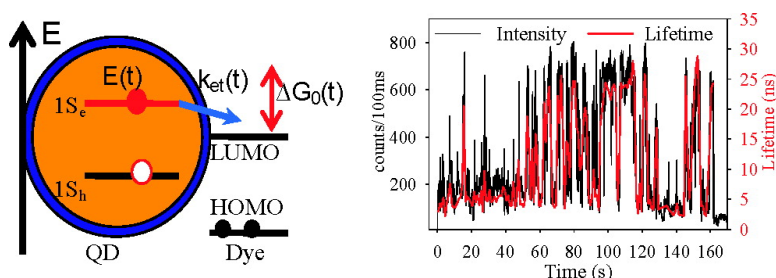


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Intermittent Electron Transfer Activity From Single CdSe/ZnS Quantum Dots

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Charge transfer to and from quantum dots (QDs) is essential to their many applications. Interest in these processes is intensified by recent reports of multiple exciton generation (MEG) by one absorbed photon in some QDs,^{1,2} which provides a potential approach to improve the efficiency of QD-based solar cells and suggests a potential application of QDs as multiple electron/hole photosensitizers in novel photocatalytic systems. The ability to separate excitons (electron–hole pair) by ultrafast charge transfer to acceptors prior to the multiexciton annihilation is not only required for the utilization of this process, but also provides another approach to address current controversy regarding MEG.³ Previous studies of single QD “blinking” showed that, unlike molecular chromophores, QDs exhibit dynamic fluctuation of exciton lifetime.^{4–10} How does this unique property affect the dynamics of charge transfer to and from QDs? To address this question, we have studied electron transfer (ET) dynamics from single CdSe/ZnS QDs to an adsorbed electron acceptor, Fluorescein 27 (F27). We report here a pronounced intermittent ET activity and discuss its possible origins.

CdSe/ZnS cores/shell QD powders (capped by octadecylamine ligand) were obtained from Ocean NanoTech, LLC, AR. F27 was purchased from Exciton, OH. The absorption spectra of these QDs-dye complexes dispersed in heptane are shown in Figure 1a. QDs attached with different numbers of F27 were prepared by controlling the amount of F27 added to the QD solution in heptane followed by sonication and filtration to remove undissolved dyes. Since F27 is not soluble in heptane, all dissolved dyes were believed to be bound with CdSe/ZnS QDs.

Ensemble averaged fluorescence decay kinetics of CdSe/ZnS QDs-F27 complexes are shown in Figure 1b. They were measured by time correlated single photon counting (TCSPC) of QD emission between 540 and 675 nm and with excitation at 410 nm, which selectively excited QDs (see the lack of F27 emission in Figure 1a). The fluorescence lifetime of QDs decreased at higher dye-QD ratio (R), suggesting the quenching of QD excitons by the adsorbed F27. CdSe/ZnS QDs used in this study have a first exciton peak centered at 606 nm, corresponding to an estimated core radius of 2.9 nm. The estimated excited-state oxidation and reduction potentials are -0.95 V and $+1.01$ V (vs SCE), respectively.^{11–13} The reduction and oxidation potentials of F27 are at -0.81 and $+1.57$ V (vs SCE), respectively.¹⁴ As shown in the inset of Figure 1a, excitons in QDs can dissociate by ET to F27, while hole transfer is energetically not allowed. Energy transfer from QD to F27 is not expected due to the lack of spectral overlap of QD emission with F27 absorption. Previous studies of CdS/rhodamine B and CdSe/Re-bipyridyl complex showed ultrafast ET from QDs to adsorbed molecules.^{11,15} On the basis of these reported ET processes in related systems with similar energetics, we attribute the quenching shown in Figure 1b to ET from QD to F27 molecules. The ZnS shell in CdSe/ZnS core/shell QDs not only enhanced the emission yield and photostability of the CdSe core but also acted as a

