

# Complete Quenching of CdSe Nanocrystal Photoluminescence by Single Dye Molecules\*\*

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Much of the current research into semiconductor nanocrystal (NC) photochemistry has focused on their potential application as biological reporters, as light harvesting elements in solar energy conversion systems, or as tunable emitters in light-emitting diodes (LEDs). These applications all necessitate energy or charge-carrier transfer between semiconductor materials and molecular species. For example, conjugated-polymer–nanocrystal blends have displayed promise as the active layer in solar photovoltaic applications.<sup>[1]</sup> In addition, reports on the use of systems incorporating nanocrystals in the place of molecular dyes within biology are beginning to emerge. These have utilized fluorescent quantum dots (QDs), such as spherical CdSe nanocrystals. For example, energy transfer between a QD donor and dye acceptor has been used as a sensing mechanism for protein binding,<sup>[2,3]</sup> enzyme activity,<sup>[4]</sup> DNA Holliday junction dynamics,<sup>[5]</sup> and hybridization<sup>[6]</sup> as well as recognition probes for the presence of specific RNA sequences<sup>[7]</sup> or other biological moieties,<sup>[8]</sup> as reviewed recently.<sup>[9]</sup> The recent determination of structural and orientational information within a QD–protein bioconjugate system via the Förster resonance energy transfer (FRET) formalism<sup>[10]</sup> is a particularly important example of the utility of energy transfer between QDs and molecular dyes. The successful development of these applications is predicated on a firm understanding of energy transfer in nanoscale systems. However, the efficiency of energy transfer between a QD donor and dye acceptor at short donor–acceptor distances is yet to be measured.

In this Communication we report a series of experimental investigations into the efficiency of energy transfer (ET) between CdSe-based nanocrystals and covalently linked organic dyes. In contrast to earlier work investigating energy transfer between nanocrystals and molecular dyes,<sup>[11]</sup> we have chosen to chemically bind the dye molecules to the QDs. The surface chemistry of the system has been controlled by linking the dye through the same functional group (amine) as that of the stabilizer adsorbed onto the QD surface. These hybrid structures combine the high absorption cross-section of CdSe

semiconductor nanocrystals, which possess a large density of states, with the high fluorescence quantum efficiency of the acceptor molecules in a controlled system to create a super-light-absorbing hybrid species, which harvests and directs light energy to a single molecular acceptor. More importantly, we will show that a single adsorbed dye molecule can completely quench the exciton luminescence of the nanocrystal.

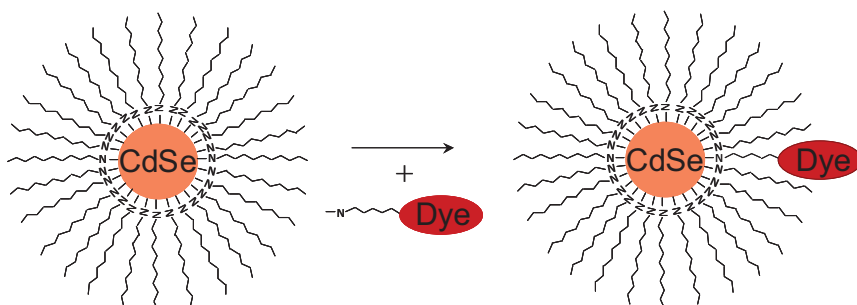
We present here results from a number of different sizes and types of nanocrystals, including cores (CdSe<sub>494</sub>, CdSe<sub>533</sub>, CdSe<sub>538</sub>, CdSe<sub>549</sub>, and CdSe<sub>580</sub>), core/shells (CdSe/CdS<sub>582</sub>), and rods (CdSeRod<sub>526</sub>), where subscripts refer to the wavelength (nanometers) of the lowest energy absorption peak. The dyes used were Texas Red Cadavarine (TexRedC5) and Lissamine Rhodamine B Ethylenediamine (LRhBen), and the QDs were prepassivated with octylamine to prevent changes in surface chemistry upon binding of the amine-functionalized dyes (Scheme 1). Both the octylamine ligands (NH<sub>2</sub>R) and dye molecules are subject to the ligation equilibrium (Equation 1). The emission spectra of the smaller nanocrystals along with the absorption and emission spectra of the organic dyes are shown in Figure 1. Whilst nanocrystals have a large absorption cross-section throughout the visible spectral region, extending down to their size-dependent band gaps, the dyes LRhBen and TexRedC5 are optically transparent around 400–450 nm, allowing selective excitation of the nanocrystals at 400 nm. In this work, the nanocrystal acts as the energy donor and the organic dye is the acceptor.



