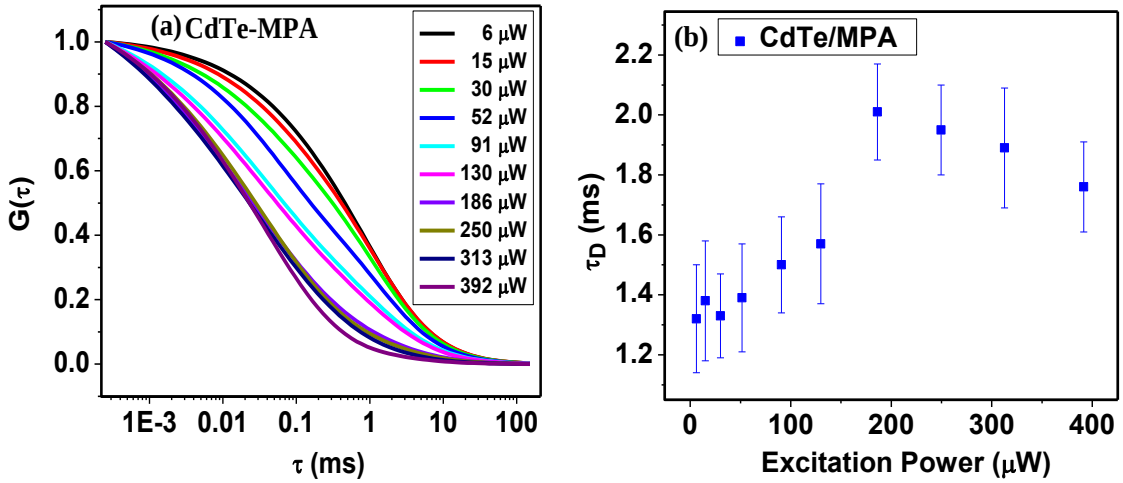

Figure 3.4. (a) Normalized fitted correlation curves of the 55 nM CdTe/MPA QDs in aqueous media for different excitation power. (b) A plot of the measured diffusion time of the QDs against excitation power.

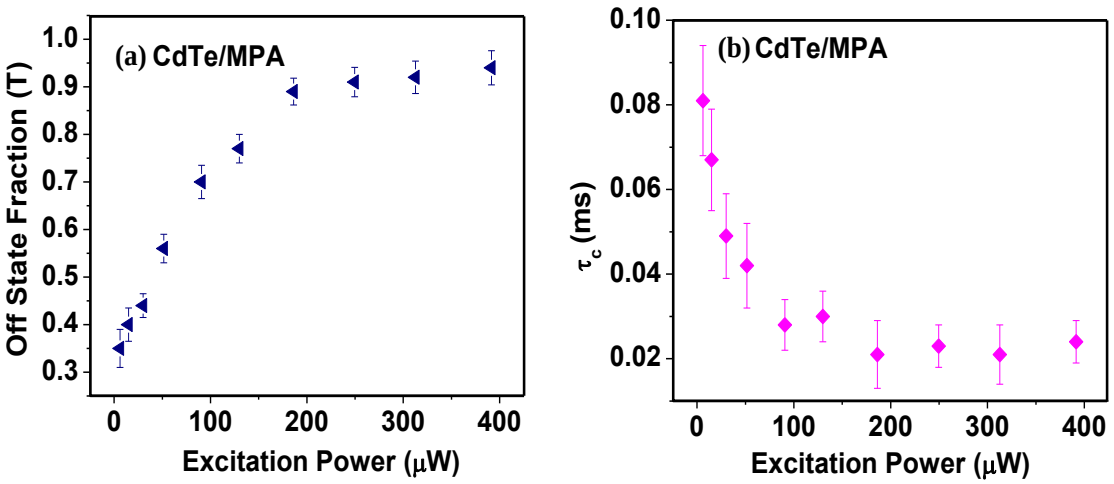

Figure 3.5. Variation of the estimated (a) off-state fraction (T) and (b) blinking time (τ_t), obtained from the fit to Equation (2.6), on the excitation power.

