Correlations between Subsequent Blinking Events in Single Quantum Dots

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Correlations between Subsequent Blinking Events in Single Quantum Dots

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ABSTRACT We explain the long-range correlations found by Stefani and his co-workers between blinking times of single colloidal quantum dot emission. Our explanation is based on the multiple recombination center model we recently suggested. The model produces positive correlations between subsequent on−on and off−off times and negative on−off correlations, as observed in the experiment. We also reproduce qualitatively the dependence of correlations between subsequent on−on, on−off, and off−off times on the number of switching events separating them.

KEYWORDS Nanocrystal, fluorescence intermittency, memory effect, long-range dependence, single molecule, nanowire

The vast majority of single fluorophores exhibit remarkable fluctuations of the emission intensity, or blinking.[1] Some of them, such as colloidal quantum dots,[2−4] nanorods,[5,6] nanowires[7,8] and even some dye molecules,[9] show an intricate dynamic behavior, blinking with long-range time correlations. Not long after blinking was reported in CdSe colloidal semiconductor quantum dots (QD),[2] an important discovery was made, namely that blinking trajectories follow scale-free statistics spanning from milliseconds to hours.[10] Indeed, if one defines a more or less arbitrary threshold of emission intensity above which the fluorophore is considered in an ON state, and conversely, below which it is considered in an OFF state, the histograms of times spent in both regions follow an inverse power law, $P_{ON/OFF}(t) \propto 1/t^m$. Subsequent studies showed evidence that the power law has an upper truncation time.[11−13]

The ubiquity of the power law has led to the suggestion that the underlying mechanism of blinking should be universal.[14] As a basis for explaining the blinking phenomenon, theories[4,10,15−17] most often invoke the charging of the QD suggested by Efros and Rosen.[18] Single photon measurements however show a continuous distribution of exciton lifetimes,[19−21] which is in contradiction with the charging mechanism. Jha and Guyot-Sionnest recently found[22] that the charged QDs are not dark; they emit with a quantum efficiency of about 10%. These experimental facts inspired several recent alternative explanations.[23−25] These novel theoretical frameworks attribute the fluctuations of the emission intensity to atomic rearrangements in the QD surface layer. As expected for a nanometer-sized system, the surface region contains a large part of the atoms building up the QD. Most recently, we proposed a phenomenological model of multiple recombination centers (MRC) to address the blinking process.[25] We have shown that this model can successfully explain several key features of QD blinking. Here we address another experimental result that shows that the blinking has a long-term memory.[26] Stefani and his co-workers measured the correlations between subsequent ON and OFF times and concluded that there are spectacularly strong correlations between blinking events (positive for ON−ON and OFF−OFF while negative for ON−OFF correlations, as shown below). They also noticed that the correlations decay slowly as they are separated by more and more switching events. This effect is not explained by other models proposed of quantum dot fluorescence fluctuation.[4,10,15−17,23]

In the present paper, we show that the MRC model can semiquantitatively reproduce the ON and OFF time correlations observed in experimentally measured fluorescence intensity trajectories. We investigate two interesting aspects of the ON and OFF correlations. First, we show (see Figure 1) how the two-point distribution function (PDF) depends on which combination of blinking events is chosen (ON−ON, OFF−OFF, ON−OFF, or OFF−ON). Second, we look at the decay of correlations as a function of the number of switching cycles separating them (also called lag[27]). The switching cycle is counted at the OFF→ON transition. The dependence on the lag parameter n is given in Figure 2.