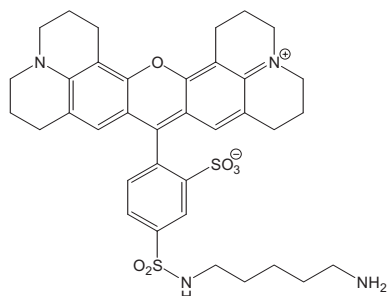
Energy transfer within a system containing a CdSe/ZnS core/shell nanocrystal and Texas Red Cadavarine has been investigated previously.<sup>[12]</sup> In this previous work, the nanocrystal was passivated with trioctylphosphine oxide (TOPO) ligands and the conjugate was found to be photochemically unstable. As a result of the instability, the energy transfer efficiency could not be quantified. Dye ligation also changed the surface chemistry of the NCs significantly. Conversely, the systems investigated here were found to be stable enough to carry out quantitative measurements, with no detectable photodegradation over 24 h in solution. However, in accord with the systems previously reported, the hybrids here were also photochemically unstable when dispersed in a poly(methyl methacrylate) matrix. The initial red emission of single

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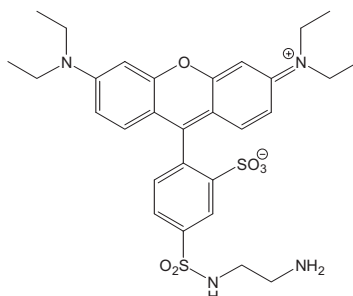
[\*\*] This work was supported through ARC DP Grant 0451651 and FF Grant 0561486. The authors thank Joel van Embden and Tich-Lam Nguyen for some QD samples and advice, as well as Lisa Smith for carrying out ICP measurements. Supporting Information is available online from Wiley InterScience or from the author.



Dye =



Texas Red C5



Lissamine Rhodamine B ethylenediamine

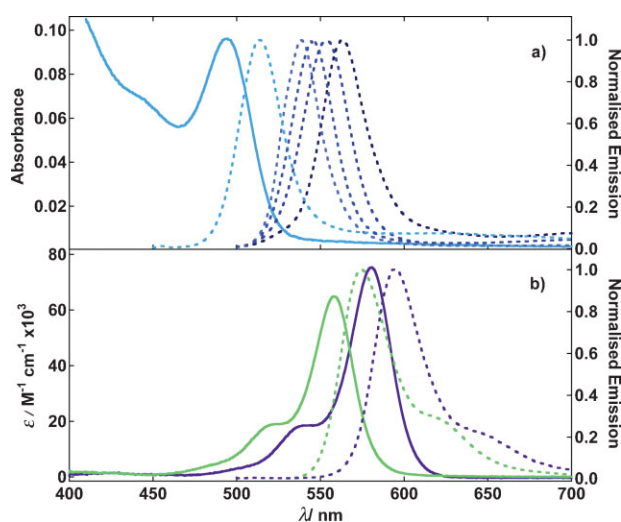
**Scheme 1.** a) Reaction scheme for adsorption of dyes onto CdSe nanocrystals. b) Structures of Texas Red C5 and Lissamine Rhodamine B ethylenediamine.

conjugates characteristic of Texas Red C5 visually changes rapidly to green, indicating photobleaching of the dye. The NCs themselves continued to emit following degradation of the dye.