However, the changes in diffusion time in the low excitation power regime (Figure 3.4) is almost negligible, and in this regime the decrease of the G(0) value is huge. A decrease in the G(0) value after 100μW excitation power can be rationalized as due to excitation saturation. However, the decrease of the G(0) value in the low excitation regime is certainly not due to excitation saturation and hence some other processes must be involved. Because the decrease of the G(0) value is much larger in the case of QDs compared to R123, an increase of background intensity with increasing excitation power is not responsible for this observation (Figure 3.3). As stated in the Introduction, Doose et al. assigned a decrease in the amplitude of the correlation curve to excitation saturation and blinking[73] but could not model the excitation power-dependent blinking of the QDs. We have successfully modeled the excitation power-dependent blinking kinetics by fitting the data to a stretched exponential model and found out that this decrease in the G(0) value is not due to blinking (as it increases the fraction of the off-state) (Figure 3.5). Under these circumstances, this decrease of the G(0) value can be explained only if N increases by exposure to light. This suggests light-induced brightening of the otherwise dark particles (which does not fluoresce), and this process is enhanced with an increase in excitation power, a process commonly termed photoactivation.[35] In this context, it is to be noted that Dong et al. attributed a decrease of the G(0) value under laser irradiation of different times to photoactivation of the quantum dots[37] resulting from facile aggregation of the QDs that led to a shift of the correlation curves to

longer correlation times.[37] However, in our study we did not observe any increase in the diffusion time in the lower excitation power region where the decrease of G(0) value is huge (Figures 3.1 and 3.4). Hence, even though photoactivation is responsible for the decrease of the G(0) value upon increasing excitation power, it is clearly not due to laser-induced aggregation. The increase in the G(0) value from 0.30 ± 0.12 (at 186 μW) to 0.45 ± 0.12 (at 392 μW) (Figure 3.1) is clearly due to photobleaching, which decreases the number of fluorescent molecules in the observation volume. This fact is also supported by the decrease in the diffusion time from 2.01 ± 0.16 ms (at 186 μW) to 1.76 ± 0.15 ms (at 392 μW) (Figure 3.4) due to a decrease in the residence time of the QDs because of photobleaching.

An important point to note here is that for low excitation power, the number of QDs in the observation volume (10^{-15} L) estimated from the FCS measurement (N) is much lower than the actual number of QDs (N_{actual}) present in this volume. For example, for a concentration of 55 nM, the actual number of QDs in the observation volume is 33. However, the number of QDs calculated from the measured G(0) value of 0.98 ± 0.13 and an off-state fraction of 0.35 is only 1.56 ± 0.25, indicating that a large fraction of the QDs remain in their dark state (absorb light but do not emit). The experiments carried out for various QD concentrations, the results of which are collected in Table 3.1, show a very similar behavior. That the concentration mismatch in the case of the QDs is indeed due to the dark fraction is further substantiated by the fact that for the molecular system, R123, no such mismatch is observed (Figure 3.6). With increasing excitation power, as the dark fractions are turned into bright ones, the G(0) value decreases despite an increase in the off-state fraction under this condition. At even higher excitation power, when almost all the QDs are turned bright and participate in the on-off transition, the saturation of the G(0) value is observed.

Table 3.1. Some FCS parameters at different concentrations of the QDs in aqueous solution for an excitation power of 6 μW.

Parameters	30 nM	55 nM	64 nM	270 nM
G(0)	3.0770 ± 0.3100	0.9800 ± 0.1300	0.8293 ± 0.0800	0.1462 ± 0.0100
N(1-T)	0.3250 ± 0.030	1.020 ± 0.150	1.201 ± 0.080	6.840 ± 0.440
T	0.42 ± 0.04	0.35 ± 0.04	0.34 ± 0.05	0.32 ± 0.04
N	0.56 ± 0.05	1.56 ± 0.25	1.83 ± 0.13	10.04 ± 0.69
$^{\dagger}N_{actual}$	18 ± 1	33 ± 2	38 ± 2	162 ± 6
*Dark Fraction	0.970 ± 0.002	0.950 ± 0.002	0.950 ± 0.002	0.940 ± 0.004

†Estimated from the concentration of QDs for an observation volume of 10^{-15} L. *N/N_{actual} gives the bright fraction of the QDs. Dark fraction = (1 - bright fraction).

