# Correlation between Fluorescence Intermittency and Spectral Diffusion in Single Semiconductor Quantum Dots

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We find a correlation between the dynamics of fluorescence intermittency and spectral diffusion in the spectroscopy of single CdSe nanocrystal quantum dots (QD). A statistical analysis of the data suggests two populations of blinking events: blinking followed by large spectral diffusion shifts and blinking with small or no spectral shifts. Although unexpected from earlier studies, the correlation between blinking and spectral shifting is consistent with a model of QD ionization as the mechanism for the blinking event, followed by a redistribution of local electric fields that results in spectral shifting.

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The photophysics of semiconductor nanocrystallite quantum dots (QD) have received a great deal of interest, as these colloidal quantum dots show promise as nanomaterials for future biological and electro-optical applications. In this Letter, we report experimental results from multidimensional, single chromophore experiments of semiconductor nanocrystals that probe the phenomenology of the optical dynamics in single QDs. These results suggest that the two separate long time dynamical processes that have been observed, fluorescence intermittency and spectral diffusion, are correlated through redistribution of charged species in and around each individual QD.

Observations of optical dynamics such as fluorescence intermittency (blinking) and spectral shifting are now ubiquitous in the literature of single chromophore systems. These dynamic processes have been observed in direct [1,2] and indirect [3] band gap semiconductor QDs, QDs grown by molecular beam epitaxy [4], and single molecules [5]. Despite numerous studies, uncertainty in the underlying physical mechanism describing single CdSe QD fluorescence dynamics remains [6,7]. Our experiments shed light on some of the basic photophysical processes determining the fluorescence dynamics of the nanocrystals and reveal a more complex picture of the emission dynamics than was assumed in earlier models. We observe a pronounced correlation between large spectral shifts and blinking events at low temperature. This surprising correlation between fluorescence intermittency and large spectral diffusion shifts suggests a "cause-and-effect" relationship that can be rationalized based on an early model developed to describe photobleaching of semiconductor nanocrystals [8]. Although blinking phenomena are prominent in many single chromophores, our model differs from previous other models which include intersystem crossings into a long-lived triplet state, spectral diffusion of the absorbing state, and interchromophoric energy transfer [9,10].

We study many individual QDs simultaneously using a homebuilt, epifluorescence microscope described in Ref. [11] coupled with fast data storage and data analysis. Under continuous wave (514 nm, Ar ion) excitation, single QD emission spectra are measured with a time resolution of 100 ms for durations of an hour. The single dot fluorescence studies were performed using a cold finger liquid helium cryostat with a long working distance air objective (N.A. 0.7). The raw data are collected in a series of consecutive images to form nearly continuous three-dimensional data sets as shown in Fig. 1. An advantage of charge-coupled device detection over avalanche photodiode or photomultiplier tube detection is that spectral data of single QDs can be obtained in one frame using a monochromator. Moreover, all of the dots imaged on the entrance slit of the monochromator are observed in parallel. If only relative frequency changes need to be addressed, then the entrance slit can be removed entirely, allowing parallel tracking of emission frequencies and intensities of up to 50 nanocrystals simultaneously. The data analysis program then retrieves the time-frequency-intensity emission trajectories for all of these QDs. The CdSe QDs are prepared following the method of Murray *et al.* [12] and protected with ZnS overcoating [13,14]. All single QD samples are highly diluted and embedded in a half-micron thin film of PMMA.

The spectrally resolved time traces shown in Fig. 2 summarize the typical phenomenology of spectral shifting and blinking for different quantum dots at low temperature (10 K). Time traces of these three QDs observed simultaneously show large variations in their spectral dynamics during the observation time. The spectrum in Fig. 2(a) shows sharp emission lines with nearly constant frequency and intensity, the spectrum in Fig. 2(b) shows some pronounced spectral shifts and a few blinking events, and the spectrum in Fig. 2(c) is fluctuating in frequency and shows a number of blinking events on a much faster time scale. The spectral information clearly shows that, for a single quantum dot under the perturbations of its environment, there are many possible transition energies (i.e., a dynamically changing emitting state). Net shifts as large as 14 nm were observed in our experiments. This observation