The fluorescence trajectories were obtained by Protasenko and Kuno on CdSe/ZnS core/shell quantum dots.[28] By applying the standard threshold procedure,[3] two finite sets of ON (bright) and OFF (dark) time durations were generated. We will denote these two sets with τ_i^{ON} and τ_i^{OFF}, where $i = 1, 2$, and so forth. Furthermore, to capture features of distributions spanning multiple orders of magnitudes, we are also introducing the following variables $y_i^{ON} = \log_{10}(\tau_i^{ON}/\tau_0)$ and $y_i^{OFF} = \log_{10}(\tau_i^{OFF}/\tau_0)$, where τ_0 is the experimental bin time. The experimental results for blinking time correlations shown in upper panels on Figure 1 and Figure 2 are calculated for a single QD trajectory that exhibits a grouping of bright and dark states, similar to the trajectories

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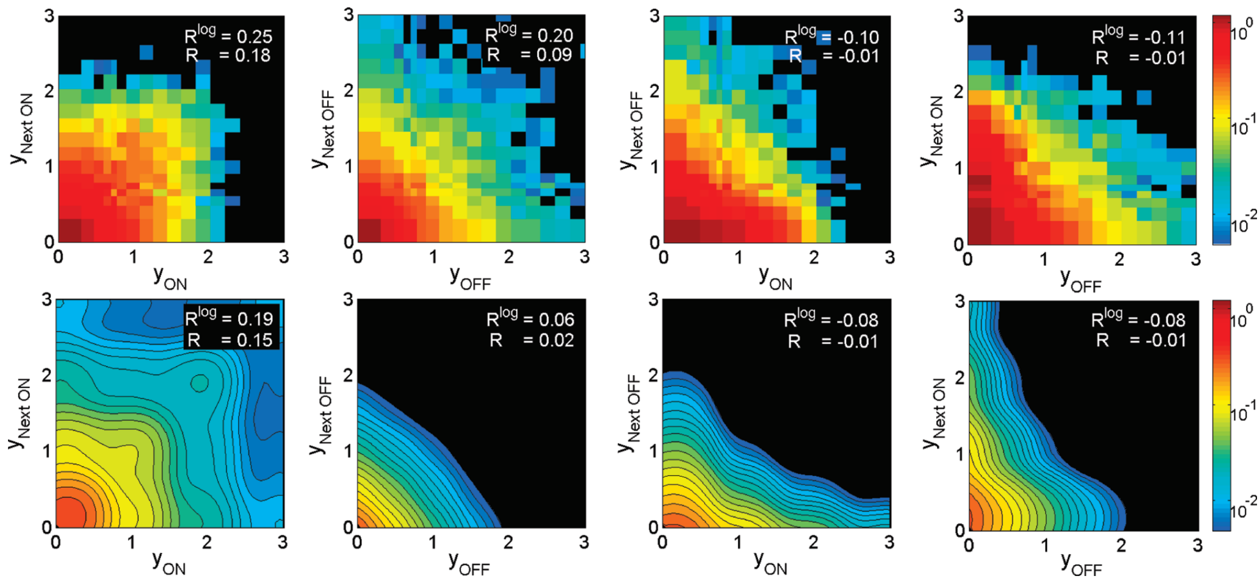

FIGURE 1. Correlation between the nearest ON−ON, OFF−OFF, ON−OFF, and OFF−ON times. The two-point probability density function is extracted from the experimental QD trajectory (upper panels) and compared to the same quantity calculated from the MRC model. From left to right: $f_{ON-ON}(y_1, y_2)$, $f_{OFF-OFF}(y_1, y_2)$, $f_{OFF-ON}(y_1, y_2)$, and $f_{ON-OFF}(y_1, y_2)$. Both time and log time correlation coefficients are shown in the upper right corner of each panel.

