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# Memory in Single Emitter Fluorescence Blinking Reveals the Dynamic Character of Nanoscale Charge Tunneling

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Luminescence blinking of single emitters is one of the most profound and intriguing issues in nano-optics and related areas. Its mechanisms and in particular the often observed deviant power-law statistics are a subject of ongoing recent debate. We examine *on*–*off* blinking in a dedicated synthetic trichromophoric assembly of perylene molecules. This trimeric system allows us to unambiguously discern blinking from photobleaching events and furthermore displays sufficient blinking events for a single-molecule analysis. An intriguing memory effect is observed, evidenced in clear correlations between successive *on*-times. In contrast, successive *off*-times are only weakly correlated and cross-correlations between *on*- and *off*-times are absent. Our results reveal the importance of nanoscale environmental dynamics on top of charge tunneling in understanding single emitter luminescence blinking. Dynamics of the polymer matrix and charge carriers therein is crucial to explain the power-law distribution of *on*-times. This result is directly relevant for related systems like semiconductor quantum dots, fluorescent proteins, and conjugated polymers.

## Introduction

Single quantum systems increasingly operate as the functional building block for nanotechnology applications in areas like sensing and detection, molecular photonics and electronics, and quantum computation and encryption. In general, such systems display a typical blinking behavior where emissive “*on*” states are randomly interrupted by non-emissive “*off*” states. A peculiar power-law distribution of *on*- and *off*-times has been observed for various systems including quantum dots and nanocrystals<sup>1,2</sup> and, recently, organic fluorescent molecules.<sup>3–7</sup> The main characteristic of power-law statistics is that, apart from frequent switching between *on*- and *off*-times with a relatively short duration, extremely long-lived *on*-, and more importantly, *off*-times can be observed.<sup>7–9</sup> For many applications relying on the optical properties of single nanosystems, such long-lived waiting times are very undesirable. Similar long-lived blinking events, indicative of power-law statistics, have also been observed on fluorescent proteins<sup>10</sup> and conjugated polymers.<sup>11</sup> Despite a considerable theoretical and experimental effort, an understanding of why and how this power-law behavior actually emerges is still lacking and subject of ongoing debate. The striking similarity in blinking behavior between these physically different systems is in this respect an important aspect. Whereas the complicated morphology of semiconductor quantum dots may give rise to a complex multi-state *on*-behavior,<sup>12,13</sup> single organic molecules exhibit a well-defined *on*-state, the duration of which still shows power-law statistics.<sup>7</sup>

The notion that charge separation is involved in entering the non-emissive state is widely accepted.<sup>1,14–19</sup> However, explaining the wide, power-law distributed range of survival times of the charge-separated state is far from trivial, and explanation of power-law distributed *on*-times has so far remained even more problematic.<sup>1</sup> Several models have been recently put forward.<sup>15–18</sup> These indeed, in several ways, predict power-law distributed *off*-times, but a unified view is still lacking and in particular problems still exist in explaining *on*-time power-laws for the variety of systems in which these have been observed. Although it has been established, both for quantum dots and organic molecules, that *on*-to-*off* and *off*-to-*on* switching events are uncorrelated,<sup>1,7</sup> the possibility of dynamic effects underlying the separate *on*- and *off*-time power-law distributions seems to have been largely overlooked. Recently, Stefani et al. have found that in a quantum dot system, correlations between successive *on*-times and successive *off*-times can exist.<sup>20</sup> This notion seems to be supported by other research.<sup>21</sup> The existence of such a memory, and in particular its characteristics for *on*- and *off*-time distributions, could provide an important clue for unraveling the nature of long-lived blinking events.

## Experimental Section

Our system consists of a perylene diimide (PD) trichromophore in a polymer matrix, which displays power-law statistics for both the *on*- and *off*-time distributions.<sup>5,7</sup> The trichromophore molecule, or in short trimer, consists of three head-to-tail oriented, rigidly linked *N,N'*-dipropyl-1,6,7,12,-tetrakis-(4'-*tert*-butylphenoxy)-3,4,9,10-perylenetetra-carboxylic diimide units (see Figure 1). The three aromatic moieties in the trimer are arranged perpendicular to each other, thus preventing electronic delocalization over the entire trimer. Instead, the three PD units are strongly coupled by dipole–