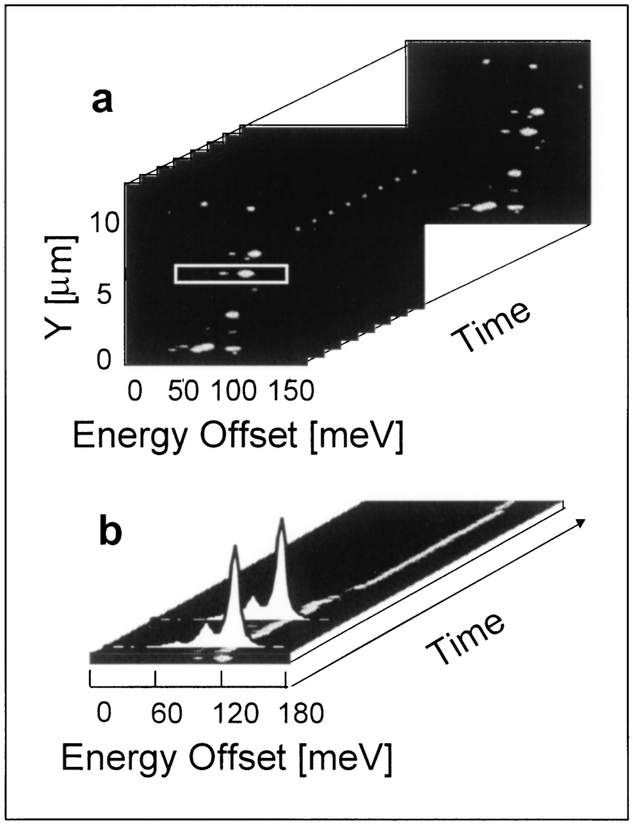

FIG. 1. Low temperature (10 K), spectrally dispersed image of multiple dots. (a) The dots are spatially separated along the vertical axis and spectrally resolved along the horizontal axis. Nearly continuous frames (100 ms integration time) allow for tracking of optical dynamic behavior. (b) A single QD marked in (a) is followed in time and its spectral trajectory is plotted.

immediately questions the application of static three (or four) level models to describe the emission dynamics observed from single QDs strongly coupled to the immediate environment. Rather, these emission dynamics suggest a QD intimately coupled to and reacting to a fluctuating environment. We expect from this observation that physical properties like fluorescence lifetimes or quantum efficiency, even when measured on a single dot basis, will provide average values over a large number of different states of the QD/environment system. Zooming into the time traces of Figs. 2(b) and 2(c) reveals that blinking and shifting between these multiple emitting states is *correlated.* As shown in Fig. 2(d), magnifying the marked region in the time trace of Fig. 2(b) reveals a pronounced correlation between individual spectral jumps and blinking: Following a blink-off/blink-on event, the energy of the emitted photons is changed. At first glance, this does not seem to hold for the dot shown in Fig. 2(c). However, as shown in Fig. 2(e), zooming into the time trace of Fig. 2(c) reveals a similar correlation. As in Fig. 2(d), the trace shows dark periods that are accompanied by discontinuous jumps in the emission frequency. The periods between shifts in Figs. 2(d) and 2(e), however, differ by nearly an order of magnitude in time scales. Because of our limited time resolution, no blinking events shorter than 100 ms can be detected. Any fluorescence change that is faster than the "blink-and-shift" event shown in Fig. 2(e) is not resolved by our apparatus and appears in a statistical analysis as a large frequency shift during an apparent on-time period. This limitation weakens the experimentally observed correlation between blinking and frequency shifts. Nevertheless, a statistically measurable difference between shifts following on and off times can be extracted from our results.