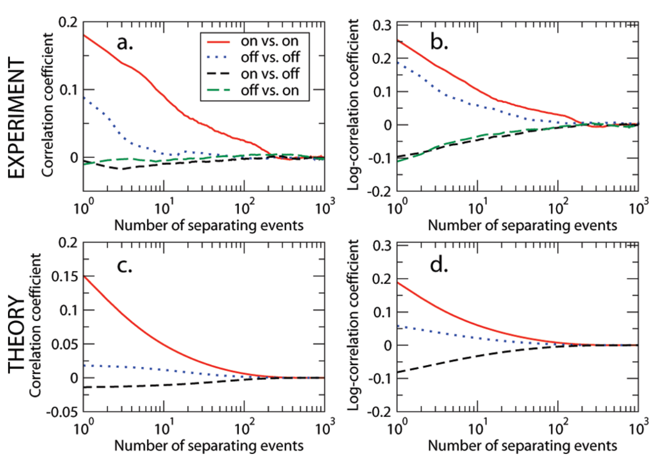

FIGURE 2. Decay of correlation and log−correlation coefficients as a function of the number of switching cycles elapsed between the correlated times. The following combination of ON and OFF times are positively correlated: continuous line (red), ON vs next ON; dotted line (blue), OFF vs next OFF. The remaining combinations are negatively correlated (anticorrelated): short-dashed line (black), ON vs next OFF; and long-dashed line (green), OFF vs next ON. Panels a and b show time−time correlations and respectively log time−log time correlations (log−correlations) from experiment. Panels c and d show the same quantities but now calculated with the MRC model.

of ref 26. While the choice of the particular trajectory that we analyze is somewhat arbitrary, it is representative of the experimental fluorescence trajectories available to us. In fact, we extracted the correlation coefficients for more than fifty QD trajectories and found similar results. The theoretical predictions shown in the lower panels on Figure 1 and Figure 2 are found within the MRC model. A detailed description how PDFs and correlation coefficients are extracted from the experimental fluorescence trajectory and calculated for the MRC model can be found in the Supporting Information. Most importantly, we would like to point out that the theoretical results for the correlations are robust: they remain qualitatively unchanged for the entire region of physically relevant parameter space. Note that a similar theoretical formalism for the calculation of the correlations between blinking events has been applied elsewhere in the context of single molecule kinetics.[29,30]

In Figure 1, we present the correlation between ON/OFF times and the next nearest ON/OFF times. The upper panels show the two-point probability density function extracted from the experimental data sets. The figure shows plots for all four combinations of blinking states: $f_{ON-ON}(y_1, y_2)$, $f_{OFF-OFF}(y_1, y_2)$, $f_{OFF-ON}(y_1, y_2)$, and $f_{ON-OFF}(y_1, y_2)$. The lower panels show the PDFs obtained from the MRC model.

Both the experimental and theoretical plots show marked features along the diagonal. For the ON−ON distributions, the plotted PDFs are large along the diagonal, which is a signature of positive correlation. This feature is also clearly present for the experimental OFF−OFF distribution and weakly in the corresponding theoretical results. The ON−OFF distributions show high PDF values along the horizontal axis that in turn corresponds to a negative correlation. The OFF−ON distribution has a similar form, showing high PDF values along the vertical axis. Interestingly, the experimental OFF−ON distributions can be used to qualitatively reproduce the experimental ON−OFF distribution by switching the two variables of the PDF. This mapping (in essence, a reflection with respect to the diagonal) is exact for the theoretically obtained PDFs. Similarly, the experimental ON−ON and OFF−OFF distributions are qualitatively symmetric with

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respect to reflection along the diagonal, whereas for the theoretically calculated PDFs this reflection symmetry is exact.

Following Stefani et al.,[26] we introduce the Pearson correlation coefficient for blinking times separated by n switching cycles

$$R_{\mathrm{gr}}(n) = \frac{\langle(\tau_i^{\mathrm{g}} - \bar{\tau}^{\mathrm{g}})(\tau_{i+n}^{\mathrm{r}} - \bar{\tau}^{\mathrm{r}})\rangle}{\sqrt{\langle(\tau_i^{\mathrm{g}} - \bar{\tau}^{\mathrm{g}})^2\rangle\langle(\tau_{i+n}^{\mathrm{r}} - \bar{\tau}^{\mathrm{r}})^2\rangle}} \tag{1}$$

There $\langle \cdot \rangle$ stands for the averaging operator, and indices g and r denote ON or OFF. Clearly, $-1 \le R \le 1$, making R suitable for comparison between all four combination of ON–ON, OFF–OFF, ON–OFF, and OFF–ON correlations. Since Figure 1 is for subsequent blinking events, the correlation coefficients in the upper right corner of each panel thus correspond to a lag value $n = 1$, except for ON–OFF correlation ($n = 0$). Both positive and negative (anti) correlations can be detected by the correlation coefficient defined in this manner. We also calculate[26] the correlation between the logarithms of the ON and OFF times, which is especially well-suited for the power law distribution of blinking times in quantum dots. The resulting log–correlation coefficient, $R_{\mathrm{gr}}^{\log}(n)$, is defined formally the same way as $R_{\mathrm{gr}}(n)$, by applying the change of variables $\tau \to y = \log_{10}(\tau/\tau_0)$ in eq 1. Note that $R_{\mathrm{gr}}^{\log}(n)$ does not depend on τ_0. While a change in τ_0 generates a linear shift in all logarithmic time variables y, these shifts do not influence the log–correlation coefficient defined above.