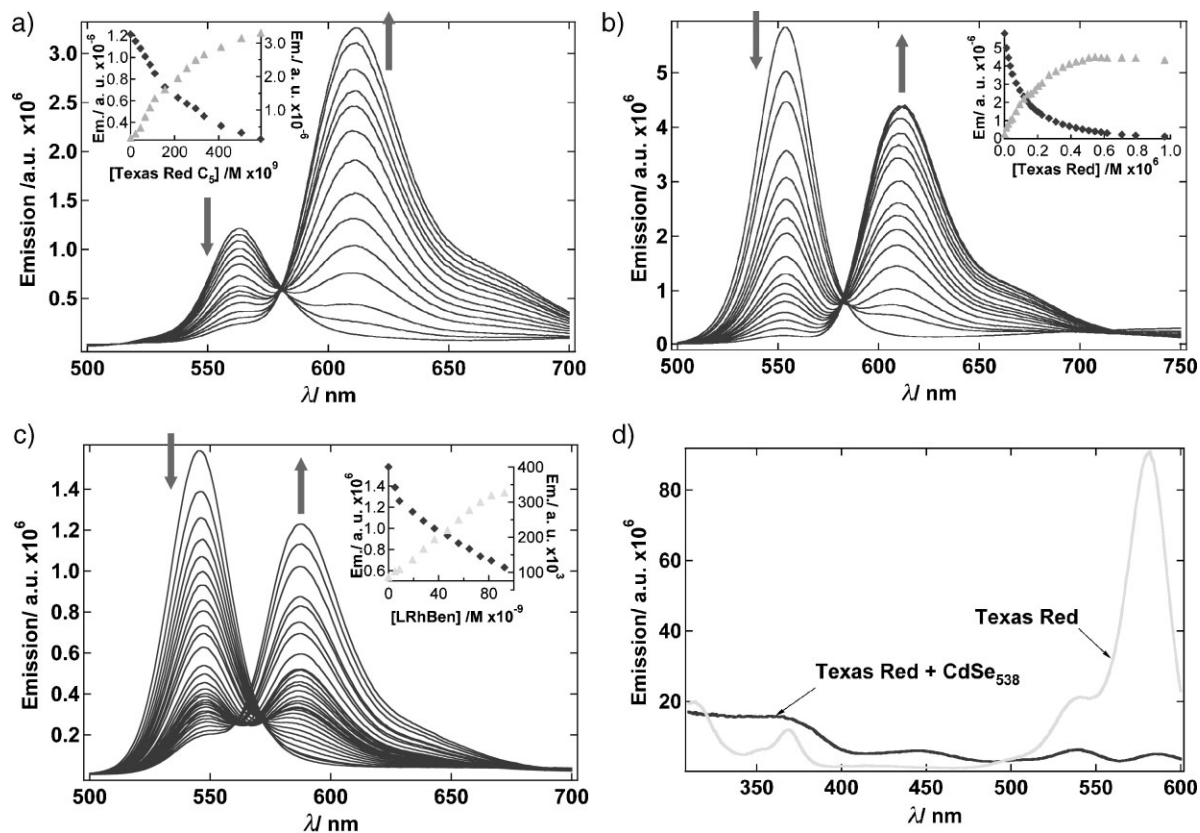
Titration of either TexRedC5 or LRhBen into a solution of CdSe nanocrystals leads to a decrease in the fluorescence from the QD and an increase in fluorescence characteristic of the organic dye. These titrations exhibited extremely clean isosbestic points. The fluorescence spectra during titrations of TexRedC5 into a solution of CdSe<sub>549</sub> and CdSe<sub>538</sub> as well as that of LRhBen into CdSe<sub>533</sub> are shown in Figure 2a–c, respectively. It is obvious from these data that the increase in fluorescence of the organic dye tracks the decrease in the fluorescence of the QD extremely closely and that for every decrease in fluorescence intensity of the CdSe nanoparticles, there is a concomitant and relative increase in fluorescence intensity of the dye (insets Figure 2a and b). The excitation spectrum of TexRedC5 in the presence and absence of CdSe<sub>538</sub> is shown in Figure 2d. In the absence of QDs, the excitation spectra (monitored at 610 nm) are characteristic of TexRedC5 with an intense maximum at 581 nm. After addition of

CdSe<sub>538</sub>, which does not fluoresce at 610 nm, the excitation spectrum exhibits features characteristic of the CdSe QDs. This indicates that the emission at 610 nm is occurring upon excitation of the QDs, and allows us to conclude unequivocally that energy transfer from the QD to the dye is occurring.

