Memory in quantum-dot photoluminescence blinking

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Abstract. We demonstrate that subsequent on- and off-times of the luminescence blinking of semiconductor quantum dots (QDs) are correlated, indicating that the process behind is not memoryless. A residual memory, which has been overlooked in previous investigations of the blinking, is found to last for several (\(\sim 40\)) detected on/off cycles. No influence of the substrate nature or the excitation intensity is observed, pointing to a process intrinsic to the QDs. These results should encourage re-analysis of existing data and may represent the key to understand the underlying physical mechanism of QD luminescence blinking.

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1. Introduction

Colloidal semiconductor nano-crystals, also known as quantum dots (QDs) are attractive chromophores which in comparison to organic dye molecules have a number of advantages such as higher photostability, wide band-edge absorption and narrow emission tunable across the complete visible spectrum. However, their performance is limited by a severe intermittency in emission; i.e. single QDs emit measurable fluorescence during limited time intervals ($t_{on}$) separated by dark periods ($t_{off}$) in which only experimental background is detected. This effect limits the brightness of QDs and their applicability in spectroscopy of single-biological molecules [1, 2] and quantum information processing using single-photon sources [3]. It has been universally observed in QDs of different compositions and structures [4]–[6] that the probability of a certain $t_{on}$ or $t_{off}$ ($P(t_{on})$ and $P(t_{off})$ respectively) follows an inverse power law. As a consequence, the QDs may stay dark for hundreds of seconds. Similar power laws were obtained for long dark periods in the fluorescence of organic chromophores [7, 8] and for the fluctuations of single-molecule Raman signals [9]. The mechanism of QDs blinking is not yet understood and represents a question of relevance not only from a fundamental point of view of confined semiconductor physics but also from a technological standpoint because it might allow us to develop strategies to obtain QDs with the highest performance.

Since the discovery of the fluorescence intermittency in CdSe QDs [10], a photo-assisted Auger ionization process was suggested as responsible for the blinking. However, all the reported experimental data show a different behaviour than predicted by such a model. While exponentials would be expected for $P(t_{on})$ and $P(t_{off})$ [11], power laws are found consistently in the experiments [4]–[6]. Furthermore, a photo-assisted Auger process predicts a quadratic dependence of the average on-time on excitation intensity, whereas the experiments show a linear behaviour [10, 12]. This resulted in the discussion of alternative mechanisms such as thermally activated ionization [4], electron tunnelling through fluctuating barriers [4] or to a uniform distribution of traps [13] and resonant electron tunnelling between the excited state of the QD and a dark trap state which wanders randomly in energy [5].
In a recent work [14], we showed that the emission blinking of QDs can be described by two completely independent mechanisms. Firstly, on-periods are shortened by a photo-induced transition from the on- to the off-state. This part of the blinking is fully described by a single-transition rate, thus leading to an exponential contribution to the on-time distribution. This contribution was found to depend not only on the excitation intensity but also on the QD’s surroundings. Secondly, a spontaneous blinking occurs independently of the excitation intensity and the environment, producing power-law distributed probabilities for \( t_{\text{on}} \) and \( t_{\text{off}} \) \( (P(t_j) = A t_j^{-m}; A = \text{constant}) \). In this framework, spontaneous blinking can be fully characterized by two parameters: the relative strength of the on \( \rightarrow \) off and off \( \rightarrow \) on transitions and the exponent \( m \) of the power law. For QDs on isolating (glass) and conducting (ITO) substrates and for excitation intensities spanning 2 orders of magnitude, we found that the spontaneous on- and off-switching processes are equally probable and the exponent of the power law \( m \) is constant and close to 1.7 [14].