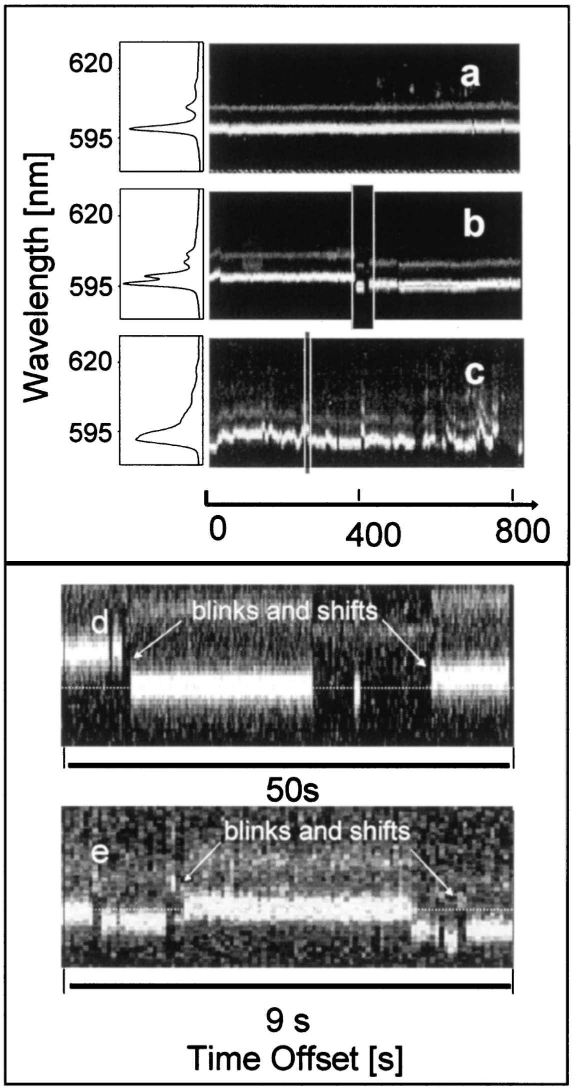

FIG. 2. Low temperature emission frequency time traces of three ZnS overcoated CdSe dots taken at the same time ($T = 10$ K, bin width = 100 ms, 200 W/cm$^2$). (a)–(c) The resulting averaged spectrum is plotted for each dot. Although all three dots originate from the same well-defined sample, they show completely different spectral diffusion patterns. (d),(e) The marked areas in the time trace of dot 2 and dot 3 are shown on an enlarged scale. The blinking "on" after a dark period is accompanied by a large spectral shift. Note the different time scales between the two dots. The white dotted line is drawn in (d) and (e) as a guide to the eye.

Since changes in the emitting state cannot be observed when the QD is off, we compare the net shifts in the spectral positions between the initial and final emission frequency of each on and off event. The histogram of net spectral shifts during the on times, shown in Fig. 3(a), reveals a nearly Gaussian distribution (dark line) with 4.2 meV full width at half maximum. However, the histogram for the off-time spectral shifts in Fig. 3(b) shows a distribution better described as a sum of two distributions: a Gaussian distribution of small shifts and a distribution of large spectral shifts located in the tails of the Gaussian profile that do not fit a simple Gaussian distribution. To illustrate the difference between the distributions of on- and off-time spectral shifts, the on-time spectral distribution is subtracted from the off-time spectral distribution shown in Fig. 3(c). Even though our measurements have a time resolution of 100 ms, this difference histogram shows that large spectral shifts occur significantly more often during off times (longer than 100 ms) than during on times; hence, large spectral shifts are more likely to accompany a blink-off event than during the time the QD is on. This statistical treatment does not try to assess the distribution of QDs that show this correlation but rather confirms the strong correlation between spectral shifting and blinking events in the QDs observed. The off-time histogram, plotted on a logarithmic scale in Fig. 3(d), shows that a Gaussian distribution (dark line) does not describe the distribution of off-time spectral shifts [15].