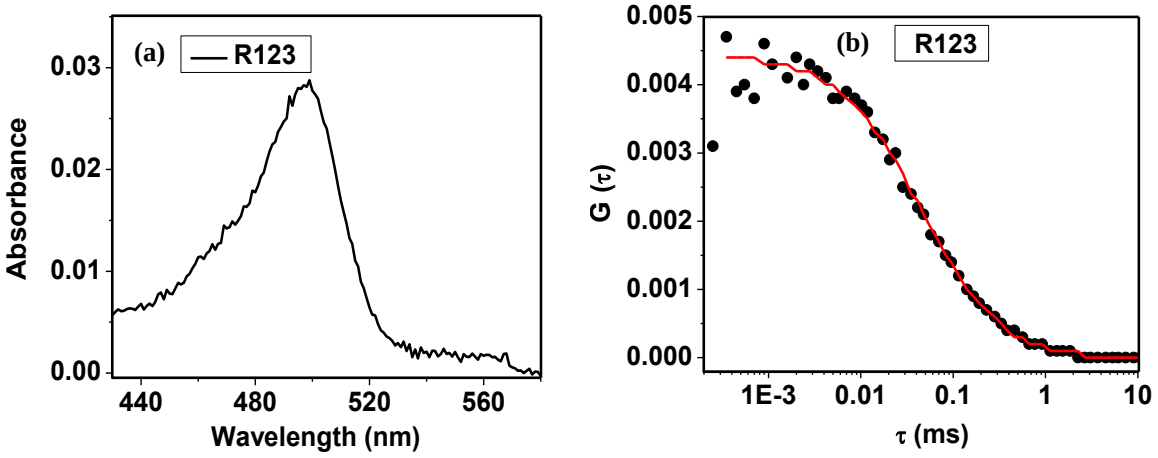

Figure 3.6. (a) Absorption spectrum of an aqueous solution of R123. Concentration of R123 obtained from absorption measurement is 379 nM. (b) Correlation curve of R123 at 379 nM concentration. Black spheres are the data and red line represents the simple 3-D diffusion fit to the data points. Exactly same G(0) value obtained in the FCS experiment as expected from the absorption measurement.

3.3. Steady state behavior of the QDs at different illumination times:

To identify the process(es) responsible for the change in luminescence behavior of the QDs, the experiments have also been performed under steady-state conditions for different irradiation periods using deoxygenated solutions of QDs (prepared by nitrogen bubbling of the solution). The effect of exposure to light on the UV−vis absorption spectrum