These two parameters that do not show any response to variations of external stimuli contain very limited information. Therefore, elucidation of the underlying mechanism of the power-law blinking on a sound experimental basis is a difficult task. In a highly complex system such as a QD, various physical processes can and have been put forward as the underlying mechanism for the blinking. Further experimental evidence requires extraction of additional, independent parameters from the experiments. One experimental measure that does reveal information on microscopic dynamics and can be used to test physical models is the memory between successive events. This approach has been recently applied to study single proteins. There, memory in the dynamics of conformational changes [15] and between successive activity/inactivity periods [16, 17] was investigated. It was first pointed by Kuno et al [4, 6] that for QDs as well, correlations between subsequent \( t_{\text{on}} \) and \( t_{\text{off}} \) would be a third independent parameter to be extracted from the blinking. In particular, if this parameter could be influenced by some external stimulus it may yield important insight into the physics behind the spontaneous process. In the analysis of Kuno, no correlation between the duration of subsequent on- or off-periods was observed, pointing towards a completely memoryless process and therefore not providing any further information about the spontaneous blinking.

In this work, we investigate the photoluminescence blinking of QDs and show that consecutive on- and off-periods are correlated. Since this effect is directly visible only on a logarithmic timescale, it has been overlooked in earlier studies. Firstly, possible artefacts that may be introduced by our data evaluation and may lead to a correlation are discussed. Secondly, the distribution of the responses of individual dots is investigated as well as the duration of the memory effect. The influence of excitation intensity and electronic properties of the substrate is addressed.

2. Experimental

Monocrystalline \( \text{Zn}_{0.42}\text{Cd}_{0.58}\text{Se} \) QDs with an average diameter of 6.2 nm were prepared as described in [18], presenting an ensemble band-edge absorption peaking at 515 nm and an ensemble emission maximum at 545 nm. They were diluted in toluene (\( \geq 99.7\% \); Riedel-de Haën) and spin-cast onto glass (N1; Menzel-Gläser) or indium-tin-oxide (ITO)-coated glass substrates (50 nm; Fraunhofer-Institut IST, Braunschweig). The concentration was adjusted to a surface density of approximately one QD per \( \mu \text{m}^2 \). The QDs were investigated through the glass slides...
Figure 1. (a) Fluorescence micrograph of individual Zn_{0.42}Cd_{0.58}Se QDs. (b) and (c) Emission versus time traces of two different QDs (QD1 and QD2) under identical experimental conditions (on glass, equal excitation intensity) and their corresponding intensity distributions. The curves are the sum of two Poisson distributions with the same average as the experimental on- and off-intensity distributions. (e) and (f) Histograms of the $t_{\text{on}}$ and $t_{\text{off}}$ detected by means of a suitable threshold (horizontal line) from the data shown in (b) and (c) respectively. The lines are power laws with an exponent $m = 1.65$. For clarity, only 60 s of the time traces are shown but the intensity and the $t_{\text{on}}$ and $t_{\text{off}}$ histograms are computed from the complete data. (d) Emission versus time trace of a single-dye molecule (SM) and the corresponding intensity distribution. The inset shows the same data with a stretched $x$-axis. (g) Histograms of the $t_{\text{on}}$ and $t_{\text{off}}$ detected by means of a suitable threshold (horizontal line) from the SM data shown in (d).

on a home-built sample scanning confocal microscope. A region of the samples was imaged (see figure 1(a)), a single QD was moved into the focus and the photoluminescence emission was recorded as a function of time. Circularly polarized light (Ar-ion laser, CW, coherent, $\lambda = 514.5 \text{ nm}$) was used to excite the QDs through a 1.4 NA oil-immersion objective. Photons emitted by the QDs were collected by the same objective, separated from the excitation light by suitable dichroic and notch filters and their arrival times were recorded with a resolution of 50 ns by a single-photon counting system (avalanche photodiode ‘Perkin Elmer SPCM-AQR-13’ + time-correlated single-photon counting module Becker & Hickl SPC-630). Measurements on single-fluorescent molecules (DiI C1(5); Molecular Probes) were performed in the same way.

For the purpose of identifying the $t_{\text{on}}$ and $t_{\text{off}}$, histograms of the photon arrival times were computed and a suitable threshold (a number of detected photons per bin) was used to classify the
Figure 2. Correlations of adjacent on- and off-times (in seconds) detected from the photoluminescence blinking of 15 QDs on glass plotted on linear (top) and logarithmic (bottom) scales. The excitation intensity was $P = 0.75 \text{ kW cm}^{-2}$. The linear correlation coefficients $R$ and $R_{\log}$ of the times and of the logarithm of the times are shown in the corresponding graphs. The scatter plot of $t_{\text{on}}$ versus the next $t_{\text{on}}$ (not shown) is similar to the one of $t_{\text{on}}$ versus the next $t_{\text{off}}$.

