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Photodynamics of a Single Quantum Dot: Fluorescence Activation, Enhancement, Intermittency, and Decay

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Photoluminescence (PL) enhancement^{1–3} and fluorescence intermittency (FI)^{4–6} are characteristic properties of colloidal semiconductor nanocrystals or quantum dots (QDs). A need to understand these processes has been driven by an increasing range of applications. Large absorption cross-sections and high quantum yields, broad excitation spectra, and the ability to tune emission wavelengths simply by size have made QDs highly attractive for biological imaging,⁷ as single photon sources,⁸ and for charge generation in photovoltaic devices.⁹ Implicit to resolving FI has been the imaging of single QDs where blinking in the fluorescence intensity trajectories has been attributed to electron loss from the excited state (conduction band) via tunneling and/or Auger ionization, the “off-state”, followed by charge migration or recombination, the “on-state”.^{5,10} In contrast, studies of PL enhancement have been performed on QD ensembles on substrates¹ or in solution.^{2,3} PL enhancement has then been attributed to a dark fraction being rendered fluorescent under continuous illumination, with an intrinsic QD quantum yield (QY) close to unity.³ Analysis of fluorescence from individual QDs offers the ability to differentiate between PL enhancement due to a dark fraction switching-on and that due to the QY of individual dots being modified.

Here, we report the observation of fluorescence activation, enhancement, intermittency, and decay over the photochemical lifetime of a single QD. The fluorescence intensity trajectories of hundreds of individual ZnS-capped CdSe nanocrystals were recorded using total internal reflection fluorescence microscopy.¹¹ Commercially available streptavidin functionalized QDs (585 and 605 nm, Invitrogen) were used under biologically relevant conditions. In this case, a 1 nM solution in 0.1 M phosphate buffered saline was found to provide stable (>1 h) monodispersions of single QDs (<0.1 dots/ μm^2) at the coverslip/buffer interface.

In a first examination of the variation in the number of fluorescent QDs with time under continuous illumination (Figure 1a), the population envelope was found to be described by a simple consecutive elementary reactions (CER) scheme of the form $A \rightarrow B \rightarrow C$. Here, a dark QD fraction A evolves into a fluorescent population B before decaying to a non-emissive product C . The photoactivation $A \rightarrow B$ and decay $B \rightarrow C$ are then characterized by rate constants k_a and k_d , respectively. For QDs emitting with a fixed QY, the emission intensity integrated over the population is expected to follow the same temporal evolution. However, detailed analysis shows a nonlinear correlation between PL intensity and QD population (Figure 1b). A quadratic in the QD population N of the form $I_T = I_A N + I_E N^2$, has been fitted to extract the linear component, I_A (the average intensity per QD), and a nonlinear component due to enhancement and decay (per QD), I_E . Note that the exact nature of the nonlinear dependence is unclear; for example, the quadratic could approximate an exponential dependence of the form $\alpha[\exp(\gamma N) - 1]$ for small γN where $\gamma = 2I_E/I_A$ and $\alpha = I_A^2/2I_E$. By separating the total fluorescence into linear and nonlinear components, it can be seen that the average intensity per QD scales

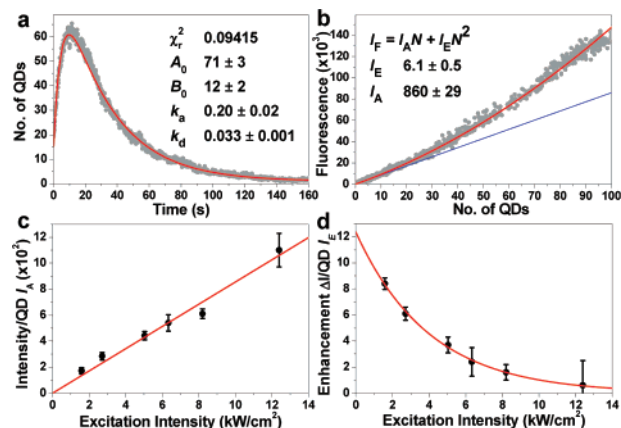


Figure 1. (a) Evolution of the fluorescent QD population under continuous 488 nm illumination at $2.7 \text{ kW}\cdot\text{cm}^{-2}$. Superimposed is a fit of the intermediate population $B(t)$ for a CER. (b) Correlation between QD population and total fluorescence intensity. Quadratic fit in the population N (red) and its linear component (blue). (c and d) Power dependence of the linear (background-corrected) and nonlinear components in the total fluorescence intensity due to enhancement and decay.

directly with laser power, as expected, while the enhancement decreases exponentially (Figure 1c and d). The reduced deviation at higher powers can be largely attributed to a lack in temporal resolution of the faster PL enhancement and decay at a fixed 10 Hz acquisition rate. At lower powers, the divergence is due to PL enhancement and decay over and above that expected from the simple activation of a dark fraction with a fixed QY and subsequent stepwise photobleaching of the population over time.