also was studied. A noticeable decrease of the absorbance throughout the entire absorption band is observed with increasing exposure time (Figure 3.7). As the absorption peak position is not well-resolved, it is difficult to figure out from the data whether light irradiation leads to any shift of the absorption maximum. Figure 3.7 depicts the effect of illumination of an aqueous solution of the QDs for different exposure times on the integrated emission intensity (I_{em}) and wavelength corresponding to the emission peak (λ_{max}^{em}). The illumination leads to a nearly 3-fold enhancement of I_{em} up to a certain time (350 min under experimental conditions) beyond which the emission intensity decreases rapidly. During this irradiation process, λ_{max}^{em} decreases slightly at the early stages, but it decreases sharply after a certain time (which coincides with the time when the I_{em} value starts dropping). To examine any possible role of oxygen on these results, the aqueous solution of the QDs in the cuvette was purged with nitrogen and the experiments were repeated in an oxygen-free environment. These results are also shown in Figure 3.7. As can be seen, also in deaerated condition the initial luminescence enhancement on exposure to light is observed, but the subsequent rapid reduction of I_{em} that is observed in aerated condition is not present. In the N_2-purged solution, the λ_{max}^{em} value, unlike that in the other case, also remains more or less constant. These findings clearly exhibit the distinct role of oxygen in the rapid reduction of I_{em} and the blue shift of λ_{max}^{em} observed following post-maximization of the luminescence intensity. The results also clearly show two competing processes; one enhances the luminescence intensity (the photoactivation of the QDs), and the other diminishes the luminescence of the system. The former is the dominant process at the early stages, and the latter dominates at longer times. It is also evident that the photoactivation process is not sensitive to oxygen, but the latter is. Oxygen-induced photocorrosion of the QDs is well-known,[22,32] and we attribute the rapid drop of luminescence of the system coupled with a blue shift of the emission maximum to photooxidation of the QDs. In this context, it is to be noted that while the overall trend of photoinduced variation of luminescence intensity is found to be very similar for QDs of different sizes, the time required for the maximization of the luminescence intensity or the subsequent rate of drop of the intensity due to photooxidation of the QDs varies from sample to sample.