Bins as on or off in a similar way as described in [6]. Figures 1(b) and (c) show such histograms for two different QDs. An experimental measure of $P(t_{\text{on}})$ and $P(t_{\text{off}})$ was obtained by computing a histogram of the detected $t_{\text{on}}$ and $t_{\text{off}}$ (figures 1(e) and (f)).

3. Residual memory in the emission blinking of an ensemble of QDs

Similarly to previous studies [4, 6], we first addressed the temporal correlation of the $t_{\text{on}}$ and $t_{\text{off}}$ by means of scatter plots of successive on- and off-times detected in the emission blinking of several QDs.

Figure 2 shows the scatter plots of the $t_{\text{on}}$ versus the successive $t_{\text{on}}$, the $t_{\text{off}}$ versus the successive $t_{\text{off}}$ and the $t_{\text{on}}$ versus the successive $t_{\text{off}}$, obtained from 15 QDs on glass. In agreement with the previous observations [4, 6], no correlation is evident from visual inspection of the graphs plotted on a linear scale. Since $t_{\text{on}}$ and $t_{\text{off}}$ are power-law distributed, this is not surprising. In a double logarithmic scale, a noticeable correlation is observed between consecutive on-times and between consecutive off-times. Remarkably, no correlation is obvious between consecutive on- and off-times. For small values of $t_{\text{on}}$ and $t_{\text{off}}$, the data points lie on lines; this artefact is due to the time discretization introduced by the histogram analysis. The apparently irregular pattern of lines observed in the graphs of figure 2 arises from the computation of data obtained from several QDs which were analysed with different optimized bin-widths.
In order to quantify this correlation, the linear (Pearson) correlation coefficient (shown in
the corresponding graphs of figure 2) was calculated between the adjacent times \((R)\) and between
the logarithm of adjacent times \((R_{\text{log}})\) as \([25]\)

\[
R = \frac{\sum(X_n - \bar{X})(Y_n - \bar{Y})}{\sqrt{\sum(X_n - \bar{X})^2 \sum(Y_n - \bar{Y})^2}},
\]

where \(X\) and \(Y\) stand for the duration or the logarithm of the duration (in any time unit) of
the corresponding time-period plotted along the \(x\)- or \(y\)-axis in the scatter plots. \(\bar{X}\) and \(\bar{Y}\) are
the averages of \(X\) and \(Y\), respectively, and the sums are performed for all the points of each
scatter plot. \(R\) and \(R_{\text{log}}\) can take values between \(-1\) and \(1\). These extreme cases would indicate
that all the \((X, Y)\) points of a scatter plot could be connected by a single straight line. \(R = 0\)
would indicate that there is no evidence of a linear relationship between \(X\) and \(Y\). The difference
between \(R\) and \(R_{\text{log}}\) is that \(R\) weights more the correlation between long times, whereas \(R_{\text{log}}\)
weighs more the correlation between short times. The obtained values of \(R\) and \(R_{\text{log}}\) indicate
clearly the correlation between consecutive \(t_{\text{on}}\) and consecutive \(t_{\text{off}}\).

### 4. Residual memory in the emission blinking of individual QDs

Next, in order to assure that the correlation does not arise from the common computation of
several different populations, we investigate the correlations on a single QD basis. Figure 3
shows the scatter plots of successive \(t_{\text{on}}\) and \(t_{\text{off}}\) for the datasets displayed in figure 1. Apart from
the poorer statistics due to the smaller datasets, both QD1 and QD2 show correlations that are
roughly consistent with the ensemble behaviour displayed in figure 2. All the 206 investigated
QDs showed similar correlation behaviour to QD1 and QD2 (see the distributions of \(R\) and \(R_{\text{log}}\)
in section 6). Nevertheless, some differences are noted between QD1 and QD2 and are discussed
below.