All other CdSe QDs, rods, and core/shell structures likewise transfer energy to the organic dye upon illumination (Supporting Information, Fig. S1) with very reproducible quenching behavior. No interplay between energy transfer and electron transfer as a function of nanocrystal size was observed, as has been reported previously for CdTe–CdTe systems crosslinked with hexanedithiol.<sup>[13]</sup> However, for all QD:dye pairs, a red-shift of the dye fluorescence was observed relative to their spectra in the absence of the QD and in the same solvent, CHCl<sub>3</sub> (compare Figures 2 and 3). The LRhBen emission maxima is at 588 nm whilst the TexRedC5 emission maxima is 610 nm compared to 571 nm and 596 nm respectively in the absence of the QD (direct excitation). A similar shift both in direction and magnitude was also observed in the absorption spectra of the two dyes. The absorption and emission maxima of LRhBen and TexRedC5 are highly sensitive to solvent polarity. In CHCl<sub>3</sub> the emission peaks are at 558 nm and 581 nm, while in hexane the broadened emission peaks are at 574 nm and 595 nm for LRhBen and



**Figure 1.** a) Absorption spectrum of CdSe<sub>494</sub> (blue, solid line) and normalized emission spectra of CdSe<sub>494</sub>, CdSeRod<sub>526</sub>, CdSe<sub>533</sub>, CdSe<sub>538</sub>, and CdSe<sub>549</sub> (dashed lines, from lightest blue to darkest blue, respectively). Emissions of CdSe<sub>580</sub> and CdSe/CdS<sub>582</sub> are omitted for clarity. b) Absorption and normalized emission spectra of LRhBen (green, solid line absorption, dashed emission) and TexRedC5 (purple, solid line absorption, dashed emission).



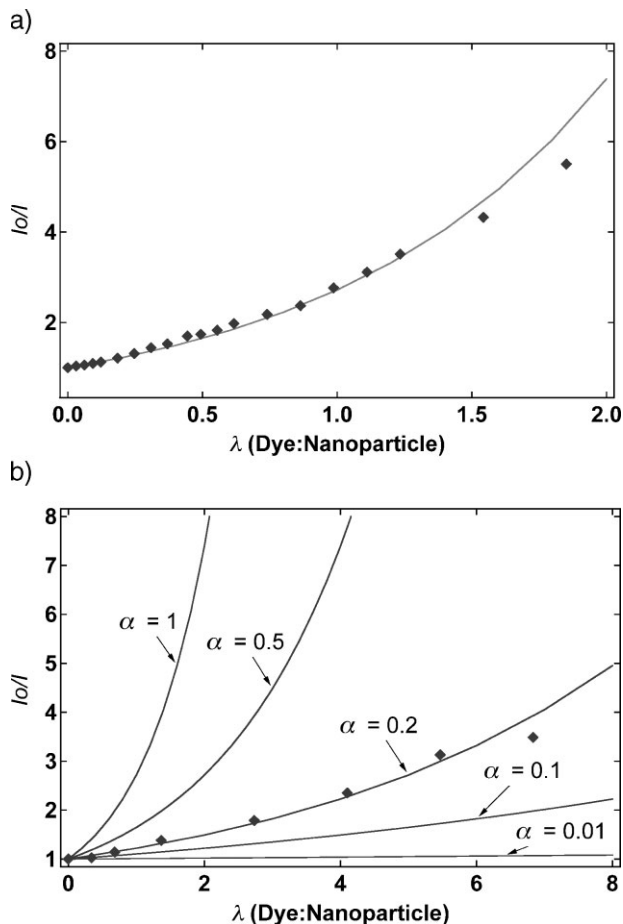
**Figure 2.** a) Energy transfer (ET) from the CdSe<sub>549</sub> nanocrystal with octylamine ligands (563 nm) to the ligated dye Texas Red C5 (610 nm) with increasing dye concentration to 0.6  $\mu\text{M}$ , nanocrystal concentration 0.36–0.32  $\mu\text{M}$ . Inset: Fluorescence at 563 nm (diamonds) and 610 nm (triangles) as a function of Texas Red C5 concentration. b) ET from the CdSe<sub>538</sub> nanocrystal with octylamine ligands (554 nm) to the ligated dye Texas Red C5 (610 nm) with increasing dye concentration to 0.8  $\mu\text{M}$ , nanocrystal concentration 0.63–0.52  $\mu\text{M}$ . Inset: Fluorescence at 554 nm (diamonds) and 610 nm (triangles) as a function of Texas Red C5 concentration. c) ET from the CdSe<sub>533</sub> nanocrystal with octylamine ligands (545 nm) to the ligated dye Lissamine Rhodamine B Ethylenediamine (588 nm) with increasing dye concentration to 0.37  $\mu\text{M}$ , nanocrystal concentration 0.59–0.51  $\mu\text{M}$ . Inset: Fluorescence at 546 nm (diamonds) and 588 nm (triangles) as a function of Lissamine Rhodamine B Ethylenediamine concentration. d) Excitation spectra of a solution containing 0.14  $\mu\text{M}$  Texas Red C5 and 0.61  $\mu\text{M}$  CdSe<sub>538</sub> (dark grey) and a solution containing only 0.12  $\mu\text{M}$  Texas Red C5 (light grey). Fluorescence curves not corrected for direct excitation of the dye, measured to be an order of magnitude lower intensity (in the absence of QDs) than the signal observed here at comparable concentrations.