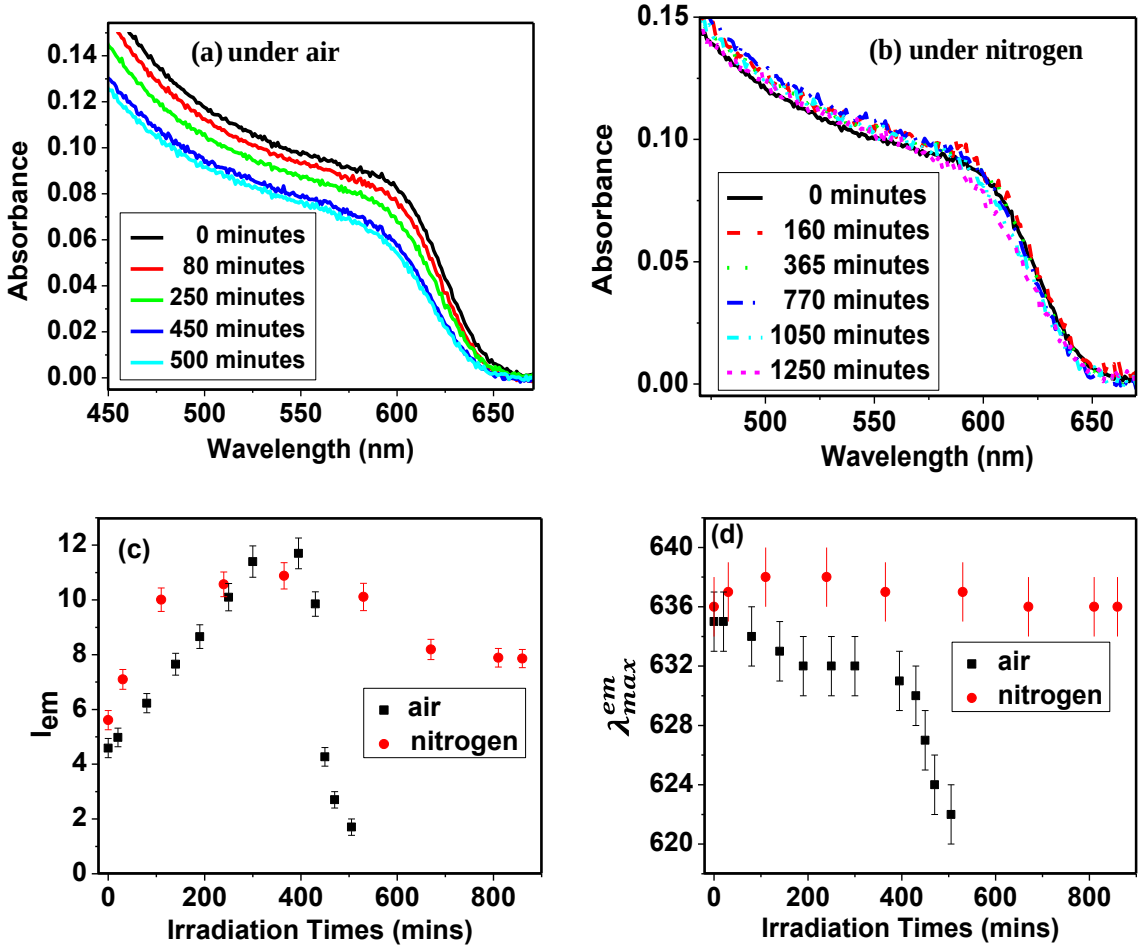

Figure 3.7. Absorption spectra of an aqueous solution of CdTe/MPA QDs at different exposure times to light in (a) air and (b) nitrogen environment. Corresponding variation of the (c) integrated fluorescence intensity (I_{em}) and (d) emission peak wavelength (λ^{em}_{max}) of the CdTe/MPA QDs as a function of irradiation times.

Insight into the mechanism of photoactivation or luminescence enhancement of the QDs can be obtained from some control experiments. Following its photoactivation in aerated or nitrogen environment, if the QD solution is kept in the dark, the luminescence intensity drops again (Figure 3.8). The decrease in luminescence and its recovery on light exposure under the experimental conditions suggests photoadsorption of water molecules on the QD surface as a possible mechanism of the photoactivation of QDs, as reported for CdSe QDs.[32,35,38,48] The photoadsorption of the water molecules passivates the surface charge carrier trap states and enhances the luminescence of the QDs. However, the fact that

luminescence intensity of the QDs does not return completely to its original state, suggests some irreversible change in the surface structure of the QDs. It is difficult to conclude at this stage about the exact nature of the change of the QD surface, but it is possible that some of the chemisorbed water molecules do not leave the QD surface when kept in the dark.

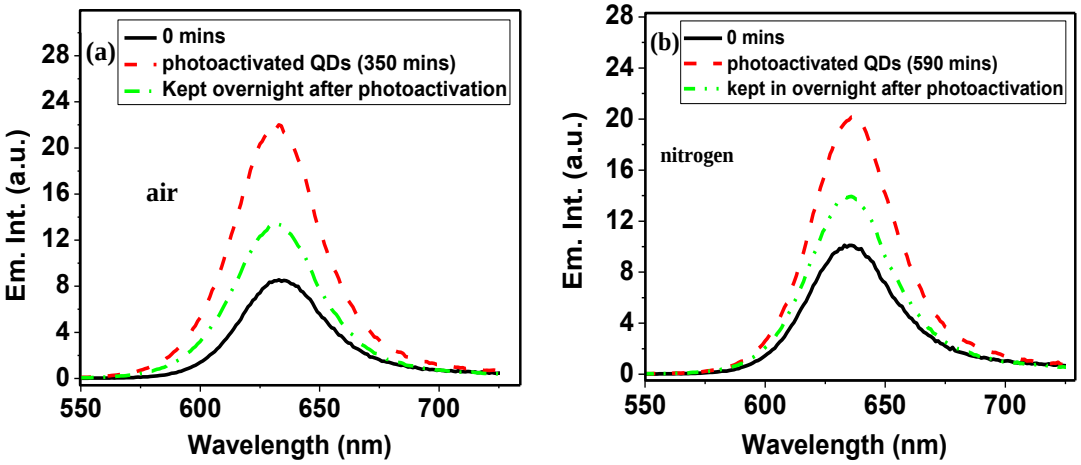

Figure 3.8: Emission spectra of the photo-activated QDs and after keeping the photo-activated QDs in dark for overnight in (a) air and (b) N_2 environment. Luminescence does not come to its original state (t=0).