In total agreement with the ensemble correlations, both QD1 and QD2 show a positive coefficient for the \(t_{\text{on}}/t_{\text{on}}\) correlation in agreement with the ensemble result. For successive \(t_{\text{off}}\), QD2 has a value of \(R\) similar to the
ensemble one, whereas QD1 presents an \(R\) significantly smaller. The values of \(R\) obtained for
the \(t_{\text{on}}/t_{\text{off}}\) correlation are for both QD1 and QD2 close to zero.

In addition, figure 3 shows as a reference the scatter plots of successive \(t_{\text{on}}\) and \(t_{\text{off}}\) detected
in the blinking of a single DiI molecule (SM). As expected for a system switching on–off
randomly, the blinking of a single molecule does not show any correlation. This reference is so
important because it shows that the experimental set-up used for this study does not introduce
artificial correlations.

Thus, the observed correlations do not arise from the common computation of \(t_{\text{on}}\) and
\(t_{\text{off}}\) detected from several QDs.
Figure 3. Scatter plots of the adjacent on- and off-times (in seconds) detected in the blinking of the QD1, QD2 and SM of figure 1. In all cases, linear and logarithmic plots are shown with the corresponding values of $R$ and $R_{\text{log}}$. 

|       | $t_{\text{on}}$ vs. next $t_{\text{on}}$ | $t_{\text{off}}$ vs. next $t_{\text{off}}$ | $t_{\text{on}}$ vs. next $t_{\text{off}}$ |
|-------|----------------------------------------|------------------------------------------|----------------------------------------|
| QD1   | ![Plot](image1)                         | ![Plot](image2)                          | ![Plot](image3)                         |
|       | $R=0.21$                                | $R=0.07$                                 | $R=-0.04$                              |
|       | $R_{\text{log}}=0.40$                   | $R_{\text{log}}=0.27$                    | $R_{\text{log}}=-0.09$                 |
| QD2   | ![Plot](image4)                         | ![Plot](image5)                          | ![Plot](image6)                         |
|       | $R=0.27$                                | $R=0.17$                                 | $R=-0.01$                              |
|       | $R_{\text{log}}=0.50$                   | $R_{\text{log}}=0.48$                    | $R_{\text{log}}=-0.23$                 |
| SM    | ![Plot](image7)                         | ![Plot](image8)                          | ![Plot](image9)                         |
|       | $R=0.07$                                | $R=-0.05$                                | $R=-0.005$                             |
|       | $R_{\text{log}}=-0.09$                  | $R_{\text{log}}=-0.02$                   | $R_{\text{log}}=0.04$                  |
5. Limitations of the time-binning analysis

It is known that the time-binning analysis used to detect \( t_{\text{on}} \) and \( t_{\text{off}} \) might introduce artefacts [14]. In the case of the blinking of QDs, two issues need to be addressed. Firstly, since \( P(t_{\text{on}}) \) and \( P(t_{\text{off}}) \) are power laws, there is a very large number of very short \( t_{\text{on}} \) and \( t_{\text{off}} \) and artefacts may arise from the limited time resolution of this method which is unable to detect them. Secondly, the QDs show a super-Poissonian on-intensity that may render the discrimination of on- and off-states difficult. In the following, we address these two issues.

5.1. Limited time resolution

The time-binning analysis we used to detect the \( t_{\text{on}} \) and \( t_{\text{off}} \) has an unavoidably limited time resolution. The time-bins for a perfect on/off binary system can be classified into three groups: ‘on-bins’ where the system stays in the on-state for the complete bin, ‘off-bins’, where the system stays in the off-state for the complete bin and ‘mixed bins’, where the system spends a fraction of the bin-time in each state. The fluorescence blinking of single fluorescent molecules is a good example of such a binary on/off system [19]. Figure 1(d) shows data corresponding to the fluorescence blinking of a single DiI molecule. The intensity distribution (histogram of photons per bin) for single molecules is dominated by the sum of two Poissonians with mean values corresponding to the on- and off-intensity, respectively. Nonetheless, due to the mixed bins, the probability to find a bin with an intermediate number of photons is increased (see the inset in figure 1(d)).