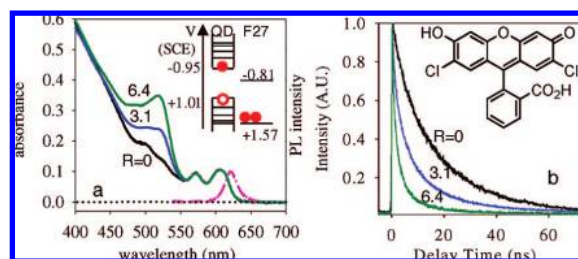


Figure 1. (a) UV-vis absorption spectra and (b) QD fluorescence decay of CdSe/ZnS-F27 complexes in heptane with dye/QD ratios (R) of 0 (solid black line), 3.1 (blue), and 6.4 (green). Also shown in panel a is the absorption spectrum of F27 in heptane without QD (black dotted line) and the emission spectrum of the QD-dye complex ($R \approx 6.9$) on a glass coverslip (pink dash-dot line) obtained with 410 nm excitation. Inset in panel a shows redox potentials of F27 and QD. Inset in panel b shows schematic structure of F27.

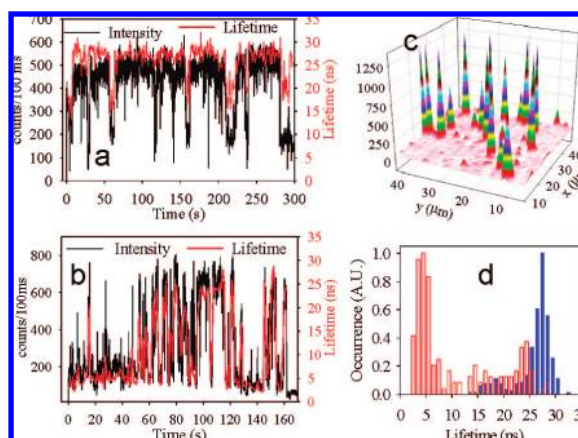


Figure 2. PL (black) and lifetime (red) transients of single CdSe/ZnS QDs with (a) 0 and (b) 6.4 adsorbed F27; (c) raster scan image of single QDs on glass coverslip; (d) histogram of lifetime transients for QDs shown in panels a (blue) and b (red).

tunneling barrier to slow down ET to the acceptor, enabling their study on the single particle level.

ET on a single QD level was studied using a confocal microscope attached with TCSPC module. Details of the experimental setup can be found in the Supporting Information section. Figure 2c shows a raster scan fluorescence image of CdSe/ZnS on a glass coverslip. Figures 2a and 2b show typical fluorescence intensity and lifetime transients of a single CdSe/ZnS QD on a glass coverslip prepared from samples with $R = 0$ and $R = 6.4$, respectively. Lifetimes were calculated using photons within a 1 s bin time. The lifetime of the particular QD shown in Figure 2a fluctuates between 15–30 ns. However, the amplitude of lifetime fluctuation is much larger for a QD-dye complex. As an example, the QD-F27 complex illustrated in Figure 2b shows lifetime fluctuations between 2.5–29 ns. In both cases, lifetime shortens when the intensity decreases, sug-

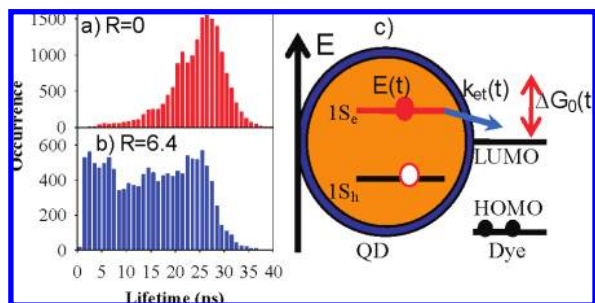


Figure 3. Histogram of single particle lifetime transients of an ensemble of 50 QDs with (a) 0 and (b) 6.4 adsorbed F27. (c) Schematic representation of dynamic fluctuation of energetics and ET rate in QD-F27.

gesting the fluctuation of nonradiative rates.⁴ The distributions of lifetimes along the trajectories of these two QDs are shown in Figure 2d. It is clear from the histogram that the CdSe/ZnS QD resided most of the time in high emitting states with lifetimes around 25–30 ns. However, for the QD-F27 complex, the QD remained mostly in low-emitting states with much shorter lifetimes (2.5–8.5 ns). Such short-lived states are attributed to configurations of the QD-F27 complex for which ET from QD to F27 is fast. It is interesting to note in the ET active complex, the QD spent a considerable amount of time in states with long lifetimes (25–30 ns), for which the ET rate was much slower. The overall fluorescence decay (average over the whole trajectory) of these two QDs is shown in Figure S1, indicating that the average lifetime decreases from 25.9 ns for $R = 0$ to 10.9 ns for QD with adsorbed F27.