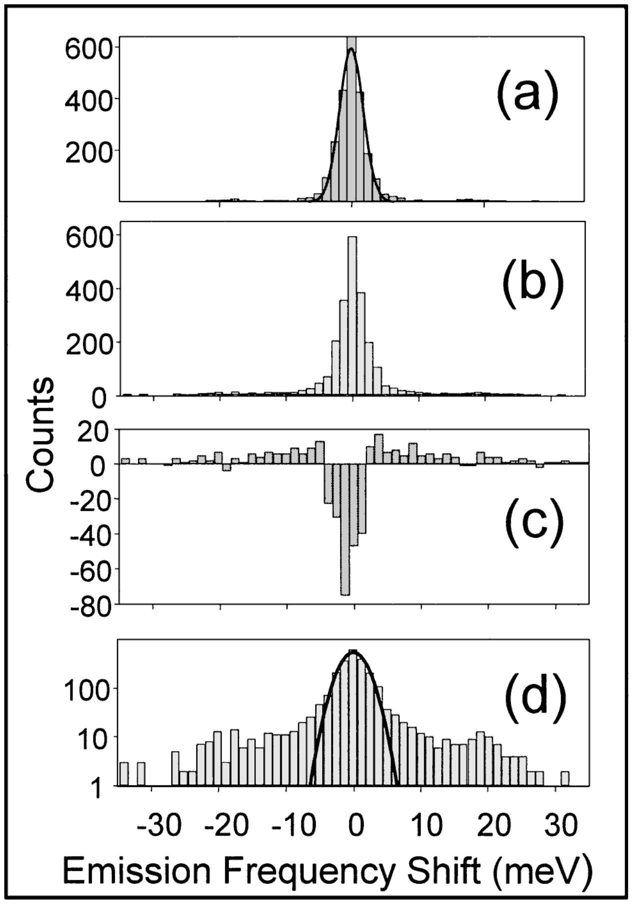

FIG. 3. Distribution of net spectral shifts between the initial and final emission frequency for 2400 on and off periods of 9 CdSe/ZnS QDs at 10 K. (a) Histogram of net spectral shifts for the on period shows a Gaussian distribution of shifts. The dark line is a best fit to Gaussian profile. (b) Histogram for off periods displays large counts in the wings of a similar Gaussian distribution. (c) Subtracting the on-period distribution from the off-period distribution magnifies the large counts in the wings of the Gaussian distribution. This quantifies the correlation that the large spectral shifts accompany an off event (longer than 100 ms) more than an on event. (d) A logarithmic plot of the histogram shows a clearer indication of the non-Gaussian distribution in the net spectral shifts during the off times. The dark line is a best fit to Gaussian profile.

The correlation observed between blinking and spectral shifting events elucidates the possible mechanisms behind these dynamical processes. The two behaviors have been described as a consequence of the interaction between the QD and the local environment, but a correlation between blinking and spectral shifting events had not been predicted. This correlation differs from blinking *caused* by spectral shifting observed in single molecules such as pentacene in a $p$-terphenyl matrix [9,16]. In single molecule experiments, the chromophore is resonantly excited into a single absorbing state and a spectral shift of the absorbing state results in a dark period since the excitation is no longer in resonance. In our experiments, we excite nonresonantly into a large density of states above the band edge [17]. An early model [1] described the fluorescence intermittency results based on a photoionization process. The transition from a bright to a dark QD occurs through the trapping of an electron or hole leaving a single delocalized hole or electron in the QD core. Upon further excitation of the QD, fast nonradiative relaxation follows due to energy transfer from the exciton to the delocalized charge carrier through the Auger mechanism [8]. The switch from a dark to a bright QD then occurs through recapture of the initially localized electron (hole) back into the QD core or through capture of another electron (hole) from nearby traps. When the electron-hole pair recombines, the QD core is no longer a site for exciton-electron (exciton-hole) energy transfer. Conversely, Empedocles and Bawendi [18] showed evidence that spectral diffusion shifts were caused by a changing local electric field around the QD. The magnitude of the changing local electric field was consistent with a single electron and hole trapped near the surface of the QD.

We can now combine both models to explain the correlation as shown in Figs. 2(d) and 2(e) between large spectral jumps and blinking. Using the assumption that a charged QD is a dark QD [19], there are four possible mechanisms for the transition back to a bright QD. Electrostatic force microscopy studies on single CdSe QDs recently showed positive charges present on some of the QDs [20] even after exposure to only room light. In our model, after cw laser excitation and exciton formation, the QD turns "off" when an electron or hole from the exciton localizes near the surface of the QD leaving a delocalized charge carrier inside the QD core. Following this initial charge localization or ionization, the QD turns back "on" as a result of the following possible mechanisms: (a) The delocalized charge carrier can also become localized near the surface leading to a net neutral QD. This localization may be thermally driven, or more likely driven through the Auger process itself. If the QD environment is decorated by charges following process (a), then after subsequent ionization, (b) a charge localized in the QD's nearby environment can relax back into the QD core recombining with the delocalized charge carrier or (c) the initial localized charge relaxes back into the core and recombines with the delocalized carrier. This last mechanism can be accompanied by a permanent reorganization of the localized charges present in the QD environment due to Coulombic interactions as the photogenerated carrier traps and detraps. Mechanisms (a), (b), and (c) would create, if not alter, a surface dipole and lead to a net change in the local electric field. The single QD spectra express this change as a large Stark shift in the emission frequency. However, the model does not necessarily require that a blinking event be followed always by a shift in emission frequency. If the dark period is produced and removed by a localization and recapture of the same charge without a permanent reorganization of charges in the environment [mechanism (d)], the emission frequency does not change. Any changes in the emission frequency during this mechanism would be entirely thermally induced and such small spectral shifts are observed. Indeed, this pathway for recombination dominates very strongly, as most dark periods are not accompanied by large frequency shifts. The processes described under mechanisms (a), (b), and (c) appear much less likely to occur. Nevertheless, these processes can introduce an increased complexity to the observed dynamics.