Obviously, an assignment of bins as on or off based on a suited threshold is prone to errors due to mixed bins which are neither of the two possibilities. However, it turns out that for the single molecule this evaluation method yields a robust measure of \( P(t_{\text{on}}) \) and \( P(t_{\text{off}}) \) as was shown by Monte Carlo simulations [19]. This is illustrated again here experimentally: the on/off blinking of single DiI molecules corresponds to excursions of the excited molecules to the long-lived triplet state [19]–[22], the on- and off-times are exponentially distributed (figure 1(g)) and uncorrelated as is expected for a random process (figure 3).

For the extraction of different parameters from a system with different photophysics, it must be proved again that the occurrence of mixed bins does not significantly influence the result. This is especially important in the case of QDs because, since \( t_{\text{on}} \) and \( t_{\text{off}} \) are power-law distributed, there is a large (theoretically infinite) number of \( t_{\text{on}} \) and \( t_{\text{off}} \) smaller than the bin width at every detected switching event. In order to test the influence of the mixed bins on the observed correlations, we performed Monte Carlo simulations of a power-law distributed random blinking for a binary on/off system as described in [14]. The simulated photon arrival times were analysed in the same way as the experimental ones. As shown in figure 4, the simulated QD presents an intensity distribution showing the Poisson components and ‘mixed bins’ as in the case of a single molecule. The detected \( t_{\text{on}} \) and \( t_{\text{off}} \) are power-law distributed and no correlation is observed. Thus, we conclude the observed correlation does not arise from the limited time resolution of the time-binning analysis.

5.2. Blinking statistics for fluctuating on-intensities

The off-intensity observed in the emission blinking of QDs is Poisson-distributed with an average equal to the experimental background intensity, showing that the QDs do stop emitting during the
Figure 4. (a) Time trace of a simulated on/off binary QD and the corresponding intensity distribution; the solid lines are Poisson distributions. (b) Histograms of the $t_{on}$ and $t_{off}$ detected by means of a suitable threshold (horizontal line) from the simulated data shown in (a). The line is a power law with an exponent $m = 1.67$. (c) Scatter plots of the adjacent $t_{on}$ and $t_{off}$ (in seconds) detected in the blinking of the simulated QD, both on a linear and on a logarithmic scale. The values of $R$ and $R_{\log}$ are shown in the graphs.

off-periods. On the other hand, QDs present in general a distribution of on-states which leads to a super-Poissonian distribution of photons per bin in the on-bins [23, 24]. Even the on-intensity of the cases resembling mostly a binary on/off system (e.g. QD1, figure 1(b)) does not reach the similarity to a Poisson distribution that is observed for a well-defined on-state as in the case of single-dye molecules. As a consequence, on-bins with low intensities are wrongly classified as off. This could lead, for example, to the interpretation of a true long on-period as being composed of several shorter on-periods separated by single off-bins. In the following, we consider possible implications of this effect on the measured correlations.

Since there is no knowledge about how the on-intensity fluctuations occur, it is not possible to perform proper simulations to compare to the experiments. One approach to investigate experimentally the influence of the broad on-intensity distribution on the blinking parameters extracted from a time-binning analysis, is based on a comparison of the results obtained from experimental datasets with on-intensities with minor and major deviations from a Poisson distribution. It is expected that any artefact due to the fluctuating on-intensities should become more pronounced if the intensity distribution gets broader. The two QD examples shown in figures 1(b) and (c) were chosen to illustrate this. These QDs were studied under identical experimental conditions and present extreme cases of the distribution of on-states. The QD1, has an almost Poisson-distributed on-state which can be clearly separated from the off-state by the
threshold, thus permitting an optimum detection of $t_{\text{on}}$ and $t_{\text{off}}$. On the other hand, the QD2 presents a more typical broad on-intensity distribution. For the determination of $P(t_{\text{on}})$ and $P(t_{\text{off}})$, it is found that as long as the maximum of the Poisson-distributed off-intensity can be detected, a satisfactory discrimination between on- and off-bins can be performed by choosing an optimum set of bin-width and threshold as if the on-intensity were Poisson distributed. This is verified by the identical power laws of $P(t_{\text{on}})$ and $P(t_{\text{off}})$ obtained for the QD1 and QD2 (figures 1(d) and (e)). In this work, only datasets for which the Poisson-distributed off-intensity could be identified (and thus a proper threshold could be set) were considered.