Figure 2 displays R_{gr} and $R_{\mathrm{gr}}^{\log}$ as a function of the lag parameter n and demonstrates that there is finite correlation between subsequent ON and OFF times. This correlation is a measure of the residual memory present in the fluorescence fluctuation which slowly decays to zero as the number of separating switching events increases. The lag parameter is related to the time elapsed between the correlated ON and OFF events. Thus the decay of $R(n)$ is a measure of the gradual memory loss of the fluorescence fluctuation process. Any significant memory is lost in roughly 100 ON–OFF cycles. The ON–ON and OFF–OFF correlations are positive and well pronounced. Meanwhile the ON–OFF and OFF–ON correlations are much less pronounced and negative. Note, however, that the correlations $R_{\mathrm{ON-OFF}}$ or $R_{\mathrm{OFF-ON}}$ are very close to zero. The advantage of the logarithmic time correlation becomes evident here: With the help of $R_{\mathrm{gr}}^{\log}$ we find evidence for a finite anticorrelation between ON and next OFF (or OFF and next ON) times. All these features are qualitatively reproduced by the MRC model. Theory and experiment also agrees in the general trend of ON–ON correlations being stronger then OFF–OFF correlations. Note that the theoretical ON–OFF and OFF–ON correlation coefficients are identical. However, numerical agreement has not been achieved in the present form of the MRC model. The theoretical values for the correlation coefficients are systematically smaller compared to the experimental data. We wish to reemphasize here that we have not fine-tuned the MRC model parameters. A detailed comparison between theory and experiment will most likely require a microscopic model.

In the MRC model,[25] we suggest that for every QD there is a given number N of nonradiative recombination centers (deep traps). These centers are most likely associated with surface defects. The carrier trapping ability, or rate, of each center can randomly change between a high and a low value, corresponding to an active and a passive state, respectively. The total trapping rate fluctuates in time according to the expression

$$k_{\mathrm{t}}(t) = k_0 + \sum_{i=1}^{N} k_i \sigma_i(t) \tag{2}$$

The individual trapping rates in active configuration are k_i while the background k_0 is the total trapping rate if all RCs are passive plus any other constant rate of all other nonradiative channels. Accordingly, the state σ_i of each center can be 0 or 1. The switching process for the ith center is defined by two rates. The rate γ_i^+ corresponds to the transitions $0 \to 1$, while γ_i^- describes the inverse transition $1 \to 0$.

The fluctuation in the trapping rate results in quantum efficiency and fluorescence emission intensity fluctuations. Variation of k_{t} is slow on the time scale of electronic processes and the radiative rate of the exciton recombination k_{r} is constant.[21] Within the steady-state approximation the emission intensity time dependence can be expressed as[23,25]

$$I(t) \sim \frac{1}{1 + k_{\mathrm{t}}(t)/k_{\mathrm{r}}} \tag{3}$$

By introducing some threshold level for the intensity I_{th}, we define the state of the QD as ON when $I(t) \ge I_{\mathrm{th}}$, and OFF otherwise. The intensity threshold corresponds to a threshold value for the nonradiative rate k_{th}. Indeed, if $k_{\mathrm{t}}(t) \le k_{\mathrm{th}}$ the QD is ON and OFF otherwise.