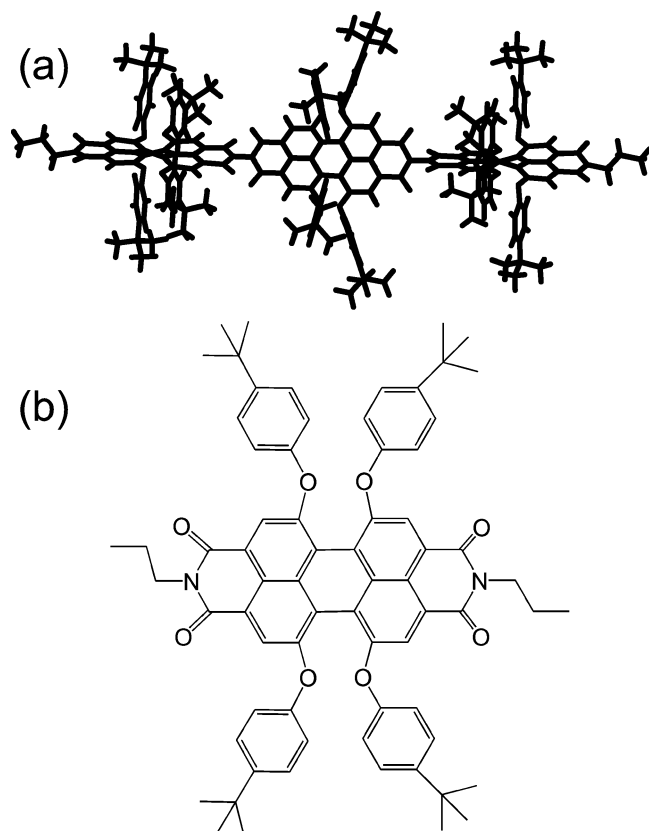
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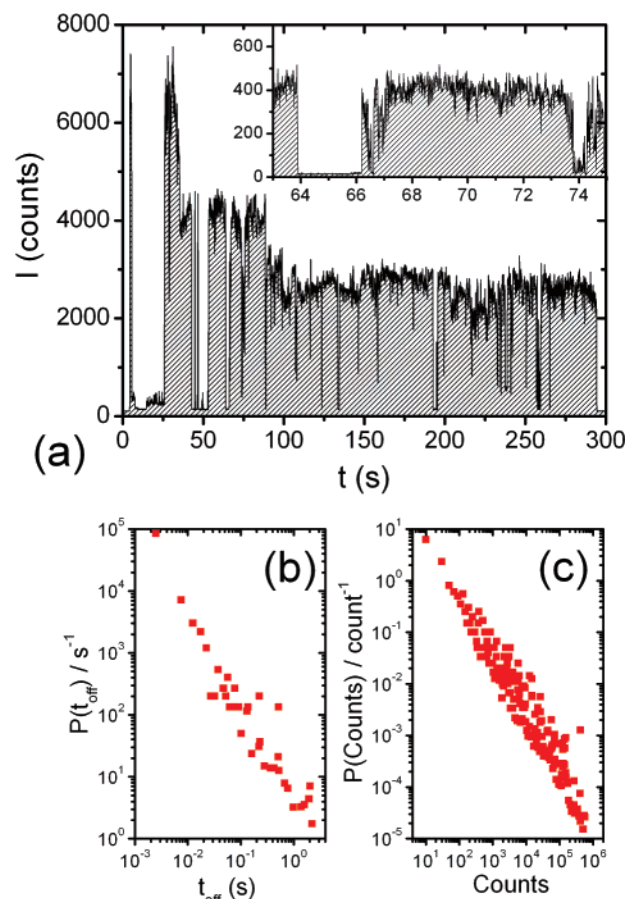
<sup>||</sup> ICREA.



**Figure 1.** (a) Geometry of the trimer molecule, consisting of three perylene diimide (PD) chromophore units. The geometry was calculated using the semiempirical MNDO (Modified Neglect of Differential Overlap) method in the Gaussian98 package with gas-phase optimization. (b) Molecular structure of a single PD chromophore. In the trimer, PD units are linked through covalent attachment of the nitrogen atoms, replacing the propyl groups.

dipole interaction, which leads to excited state, or exciton, delocalization over the entire trimer molecule. The trimer thus behaves as a single emitter in which, as reported previously, the signature of coupling can be observed in absorption and emission spectra,<sup>7</sup> fluorescence lifetime and photon antibunching,<sup>22</sup> and ultrafast excited-state dynamics,<sup>23</sup> both in the bulk and at the single-molecule level at room temperature. The strong coupling and the concomitant emission changes allow us to unambiguously discriminate between blinking and photobleaching events.<sup>5</sup>