The same approach as for the $P(t_{j})$ is used here to validate the extraction of the correlation coefficients. As seen in figure 3, a similar appearance of the scatter plots as well as values for $R$ and $R_{\log}$ are obtained for QD1 and QD2. Figure 5 displays two further examples of QDs (QD3 and QD4) with well-separated on- and off-states. Although the on-intensity distribution is in all cases broader than a Poissonian, only the bins containing less photons than the threshold are important for the wrong assignment of an on-state as off. In this region, the deviations from the double Poissonian observed in QDs such as QD1, QD3 and QD4 are indistinguishable from the deviations observed in a perfectly binary system such as the simulated on/off binary QD (figure 4). This indicates that these deviations are predominantly due to mixed bins, whereas a low-intensity tail of the on-intensity distribution which would cause problems is, if exists, negligibly weak. Further evidence that the on- and off-states are properly separated in these cases is found in the fact that the results obtained are independent of the choice of the threshold, as long as it is chosen within the mixed-bin region. For example in the case of QD4, identical results for $P(t_{\text{on}})$, $P(t_{\text{off}})$, $R$ and $R_{\log}$ are obtained with any threshold within 7 and 14 photons per bin (transparent window in figure 5). Although it cannot be excluded with absolute certainty, an effect of a fluctuating on-intensity seems highly improbable in these cases. In cases where the on- and off-states are not well separated, the obtained correlation coefficients depend on the chosen threshold and this has an influence in the distributions of $R$ and $R_{\log}$ (see section 6).

The correlations obtained for QD1, QD3, QD4 and other QDs with alike intensity distributions are very similar. From the differences with respect to QDs with broader on-intensities such as QD2 (discussed in section 4), it can be deduced that a fluctuating on-intensity has an influence on the detected correlations. Nevertheless, the observation of clear correlations for the QDs with well-separated off- and on-states strongly supports the interpretation that the principal component of the memory effect arises from the on/off blinking itself and not from the on-intensity fluctuations.

Based on the observations described in the previous two sections, we conclude that the residual memory is a genuine characteristic of the blinking of QDs and proceed to further characterize this effect.

6. Independence of the substrate nature and excitation intensity

Since most of the physical mechanisms for QD blinking that are currently discussed in literature predict an influence of excitation intensity and/or environment, we investigated the correlations for QDs on glass and ITO substrates under different excitation intensities. Figure 6 shows the distributions of $R$ and $R_{\log}$ for the on/on, off/off and on/off correlations obtained from QDs on glass and ITO substrates. Practically identical behaviour is observed for the QDs on glass and ITO.
Figure 5. Blinking data of two QDs (QD3 and QD4) with a very small number of wrongly assigned bins. The time trace, the corresponding intensity distribution, the histograms of the detected $t_{on}$ and $t_{off}$ and the scatter plots of adjacent $t_{on}$ and $t_{off}$ are shown in the same fashion as in figure 4. Only a fraction of the complete time traces are shown for clarity. The $P(t_{off})$ of QD3 and QD4 are fitted by a power law with exponents 1.52 and 1.53, respectively. The values of $R$ and $R_{\log}$ are shown next to the scatter plots. In the case of QD4, the semi-transparent window in the time trace shows the range of thresholds that retrieve identical power laws and correlation coefficients.
Figure 6. Distributions of the $R$ and $R_{\log}$ obtained from the blinking of QDs on glass and ITO and of single DiI molecules. In the case of QDs, experiments were carried out at six different excitation intensities $P$ (0.026, 0.18, 0.75, 0.95, 1.60 and 2.05 kW cm$^{-2}$). The overall distribution (All P) and the distribution for $P = 0.75$ kW cm$^{-2}$ (One P) are shown.
In a logarithmic evaluation, the off/off and the on/on correlation coefficients are distributed around \( \langle R_{\text{log}} \rangle = 0.37 \) with a standard deviation of \( \sigma = 0.06 \). This shows that the observed values represent with some scatter a general feature of all observed dots. No events are found with \( R_{\text{log}} = 0 \) and all the QDs with well-separated on- and off-states (such as QD1, QD3 and QD4) show coefficients close to the average, indicating that this is a true on–off blinking memory. The distribution of \( R_{\text{log}} \) for the on/off correlation is shifted from zero to negative values; a mean of \(-0.13\) \((\sigma = 0.07)\) is determined from the data. It is observed that the values of \( R_{\text{log}} \) obtained for the on/off correlation of QDs with well-separated on- and off-states lie at the tail of the distribution close to zero. This indicates that the observed on/off anti-correlation might be caused by the fluctuating on-intensity.