TexRedC5, respectively. The emission of the dyes adsorbed onto the NCs reflects the local polarity around the particle. Conjugation of the dyes to the QD surface places them in a non-polar local environment, composed of octyl groups from the passivating octylamine ligands, similar to that of hexane. We suggest that this effect solvatochromically red-shifts and broadens the absorption and emission of the dyes.

For the smaller nanocrystals, CdSeRod<sub>526</sub> and CdSe<sub>494</sub>, there was, respectively, an initial, small increase in CdSe NC photoluminescence (PL) or a disparately small decrease in the fluorescence of CdSe following addition of the first few aliquots of dye (Supporting Information, Fig. S2). A small broadening and blue-shift in the absorption and emission of the nanocrystal was also observed at higher dye concentrations (Supporting Information, Fig. S1a). These effects may be rationalized by considering the surface chemistry of the nanocrystals. CdSeRod<sub>526</sub> and CdSe<sub>494</sub> exhibit some trap emission, indicat-

ing incomplete surface passivation. The initial addition of the free bifunctional amine-linked dyes leads to greater passivation of the QD surface within the equilibrium shown in Equation 1, where the concentration of free amine is the concentration of ligand plus dye, and a blue-shift and higher PL quantum yield. It is possible that at higher dye concentrations the small QDs also slightly dissolved, leading to a loss of monodispersity. However, following this initial induction, the PL titration spectra were similar to the spectra observed for larger NCs and energy transfer dominated. Hence our subsequent discussion and analysis will focus on the systems with QDs with diameters of 2.5 nm or more and with an energy difference of at least 20 nm between the donor and acceptor emission fluorescence.

As the dye is appended directly to the nanocrystal to form a donor–acceptor complex, energy transfer within the donor–acceptor complex itself from the QD to the linked dye will



**Figure 3.** a) Theoretical prediction of dye quenching without excess octylamine ( $\alpha = 1$ , see text) and experimental data points (diamonds) for CdSe<sub>549</sub> titration with TexRedC5, and b) theoretical predictions of dye quenching with excess octylamine for different values of  $\alpha$ , see text, and experimental data points (diamonds) for CdSe<sub>533</sub> titration with TexRedC5 in the presence of 4 mM excess octylamine.

occur, resulting in quenching of the QD PL, known as static quenching. This interpretation is supported by the prompt reduction in fluorescence intensity observed in time-resolved measurements, indicative of an immediate energy transfer ( $<0.3$  ns) owing to the formation of the bound CdSe–dye system, and the lack of significant change in lifetime of the NC fluorescence (Supporting Information, Fig. S3). Control experiments employing CdSe and organic dyes without an amine linking group (for example Rhodamine 6G) showed no significant energy transfer under the conditions used here for the bound dyes, also confirming the lack of diffusional quenching. Finally, we can estimate the diffusion-limited rate constant for dye–QD collisions to be in the order of  $2 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ , assuming  $R = 3 \text{ nm}$  and  $D = 1 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ . However, we obtain Stern–Volmer constants,<sup>[14]</sup> reported in Supporting Information Table S1 to allow comparison to other systems, of around  $10^6$ – $10^7$ , giving a quenching rate constant of around  $10^6 / (2 \times 10^{-9} \text{ s}) \sim 5 \times 10^{14} \text{ M}^{-1} \text{ s}^{-1}$ , far in excess of the

diffusion-limited rate constant. These results demonstrate unambiguously that QD–dye ET occurs only between adsorbed dye molecules and the excited QD.

Whilst FRET has been used previously to successfully quantify energy transfer (ET) in QD–dye systems, within those systems the donor and acceptor moieties were relatively distant and bound at a well-defined distance. Under these conditions the dipole approximation within the FRET formalism is reasonable. Our systems, however, contain very flexible, short linkers between the donor and acceptor with ill-defined donor–acceptor distances. The highly delocalized wavefunctions of the nanoparticle combined with the close proximity of the donor and acceptor brings into question the FRET dipole approximation. Owing to these considerations we analyze our energy transfer results in terms of a simple Langmuir ligation isotherm.