The parameters of the model were introduced in ref 25 and are in compliance with basic physical properties of the QD blinking phenomenon. N is set to be 10, which is in agreement with the experimentally obtained estimate for the number of surface traps in the QD.[31] We further reduce the number of parameters by assuming equal rates for trapping, $k_i = k$ and $k_0 = 0$. The switching times have to be widely distributed to explain the many orders of magnitude that the fluorescence fluctuation process spans in time: from milliseconds to hours. So, we suggested that "bare" switching times (without interaction) follow the geometric sequence

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$$\gamma_i = \gamma_1 a^{i-1} \tag{4}$$

The parameter a is set to be $10^{-1/2}$ so as to cover at least 5 orders of magnitude in time domain. The switching rate of the first RC γ_1 determining the scale of time in the model is set to be $1/\tau_0$.

The mean-field interaction between RCs

$$\gamma_i^{\pm} = \gamma_i \exp(\pm\alpha \sum (\sigma_i - 1/2) \pm \beta) \tag{5}$$

is characterized by the positive parameter α and has been introduced to reproduce qualitatively the commonly seen two-peak form of the distribution of the emission intensities. The bias parameter β tunes the relative weights of these two peaks. It has to be negative to make the ON peak reasonably large. We have shown in ref 25 that the introduction of the interaction and the bias to the model also helps to reproduce qualitatively the threshold dependence of the exponents in the ON and OFF time distributions. The values of these parameters $\alpha = 0.3$ and $\beta = -0.2$ utilized in the manuscript are slightly different from the ones used in ref 25 ($\alpha = 0.27$ and $\beta = -0.13$). We found that the model predictions for the correlation coefficients depend on these parameters very weakly. The same qualitative behavior is seen when their values vary within a wide range ($0 < \alpha < 0.5$ and $-0.5 < \beta < 0$). The dimensionless parameter $k_{tt} = k_{th}/k$ determines a threshold value for the nonradiative rate. We set $k_{tt} = 4$, which is close to the median value ($0 < k_{tt} \leq 10$), but our analysis revealed that if it is kept within the neighborhood of the median, the results are qualitatively unchanged.

In conclusion, we demonstrated that the MRC model predicts long-range correlations between consequent blinking events. This is in contrast to all the previous models of the QD blinking.[4,10,15−17,23] The physical reason for the long correlations between blinking times in our model is in the hierarchy of the RC switching times. The longest OFF events, for example, correspond to the configuration where almost all RCs are in active conformation. The QD could become bright again only if some number of RCs would switch to the inactive conformation. Immediately after a long OFF event, the OFF−ON transition would most likely be caused by a couple of "fast" RCs (with short switching times) switching to inactive conformation. It is then natural to expect a fast switching back to the OFF state in this case, when one of these "fast" RC jumps back to active conformation. The "slow" RCs need much more time to switch. Thus most probably a short ON event would follow a long OFF event. The "slow" RCs are still in the active conformation, so next OFF event has quite large probability to be long again. This reasoning leads us to the conclusion that there is a positive correlation between consequent OFF times and negative OFF−ON correlation. Analogously, we expect positive ON− ON and negative ON−OFF correlations. The correlations have to be kept on the time scales corresponding to the "slow" RCs switching times. That is exactly the behavior seen on Figure 2. As demonstrated in this paper, the observation of correlations in the QD blinking first proposed by Stefani et al.[26] proves to be an important experiment that sheds light on the nature of the underlying physical process. Note that analogous correlations were found recently in the fluorescence emission of the single perylene diimide molecule,[27] which is another sign that there is an universal molecular mechanism behind the fluorescence intensity fluctuation of fluorophores. The key features of the ON and OFF correlations in the intensity fluctuation process are in qualitative agreement with the MRC model. These are (1) the positive OFF−OFF and the especially well pronounced ON−ON correlations, (2) the negative and small ON−OFF and OFF−ON correlations, and (3) the residual memory duration of 100 ON−OFF cycles.

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Supporting Information Available. Details of the statistical analysis of the experimental trajectory. Statistics of the log-correlation coefficients for the single quantum dot fluorescence trajectories. Detailed description of the theoretical calculations within MRC model. Discussion on influence of the finite trajectory length to the correlations between blinking times. This material is available free of charge via the Internet at http://pubs.acs.org.

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