The linear evaluation shows a different behaviour. The distributions of \( R \) for the on/on correlation are clearly positive with an average around \( 0.2 \) \((\sigma = 0.07)\) and very few events close to zero. As in the case of \( R_{\text{log}} \) for the on/on and the off/off correlations, all the QDs with well-separated on- and off-states show values of \( R \) for the on/on correlation which are positive and very close to the average. The distribution of \( R \) for the off/off correlation is significantly broader. Similarly to the case of \( R_{\text{log}} \) for the on/off correlation, we found here that the QDs with well-separated on- and off-states present the lowest values of \( R \); in any case, although small, the obtained values are always positive. This indicates that the greater values of \( R \) for the off/off correlations have a contribution which arises from the fluctuating on-intensities. One possible reason for the real lower value of \( R \) in the off/off correlation may be the stronger weight on long times applied in the calculation of \( R \). It seems that the memory may be lost after very long off-times while the on-times are generally short enough to preserve some memory. In the case of the on/off correlation, both QDs on glass and ITO show a sharp distribution of \( R \) peaking at zero \((\langle R \rangle = 0.007, \sigma = 0.045)\).

Experiments were performed at six different excitation intensities \( P \) spanning two orders of magnitude and no obvious influence of \( P \) was observed. This can be seen in figure 7, for all correlation coefficients and for both substrates, by the high similarity between the distributions obtained at an excitation power of \( 0.75 \text{ kW cm}^{-2} \) and the accumulated histogram, over all employed excitation intensities. The mean values of \( R \) and \( R_{\text{log}} \) are shown for the two substrates under investigation in figure 7. No significant effect of varying power is observed.

The lowest part of figure 7 shows, as a reference, the distribution of \( R \) and \( R_{\text{log}} \) obtained from the blinking of several DiI molecules. Once more, the on–off switching of the organic chromophores appears to be memoryless.

### 7. Duration of the memory

Another interesting property of this residual memory is its typical timescale. In order to address this question, \( R \) and \( R_{\text{log}} \) were calculated between on- and off-periods separated by a given number of experimentally detected periods \( \Delta n \) and by a minimum time \( \Delta t \).

The correlation coefficient \( R(\Delta n) \) for the on-times is calculated in a straightforward manner by correlating on-times that are separated by a time interval containing \( \Delta n \) other on-times. It should be noted that this experimentally observed \( \Delta n \) does not correspond to the true number of switching events between two on-times which are theoretically infinitely many due to the power law.
Figure 7. Average correlation coefficients as a function of the excitation intensity $P$ for QDs on glass and ITO substrates.

In order to directly access a typical time of this memory effect, $R(\Delta t)$ was calculated by correlating a certain on-time with another one separated by a number of $t_{on}$ and $t_{off}$, so that the time elapsed in between was equal or larger than $\Delta t$. Obviously, this algorithm does not yield a precise time-dependence of the correlation but provides nonetheless some information on typical times. The situation for the correlations between $t_{off}$ and $t_{on}$ as well as between $t_{on}$ and $t_{off}$ is analogous.