For high-affinity, amine-functionalized dyes such as those used here, at low surface coverage the equilibrium adsorption constant of the Langmuir binding isotherm,  $K_{ads}$ , approaches infinity and every dye molecule is in the adsorbed state. Assuming that only unlabelled nanocrystals fluoresce and incorporating a Poisson distribution of the quencher dye molecules amongst the nanocrystals, the probability of a nanocrystal having one or more adsorbed dye molecules is:

$$\Pr(n > 0) = \sum_{n=1}^{n=\infty} \frac{e^{-\lambda} \lambda^n}{n!} \quad (2)$$

where

$$\lambda = \alpha \left( \frac{[\text{dye}]_o}{[\text{NC}]} \right) \quad (3)$$

and  $\alpha$  is the fraction of the dye in solution that is adsorbed onto the QD according to the equilibrium in Equation 1, where both ligand and dye contribute to the total amine concentration; this fraction is distributed according to the Poisson distribution amongst the NCs. For the case of quantitative adsorption of the dye,  $\alpha = 1$ .

The PL intensity then obeys

$$\frac{I_o}{I} = \frac{1}{1 - \sum_{n=1}^{n=\infty} \frac{e^{-\lambda} \lambda^n}{n!}} \quad (4)$$

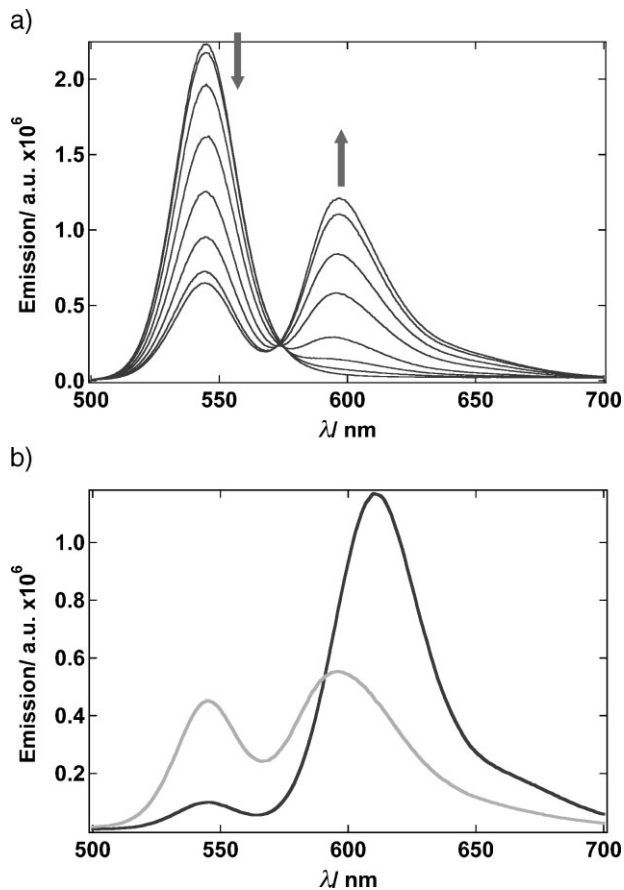
where  $I_o$  and  $I$  are, respectively, the fluorescence intensity of the donor in the absence and presence of the acceptor (see Supplementary Information for complete derivation). Figure 3a displays a plot of  $I_o/I$  vs  $[\text{dye}]/[\text{NC}]$  for the titration of TexRedC5 and CdSe<sub>549</sub> shown in Figure 2a. The solid line represents Equation 4 with quantitative adsorption of the dye ( $\alpha = 1$ ). Under the conditions used in this titration, we can conclude that we achieve quantitative energy transfer from the QD to the conjugated dye, viz. just one dye conjugated to one QD is required to achieve complete transfer of energy

from the QD to the dye. For this system, the emission from TexRedC5 for the QD–dye system with 1.85 TexRedC5 molecules per QD has an area 3 times greater than the emission from the QD only, hence the relative quantum yield for fluorescence of the QD–dye system is greater than for the QD alone. This indicates that the rate of energy transfer is sufficiently rapid to compete effectively with energy loss via non-radiative channels in the QD, thus intercepting energy which would usually be lost non-radiatively and transferring it to the dye molecule from which it is emitted radiatively. Hence the dye acts as an energy funnel when adsorbed onto the QD surface, effectively resulting in an increase in the quantum yield of fluorescence compared to the QD alone.