To quantify the fluorescence lifetime distribution in an ensemble of single QDs, Figure 3a shows a histogram of lifetimes obtained from the lifetime transients of 50 single QD (without F27) trajectories. The intrinsic lifetime ($k_0 = k_r + k_{nr}$) distribution of the ensemble has a mean of 24.6 ns and a standard deviation of 5.4 ns. However, as shown in Figure 3b, the histogram for an ensemble of 50 single QD-F27 complexes ($R = 6.4$) is much broader, with a mean lifetime of 15.4 ns and a standard deviation of 8.7 ns. The shortening of the average lifetime is attributed to quenching by ET from QD to F27, and the broadening is attributed to the distribution of ET rates ($k = k_0 + k_{ET}$). This observation is consistent with nonsingle-exponential ensemble averaged kinetics of photoinduced ET from CdS and CdSe QDs to acceptors measured by ultrafast transient absorption spectroscopy.^{11,15,16}

The fluctuation of the intrinsic lifetime ($1/k_0$) of QDs hinders a quantitative determination of the ET rate from the measured fluorescence lifetime alone. To provide an estimate of the range of ET rate distribution, we assume an intrinsic lifetime of $1/k_0 = 40$ ns (longest lifetime of the ensemble). The distribution of lifetime shown in Figure 3b corresponds to a variation of k_{ET} from 0 to $<5 \times 10^8 \text{ s}^{-1}$. This distribution of ET rates contains both static and dynamic contributions. The latter can be estimated from single QD trajectories. For the single QD shown in Figure 2b, the estimated ET rate fluctuates from $\sim 4 \times 10^8$ to $<1 \times 10^7 \text{ s}^{-1}$.

The observed fluctuations of single QD (without acceptors) emission intensity (i.e., “blinking”) and lifetime are consistent with previous reports.^{4–10} A positive correlation between intensity and lifetime was observed and attributed to the fluctuation of nonra-

diative decay rates. These fluctuations have been attributed to the variation of trapped charges in and around the QD and their effect on exciton lifetimes.¹⁷

The surprising finding in this study is the large dynamic fluctuation of ET rate in single QD-F27 donor–acceptor complexes. One possible reason for the intermittent ET activity is the fluctuation of adsorbate adsorption conformation on QD, which affects their electronic coupling strength. Another possibility is the fluctuation of charge in QDs, which is already present in QDs without acceptors and is responsible for their blinking.^{4,17} The presence of charge can affect the wave function of excitons in QDs, thus changing the strength of electronic coupling with the adsorbate.¹⁸ It may alter the excited-state energy of QDs, as evident in the observation of spectral diffusion of up to 50 meV for single CdSe/ZnS QDs.⁴ We speculate that in QD-F27 donor–acceptor complexes with small ET driving force (~ 140 meV in this case), the fluctuation in QD energy levels may lead to a large fluctuation in ET activity, as indicated in Figure 3c.

In summary, we demonstrate that ET between single CdSe/ZnS QDs and molecular acceptors can be studied by single QD fluorescence spectroscopy. On the single QD-acceptors level, ET activity undergoes large fluctuation. We speculate that this fluctuation is caused in part by change of charge states in QDs, which may affect the driving force and/or electronic coupling strength of electron transfer to acceptors. Since blinking has been observed in many QDs, the observed intermittent ET activity is likely relevant to ET dynamics in many other QDs.

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Supporting Information Available: Experimental methods, PL decay of single QD and QD-F27 complexes. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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