Figure 8 shows $R$ and $R_{\log}$ for the QDs on glass and ITO as a function of $\Delta n$ and $\Delta t$. As $\Delta n$ or $\Delta t$ increase, $R$ and $R_{\log}$ approach zero indicating that the residual memory in all correlations under investigation vanishes after $\sim 40$ detected switching cycles or at $\Delta t \approx 3$ s, leaving only statistical fluctuations of $R$ and $R_{\log}$ for large $\Delta n$ or $\Delta t$. The anti-correlation observed in $R_{\log}$ between a given $t_{on}$ and the next $t_{off}$ presents a similar behaviour. Remarkably, all non-vanishing correlations exhibit similar decay curves.

Although $R(\Delta t)$ and $R_{\log}(\Delta t)$ do not permit to determine exactly how long the memory on the blinking lasts in terms of time, it is nevertheless possible to estimate that that the blinking memory does not vanish before 3–4 s.

8. Conclusions

In conclusion, we have found a correlation in the on- and off-times of the blinking of QDs as extracted from a time-histogram analysis. The correlations were analysed by means of the linear
correlation coefficient calculated between the length and between the logarithm of the length of the successive on- and off-periods. By means of Monte Carlo simulations, it was shown that the observed correlations do not arise artificially from the limited time resolution of the time-binning analysis. In order to determine the influence of the fluctuating on-intensity observed in QDs on the correlations, experimental data from QDs with well-separated on- and off-states was analysed separately.

On a logarithmic scale, it was found that subsequent on-periods and subsequent off-periods of the luminescence blinking of QDs are correlated, indicating that the processes behind the on/off blinking is not completely random but have a certain residual memory. These correlations are found to be independent of the shape of the on-intensity distribution, which is different for each QD and seems to be produced by local environmental changes [23]. Moreover, no influence of the substrate (ITO or glass) or the excitation intensity was observed pointing towards a process intrinsic to the QDs. The fact that $t_{on}$ and $t_{off}$ show similar correlation behaviour suggests that

**Figure 8.** Average correlation coefficients of on- and off-times separated by a certain number of detected on–off switching events $\Delta n$ and by a minimum time $\Delta t$. 

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both the on \(\rightarrow\) off and the off \(\rightarrow\) on processes follow a similar mechanism. Since all the QDs with well-separated on- and off-states show values of \(R_{\log}\) very close to zero for the on/off correlation, the weak anti-correlation in the distribution of \(R_{\log}\) seems to be an effect introduced by the fluctuating on-intensity of the majority of the analysed QDs. In that case, adjacent \(t_{on}\) and \(t_{off}\) would be uncorrelated indicating that the on \(\rightarrow\) off and the off \(\rightarrow\) on switching processes occur independently.

On a linear scale, it was found that subsequent on-periods are correlated independently of the shape of the on-intensity, the substrate and the excitation intensity. In the case of subsequent off-periods, a weaker correlation was observed since the higher values of \(R\) seem to be a product of the fluctuating on-intensity. Adjacent on- and off-periods appear absolutely uncorrelated in the linear analysis.

The memory of the blinking is found to last typically \(~40\) detected on/off cycles (\(\sim 3\text{–}4\text{ s}\)) and is observed in a linear and in a logarithmic scale, showing that this effect occurs in a wide range of time-scales. The obtained correlation coefficients \(R\) and \(R_{\log}\) are found to be invariable upon changes on excitation intensity and electronic states of the substrate. In the context of the blinking mechanism based on two-processes that was discussed recently [14, 29], these results imply that the residual memory is a characteristic of the spontaneous, power-law distributed component of the blinking which seems to be due to processes occurring inside or immediately at the surface of the QDs [14].

The correlation coefficient between successive on- and off-times introduced here provides an additional measurable quantity to characterize the blinking of QDs which should trigger additional experiments and re-analysis of existing data to reveal its dependence on temperature and other external stimuli. While this work presents first experimental evidence, a quantitative model taking account of correlations produced by the fluctuating on-intensities and the independent memory in the on/off blinking remains to be developed. This should provide new hints for the development of a consistent physical picture of the process behind the intriguing blinking luminescence of QDs.

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