In conclusion, we have shown a strong correlation between large spectral shifting events and blinking of single nanocrystals by measuring simultaneously fluorescence intensity and fluorescence frequency of single dots. This dynamical behavior can be explained by extending the photoionization model that describes blinking in semiconductor nanocrystals as a result of a QD ionization and Auger electron-exciton (hole-exciton) energy transfer, a mechanism that differs from the process known to cause blinking in single molecules.

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[1] M. Nirmal, B. O. Dabbousi, M. G. Bawendi, J. J. Macklin, J. K. Trautman, T. D. Harris, and L. E. Brus, Nature (London) **383**, 802 (1996).
[2] S. A. Empedocles, R. Neuhauser, K. Shimizu, and M. G. Bawendi, Adv. Mater. **11**, 1243 (1999).
[3] M. D. Mason, G. M. Credo, K. D. Weston, and S. K. Buratto, Phys. Rev. Lett. **80**, 5405 (1998).
[4] B. P. Zhang, Y. Q. Li, T. Yasuda, W. X. Wang, Y. Segawa, K. Edamatsu, and T. Itoh, Appl. Phys. Lett. **73**, 1266 (1998).
[5] R. M. Dickson, A. B. Cubitt, R. Y. Tsien, and W. E. Moerner, Nature (London) **388**, 355 (1997).
[6] U. Banin, M. Bruchez, A. P. Alivisatos, T. Ha, S. Weiss, and D. S. Chemla, J. Chem. Phys. **110**, 1195 (1999).
[7] M. Kuno, D. P. Fromm, H. F. Hamann, A. Gallagher, and D. J. Nesbitt, J. Chem. Phys. **112**, 3117 (2000).
[8] D. I. Chepic, A. L. Efros, A. I. Ekimov, M. G. Vanov, V. A. Kharchenko, I. A. Kudriavtsev, and T. V. Yazeva, J. Lumin. **47**, 113 (1990).
[9] T. Basche, J. Lumin. **76–77**, 263 (1998).
[10] W. T. Yip, D. H. Hu, J. Yu, D. A. Vanden Bout, and P. F. Barbara, J. Phys. Chem. A **102**, 7564 (1998).
[11] S. A. Empedocles, D. J. Norris, and M. G. Bawendi, Phys. Rev. Lett. **77**, 3873 (1996).
[12] C. B. Murray, D. J. Norris, and M. G. Bawendi, J. Am. Chem. Soc. **115**, 8706 (1993).
[13] M. A. Hines and P. Guyot-Sionnest, J. Phys. Chem. **100**, 468 (1996).
[14] B. O. Dabbousi, J. RodriguezViejo, F. V. Mikulec, J. R. Heine, H. Mattoussi, R. Ober, K. F. Jensen, and M. G. Bawendi, J. Phys. Chem. B **101**, 9463 (1997).
[15] The on-time histogram also has weak tails on top of the Gaussian distribution because of apparent on-time spectral shifts that may have occurred during an off time faster than the time resolution (100 ms) allowed by our present setup.
[16] W. P. Ambrose and W. E. Moerner, Nature (London) **349**, 225 (1991).
[17] D. J. Norris and M. G. Bawendi, Phys. Rev. B **53**, 16 338 (1996).
[18] S. A. Empedocles and M. G. Bawendi, Science **278**, 2114 (1997).
[19] Note we make a distinction between a charged QD where the charge is delocalized in the core of the QD (a dark QD) and a charged QD where the charge refers to trapped charges localized on the surface or in the organic shell surrounding the QD (not necessarily a dark QD).
[20] T. D. Krauss and L. E. Brus, Phys. Rev. Lett. **83**, 4840 (1999).