The energy transfer between the QDs CdSe<sub>533</sub> or CdSe<sub>538</sub> and the dyes appeared to be slightly more efficient than predicted by the model, possibly due to either a small amount of dye-induced aggregation or slight errors in the extinction coefficient of the NCs. Recent calibration work in our laboratory suggests that the values determined by Peng<sup>[15]</sup> are low owing to the presence of soluble Cd ions. Despite this, the relative quantum yield for energy transfer from the QD to the dye for these systems is 90%, indicating that only 10% of the radiative energy of the QD is not transferred to the dye. This energy transfer results in an effective increase in the absorption cross-section of the dye upon conjugation to a QD compared to the dye alone.

The quantitative energy transfer measured here may be compared with measurements performed by Mattoussi et al. and Feldmann et al. on similar donor–acceptor systems.<sup>[2,11]</sup> These works employed relatively big core/shell QDs or rods with up to 10 dyes per nanocrystal, combined with donor–acceptor distances greater than 6.5 nm and up to 35 nm. The energy transfer within these systems was quantified using the FRET formalism although it was noted in all cases that application of this theory to QDs is yet to be proven. Despite this, good agreement between predictions made by FRET and experimental results were obtained. In contrast, in the systems here, the donor–acceptor distance is 2.5–3.9 nm (assuming a fully extended dye linking group) and for the specific system in Figure 3a where the QD has a diameter of 3.0 nm, the donor–acceptor distance is 2.8 nm. In addition, the conditions used here ensured for the most part fewer than one dye molecule per QD. These differences provide an explanation for the much more efficient energy transfer observed here. Unlike the previous work, we observe little increase in the energy transfer efficiency above a dye:nanocrystal ratio of 1, the small increase that was observed is due purely to the Poisson distribution of dyes across the QDs in solution, with the addition of more dye merely increasing the proportion of QDs with a dye attached. In other words, once one QD has one dye attached, the energy transfer efficiency for that conjugate is 100% and addition of more dye molecules around the same QD will not increase the energy transfer efficiency.

The data shown in Figs. 2 and 3 were obtained without additional octylamine in the solution and the smaller QDs were not fully passivated. This results in conditions where the



**Figure 4.** a) ET from the CdSe<sub>533</sub> nanocrystal with octylamine ligands (545 nm) to the ligated dye Texas Red C5 (610 nm) with increasing dye concentration to 3.8 μM, nanocrystal concentration 0.57–0.56 μM, in a solution containing 4 mM octylamine. Each solution was allowed to equilibrate for 2 h prior to measurement of the fluorescence spectrum and was prepared from the same CdSe<sub>533</sub>/octylamine stock solution. b) Fluorescence spectrum of a solution containing 0.66 μM of TexRedC5 and 0.55 μM CdSe<sub>533</sub> (dark grey) and the same solution following addition of 1 μL octylamine (to give 2 mM concentration) and equilibration (light grey).

binding of the dye to the CdSe competes only minimally with binding of octylamine and where binding occurs extremely rapidly. When there is an excess of octylamine, however, the dye adsorption will occur in competition with octylamine adsorption. Therefore, for a given concentration of dye, fewer dye molecules will be bound to the CdSe nanocrystal than in the absence of the excess ligand (Equation 1). This effect is shown in Figure 4a for titration of TexRedC5 into a CdSe solution containing 4 mM octylamine where, despite the much higher concentration of dye compared to that in Figure 2a (more than five-fold), a smaller degree of energy transfer is observed. Figure 4b displays the fluorescence spectrum of a solution containing a 1:1.2 ratio of CdSe<sub>533</sub> and TexRedC5 prior to and following the addition of excess octylamine and equilibration of the system. The fluorescence of the CdSe nanocrystal is partially restored and the fluorescence of the dye

is lessened upon addition of the excess octylamine, indicating a loss of energy transfer within the system. Thus, excess ligand may be used to control the degree of ET. For all systems, addition of excess octylamine to solutions containing the CdSe:dye complexes following titration leads to a blue-shift and sharpening in the absorption band of the dye back to its characteristic position in the absence of CdSe in  $\text{CHCl}_3$ , indicative of desorption of the dye from the nanoparticle (Fig. 4). A plot of  $I_0/I$  vs the ratio of TexRedC5:CdSe<sub>533</sub> in a system containing 4 mM excess octylamine is shown in Figure 3b. For this system, there is competition for the surface between the dye and the octylamine. The theoretical curves for  $\alpha = 1, 0.5, 0.2, 0.1,$  and  $0.01$  are also displayed and at these concentrations  $\alpha \approx 0.2$ , indicating that only approximately one in five of the dye molecules present are adsorbed onto a nanocrystal surface at any given time.