Trimer molecules were embedded in a thin poly(methylmethacrylate) (PMMA) film by spincoating a toluene solution containing a low concentration of trimer molecules ( $\sim 10^{-9}$  M) and 5 g/L of PMMA onto oxygen-plasma etched glass cover slides. Single-molecule spectroscopy was performed using a home-built confocal microscopy setup. Trimer molecules were excited using pulsed (280 fs, 8 MHz repetition rate) laser illumination (Spectra Physics Tsunami 3960 with a Spectra Physics OPAL 1100-1300 nm optical parametric oscillator) at 568 nm wavelength and with circular polarization. The sample was illuminated through a 1.3 NA oil-immersion lens (Olympus), and the collected fluorescence light was separated from the excitation beam using a dichroic mirror and a 585 nm long-pass filter (Omega Optics 580DRLP and 585ALP, respectively) and subsequently split into two orthogonal polarization directions, each of which was focused onto the detection area of an avalanche photodiode (Perkin-Elmer SPCM-AQR-14). An average power density of 2.5 kW/cm<sup>2</sup> was used. Single molecule

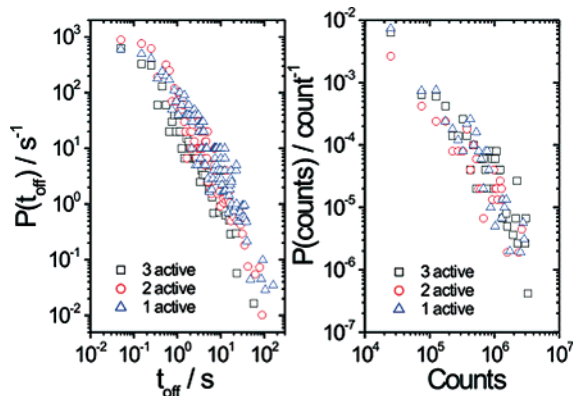


**Figure 2.** (a) Fluorescence intensity trace of a single PD trimer in PMMA (binned at 100 ms). Three intensity levels resulting from sequential photobleaching of the three PD units (at  $t = 35$  s,  $t = 88.5$  s, and  $t = 295$  s) can be discerned. *On-off* blinking occurs in all three levels with widely varying *on-* and *off-*time durations (see also inset, binned at 10 ms). (b) Probability density for the *off*-time duration for the molecule in (a), *off*-times retrieved with binning at 1 ms. (c) Like (b) but for the number of detected counts in the *on*-states. Both probability densities display a clear linear behavior corresponding to a power-law distribution.

intensity traces were recorded for a total of 300 s with a minimum binning time of 1 ms.

## Results and Discussion

Figure 2a shows a fluorescence intensity trace recorded for a single trimer molecule. Three different intensity levels can be clearly discerned, indicative of sequential photobleaching of the three PD units. This sequential photobleaching is also evidenced by simultaneous increase in the fluorescence lifetime as a result of decreased dipole–dipole coupling strength after partial photobleaching (data not shown). This has been described in detail in ref 22. The polarization ratio of the emitted light was found to remain constant, confirming the rigidity of the trimer molecule and allowing us to disregard orientational or conformational changes as the source of these intensity jumps.<sup>22</sup> Throughout the entire intensity trace in Figure 2a, *on-off* blinking can be observed, irrespective of the intensity level and thus of the number of active, non-photobleached PD units in the trimer. The probability density constructed from all 426 *on-* and *off*-time durations observed in this trace (at a binning of 1 ms) follows a clear power-law behavior (Figure 1b and c). Note that we express the *on*-time duration in the number of photon counts, that is, photoexcitation cycles, which is justified because the fluorescence quantum yield of all three intensity levels is



**Figure 3.** Probability densities per trimer intensity level for the *off*-time duration (left) and the number of counts in the *on*-times (right) for all blinking events observed in 199 trimer molecules (with minimum  $t_{\text{off}} = 25$  ms). Intensity levels have been designated corresponding to the number of non-photobleached PD units as given in the figure. For all three levels, similar power-law statistics are observed.

nearly one.<sup>22</sup> For the distributions, we find power exponents of  $m_{\text{off}} = -1.93$  and  $m_{\text{on}} = -1.25$  using maximum likelihood estimation.<sup>24</sup> Similar power-law behavior was observed for other individual trimer molecules,<sup>7</sup> as well as by adding *on*- and *off*-time durations from 199 trimer molecules<sup>5</sup> (see, e.g., Figure 3).