3.4. Fluorescence lifetime study of CdTe/MPA at different irradiation times:

The mechanism of photoinduced fluorescence enhancement is further substantiated by the fluorescence lifetime data of an aqueous solution of QDs measured after different irradiation times. Figure 3.9 shows the dependence of the fluorescence decay curves of the QDs on the illumination times. The decay curves could be best fit (as determined from the residuals and χ^2 values) to a three-exponential function. This multi-exponential decay of the fluorescence time-profiles of the QDs is due to the existence of a number of discrete relaxation pathways from the excited states with characteristic lifetime components and is consistent with the literature.[5,19,76] The individual lifetime values and the corresponding amplitudes are listed in Table 3.2. As can be seen, the fluorescence lifetime data parallels the steady state data. The average fluorescence lifetime of the QDs increases on photoexposure up to a certain time, beyond which a decrease of fluorescence lifetime is observed. Another point to note here is that the relative weightage of the 0.60 ± 0.02 and 7.12 ± 0.30 ns components vary significantly, while that of the longest lifetime component (48.07 ± 1.45 ns) remains more or less unaltered during light irradiation from 0 to 330 mins. The amplitude

associated with the 0.60 ± 0.02 ns component decreases, while that of 7.12 ± 0.30 ns component increases upon irradiation. After 330 minutes of irradiation, the weightage of the 7.12 ± 0.30 ns component decreases and that of the fastest component increases (Table 3.2).

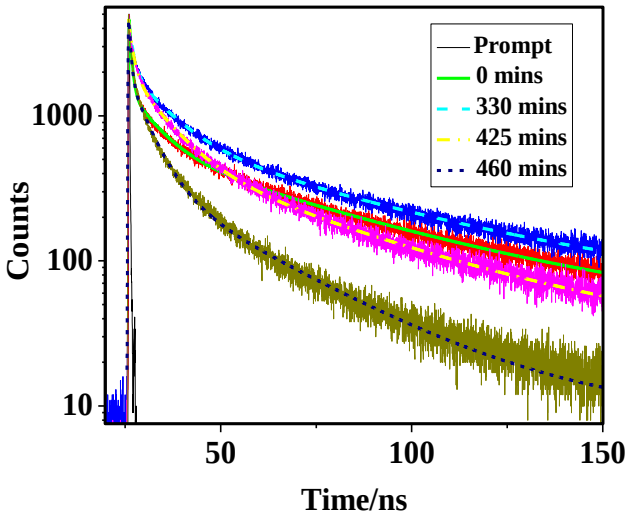

Figure 3.9: Fluorescence decay profiles of CdTe/MPA QDs in aqueous media at different irradiation times. The lines are the fit to the decay traces. In all the cases, the traces are fit to a three exponential model $I(t) = a_1 \exp(-t/\tau_1) + a_2 \exp(-t/\tau_2) + a_3 \exp(-t/\tau_3)$. Excitation wavelength is 439 nm and the emission is monitored at the peak wavelength.

The observation can be rationalized after considering the origin of the each lifetime component of the QDs. The 0.60 ± 0.02 ns component arises from intrinsic electron-hole recombination at the core with little contribution from the surface states.[19] The long lifetime component is often attributed to the involvement of the surface states where overlap of the wave functions of electron and hole is poor.[5,19] In some other instances, the long lifetime component is attributed to the involvement of the spin-forbidden optically passive states present in the band edge (dark exciton states).[36,77] The 7.12 ± 0.30 ns emission component can be considered arising from the involvement of the shallow trap states just below the band edge states and the 48.07 ± 1.45 ns component to the spin-forbidden state in the band edge. As exposure to light passivates the surface trap states and decreases the nonradiative deactivation pathways, it is understandable why the lifetimes are increased on irradiation. In order to explain the change of the amplitudes on photoexposure, one need to consider that all QDs are not bright, some are dark (having very poor surface that provides a broad distribution of the deep trap states that quenches the luminescence). Irradiation of light not