In conclusion, energy transfer from CdSe nanocrystals to a single, conjugated organic dye is observed in these well-defined systems. We have shown that a single dye molecule is capable of quantitatively quenching the exciton PL of one CdSe nanocrystal. The energy transfer can be partially switched on and off by altering the surface chemistry of the CdSe nanocrystal and is observed for CdSe “cores” and “core/shell” structures as well as CdSe nanorods. The ability of one dye molecule to capture the exciton energy from a semiconductor nanocrystal drastically enhances the effective absorption cross section of the dye molecule. This opens up possibilities to improve the efficiency of dye-based solar cells by utilizing semiconductor nanocrystals as supersensitizers. However, these results also highlight the difficulty of using QD–dye pairs as PL-based sensors, since the emission quenching efficiency is drastically dependent on the surface passivation of the QD and any changes in this passivation during an “assay” will also result in PL changes.

## Experimental

**Materials:** The dyes Texas Red Cadavarine (TexRedC5) and Lissamine Rhodamine B ethylenediamine (LRhBen) were purchased from Invitrogen. Chloroform was purchased from Acros Organics (Spectroscopy Grade, 99.8%, stabilized with ethanol) and octylamine was purchased from Fluka ( $\geq 98\%$ ). All chemicals were used without further purification. CdSe spheres and rods were synthesized according to literature procedures [16]. CdSe spheres were shelled according to the method of Van Embden [17]. The ligands of the as-synthesized nanocrystals were generally exchanged with octylamine by heating the nanocrystals at  $60^\circ\text{C}$  overnight in the presence of excess octylamine. For the smallest QDs and the CdSe rods, exchange was carried out without heating. Unbound octylamine was removed from the resultant solution by repeated extraction of the NCs. As observed previously, [18] the first excitonic absorption peak blue-shifted slightly (ca. 3 nm) following adsorption of the amine ligands. The nanocrystal size was determined from the solution absorption at the first excitonic absorbance peak [15]. The concentration of dye was determined using the molar extinction coefficients,  $8.5 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$  and  $1.22 \times 10^5 \text{ M}^{-1} \text{ cm}^{-1}$  for Texas Red Cadavarine in pH 9 buffer and Lissamine Rhodamine B ethylenediamine in methanol respectively.

**Instrumentation:** Absorption spectra were obtained using a Cary 5 UV-vis-NIR. Emission and lifetime measurements were performed on a Jobin-Yvon Fluorolog-3 spectrometer equipped with TCSPC capability. Excitation was at 400 nm with 4 nm bandpass. Emission was collected with 1 nm bandpass with a 0.5 s integration time. Photon counting was carried out with the Fluorohub. At the excitation source was a 403 nm (NanoLED-405L) diode laser, with a pulse width  $< 200$  ps and the fluorescence was detected using a multi-alkali PMT emission detector fitted with photon counting electronics. The instrument response function was 1.1 ns. Data were analyzed using Igor-Pro software with customized routines. Time-dependent data were fit with convolution. Errors are reported as  $2\sigma$ .

The fluorescence quantum yield for the octylamine passivated nanocrystals under the conditions used in these experiments range between  $< 1\%$ – $25\%$  as measured using C153 in ethanol,  $\Phi_F = 0.38$  for excitation at 422 nm [19]. The quantum yield is higher for the larger QDs owing to greater surface passivation [18]. The concentration of the nanocrystal CdSe quantum dots was determined via ICP analysis. The error in the determined concentrations was  $\pm 30\%$ . The absorbance of solutions at 400 nm for all measurements was kept within the range 0.05–0.2 to avoid reabsorption effects. Experiments were carried out in ambient conditions and in air. Samples were stored in the dark and exposed to as little light as possible.

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