Analysis of individual QD fluorescence trajectories has revealed a variety of intensity envelopes, characterized by fluorescence activation, intermittency, single-step photobleaching, as well as intensity decay, and in some cases PL enhancement (Figure 2a–d). Evidently, the integration over many single QD trajectories, distributed in time, manifests as a deviation in the total PL from that of QDs simply switching-on and eventually -off with quantized, steady-state intensities. QDs undergoing single-step activation and bleaching (Figure 2a) will largely contribute to the linear component of the ensemble fluorescence. Rapid FI is observed in all trajectories with a large number of “on–off” cycles operating at a few hertz below the acquisition rate. However, substantially longer dark periods (>5s), characteristic of QD ionization, carrier trapping, and core charging, are also evident (Figure 2c). Interestingly, prior to complete fluorescence activation, there appears, in most cases, a period of “ignition” during which short transient PL bursts are followed by relatively long dark interludes. While further investigation of this effect is required to elucidate its origin, it follows that during activation a gradual shift to shorter fluorescence-off and longer -on times will integrate during acquisition to an enhancement in the PL intensity. The reverse would then be true for the degradation of the PL, and this may be the case in the latter stages

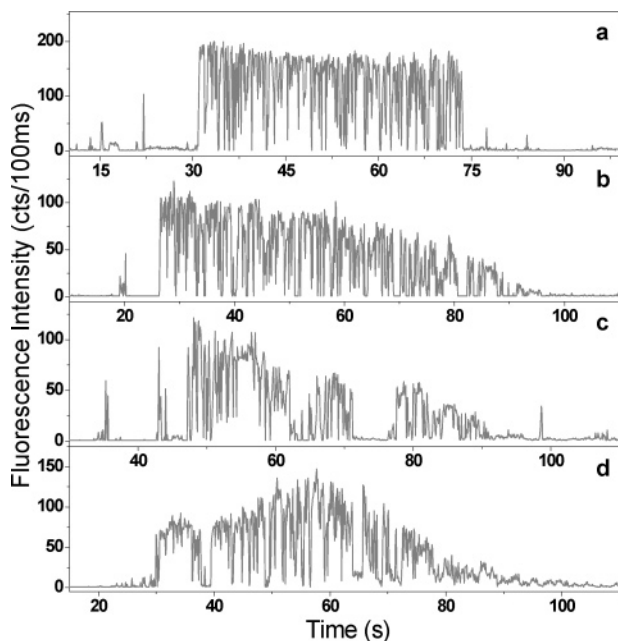


Figure 2. Single QD fluorescence intensity trajectories under continuous 514 nm excitation at $1.2 \text{ kW} \cdot \text{cm}^{-2}$ showing characteristic FI and (a) single-step PL activation and photobleaching (b) activation with continuous PL degradation. (c) FI-modulated PL activation and stepwise intensity depletion (d) activation, PL enhancement followed by continuous fluorescence decay.

of the QD's photochemical lifetime (Figure 2b). However, processes acting on individual QDs, including photoannealing and ultimately photoinduced oxidation, are also likely to contribute to QY enhancement and PL decay, respectively (Figures 2b–d).¹² Many QD trajectories were found to exhibit near-continuous intensity envelopes, interrupted only by periods of FI (Figure 2b and d). This is not entirely unexpected since single QDs of identical structure have recently been shown to possess a continuous distribution of emission states that has been attributed to a time-dependent charge migration to surface trapping sites away from the core, following photoinduced ionization.¹³ Indeed, QDs have been shown to develop positive charge under low-level excitation using electrostatic force microscopy,¹⁴ with qualitatively similar saturation of the charge on a time scale comparable (accounting for the power difference) to PL enhancement seen here (Figure 2d). Trajectories that display discrete, stepwise intensity jumps (Figure 2c) might, therefore, be associated with QDs that can support only a small number of charges at the surface or in the ZnS shell. Perhaps more surprising is the observation that, following a period of FI, emission returns to a level that does not depart significantly from the overall intensity envelope.

Dual-view imaging of the red and blue components in the fluorescence trajectories highlights this observation (Figure 3). Here, the strong correlation between blinking events in both channels confirms that the decay is associated with a single QD, while the anti-correlation in the on-state intensities shows blue shifting of the emission wavelength. Of significance is that the PL intensity degradation cannot be wholly attributed to the “blueing”¹² of fluorescence since, in this case (Figure 3, right inset), the total intensity is relatively well maintained during the shift to shorter wavelengths. Assuming this arises from QD emission blue-shifting

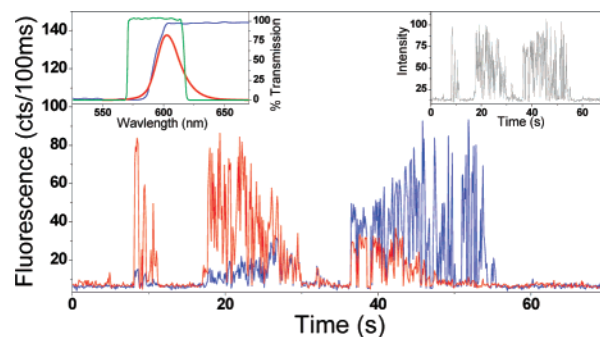


Figure 3. Single QD fluorescence trajectory spectrally separated onto red and blue channels of a dual-view imaging system with 488 nm excitation at $1.6 \text{ kW} \cdot \text{cm}^{-2}$. Total fluorescence intensity (right inset) and optical window (left inset), showing QD emission spectrum (peak 610 nm), dichroic beamsplitter (593 nm edge), and bandpass filter transmission (593 \pm 40 nm).

from the 605 nm long pass edge to the 585 nm reflection edge of the dichroic (Figure 3, left inset), then the minimum wavelength shift is 20 nm at a blueing rate of $\sim 0.5 \text{ nm/s}$. Furthermore, processes leading to the blue shift are seen to continue unabated in the dark off-state associated with a charged core of the QD. Electron–hole recombination or charge migration then reactivates fluorescence at a level that appears to maintain the intensity envelope. Continued investigation into PL modification at the level of individual QDs may ultimately lead to its control through rational chemistry or photoengineering. More importantly for quantitative assays using QDs as probes is the fact that the temporal evolution of the total PL intensity may only follow that of the true QD population within strict excitation intensity, exposure time, and environmental limits.

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Supporting Information Available: Methods and materials and discussion of the CER scheme. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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