only suppresses the nonradiative pathways of the bright QDs but also converts some dark fraction into bright QDs (as evident from the FCS data) by stabilizing the shallow trap states of the dark QDs.[36,22] Photoadsorption of water molecules stabilizes these trap states containing charge carriers (electron or hole) and increases the probability of the charge carrier to repopulate the emitting band edge state instead of undergoing nonradiative relaxation to deep trap states from where nonradiative processes dominate.[38] When photooxidation of the QDs dominates over the photoactivation process, new surface defects are introduced, which provide additional nonradiative pathways and thus decrease the emission lifetime of the components.[22, 32] As more surface trap states are now generated due to photooxidation of QDs, this decreases the lifetime as well as amplitude of the 7.12 ± 0.30 ns (t=0). So, at later stages of photoirradition the fluorescence is mainly due to the involvement of electron and hole recombination in the core as the surface becomes poor and contributes less to the total luminescence. So the lifetime studies under light irradiation corroborate the findings obtained in the FCS and steady state experiments.

Table 3.2: Time-resolved fluorescence parameters of CdTe-MPA QDs in aqueous solution after different illumination times.

Irradiation times (mins)	τ_1 (ns)	α_1	τ_2 (ns)	α_2	τ_3 (ns)	α_3	$\langle\tau\rangle$ (ns)*
0	7.12 ± 0.30	0.17	48.07 ± 1.45	0.10	0.60 ± 0.02	0.73	6.46 ± 0.21
50	7.40 ± 0.35	0.18	48.30 ± 1.40	0.10	0.71 ± 0.02	0.72	6.67 ± 0.22
110	8.09 ± 0.40	0.21	50.00 ± 1.50	0.11	0.84 ± 0.02	0.68	7.77 ± 0.26
170	8.70 ± 0.30	0.22	51.60 ± 1.35	0.11	0.93 ± 0.02	0.67	8.21 ± 0.23
220	9.38 ± 0.35	0.23	52.02 ± 1.40	0.12	1.08 ± 0.02	0.65	9.10 ± 0.26
280	9.32 ± 0.40	0.25	52.00 ± 1.45	0.12	1.05 ± 0.02	0.63	9.23 ± 0.29
330	9.67 ± 0.30	0.27	52.20 ± 1.35	0.12	1.15 ± 0.02	0.61	9.58 ± 0.26
425	8.02 ± 0.35	0.29	42.10 ± 1.30	0.10	0.80 ± 0.02	0.61	7.02 ± 0.24
460	5.30 ± 0.25	0.23	29.00 ± 1.10	0.05	0.48 ± 0.02	0.71	3.01 ± 0.13
480	4.37 ± 0.20	0.18	24.50 ± 1.10	0.03	0.40 ± 0.02	0.79	1.840 ± 0.085
500	3.83 ± 0.25	0.18	21.76 ± 1.20	0.03	0.34 ± 0.01	0.79	1.670 ± 0.089
535	3.87 ± 0.20	0.17	22.07 ± 1.10	0.03	0.31 ± 0.01	0.80	1.51 ± 0.075

*$\langle\tau\rangle$ is defined as, $\langle\tau\rangle = (\alpha_1\tau_1+\alpha_2\tau_2+\alpha_3\tau_3)/\alpha_1+\alpha_2+\alpha_3$

3.5. Conclusions:

Significant changes of the fluorescence behavior of an aqueous solution of CdTe/MPA QDs under exposure to light have been studied by using a combination of FCS, steady state and time-resolved fluorescence techniques. A faster relaxation of the correlation at higher excitation power, especially at shorter correlation time, is attributed to increasing contribution of the off-state of the QDs. A decrease in the G(0) value with increasing excitation power, despite an increasing fraction of the molecules in their off-state, is mainly attributed to light-induced brightening of the dark QDs to bright QDs because of surface passivation at higher excitation power. The simultaneous of the occurrence of two competing processes, photoactivation leading to fluorescence enhancement and photo-degradation resulting in quenching of the luminescence of the QDs, has been substantiated by the steady state and time-resolved emission measurements. It is suggested that surface passivation by photoadsorption of water molecules leads to photoactivation of the QDs and dissolved oxygen-induced photooxidation of the surfaces is responsible for subsequent drop of the luminescence intensity of the system.

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