We ascribe the occurrence of the *off*-states to the formation of a radical ion in the trimer after electron or hole transfer from the exciton level to a charge acceptor in the environment of the molecule. Recently, Zondervan et al. demonstrated using electron-spin resonance that long-lived *off*-states in a system of Rhodamine 6G dye in a poly(vinylalcohol) matrix are caused by charge transfer.<sup>19</sup> Furthermore, the occurrence of power-law statistics for the *off*-times can only be satisfactorily described by models that take into account charge separation with acceptors located in the environment. Finally, spectral overlap between emission of the neutral dye and absorption of PD radical ions,<sup>25,26</sup> together with the short distances between the PD units in the trimer ( $\sim 1.3$  nm), gives rise to Förster energy transfer within the trimer between remaining active PD units and the perylene radical ion unit. Thus, the radical ion conjecture can also explain why the trimer in the highest and intermediate intensity levels, corresponding to three and two active PD units respectively, switches off collectively (cf. Figure 2a).

As can be seen in Figure 2a, *off*-times with strongly varying duration can be observed in each of the three intensity levels. An important advantage is the fact that for the two highest levels, blinking can be clearly separated from photobleaching, which is evidenced as a change in fluorescence intensity and lifetime.<sup>5</sup> Thus, for a trimer molecule we are sure to probe all *off*-states occurring before photobleaching. For a single dye molecule, as for the lowest intensity level in the trimer, long *off*-states may be missed as they cannot be discerned from a photobleaching event. A second advantage of the use of our trimer system is the fact that the probability of observing blinking events in a trimer trace is higher than for a single dye molecule because of the increased survival time of the trimer. For instance, for a PD monomer we found *off*-states (with  $t_{\text{off}} > 25$  ms) in 48% of 78 molecules, for a PD dimer in 68% of 82 molecules, and for the trimer in 93% of 214 molecules. Obviously, also the number of observable *off*-states per molecule is larger for a trimer than for a monomer. Thus, the trimer system provides a statistically more reliable system to investigate power-law blinking at the level of single molecules. However, we first have to establish that transitions between the different intensity levels do not

**TABLE 1: Power-Law Exponents Retrieved for the Three Different Intensity Levels, Corresponding to Different Numbers of Active Chromophores, by Adding Data from 199 Trimer Molecules**

trimer level	$m_{\text{off}}$	$m_{\text{on}}$	# events
3 active PDs	1.55	1.22	148
2 active PDs	1.53	1.18	381
1 active PD	1.42	1.20	371

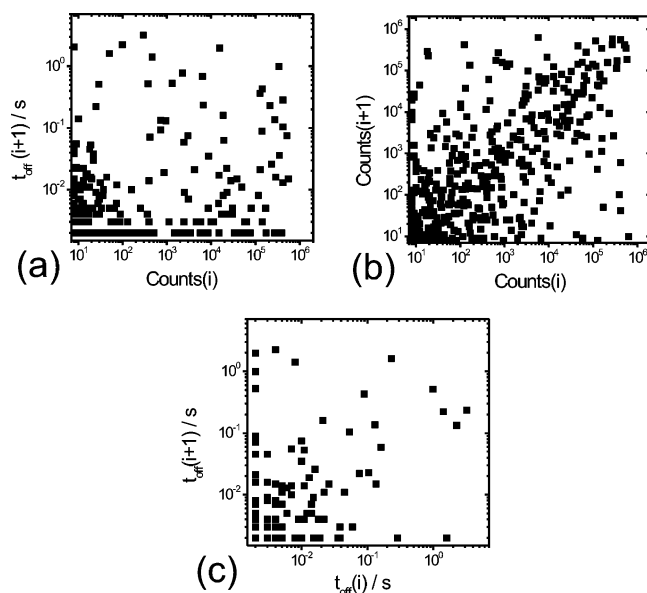
influence the *on*- and *off*-time statistics and that we can effectively treat our molecule as a two-state *on-off* blinker.

For a single trimer molecule, the number of observed blinking events per level is usually, at least for one of the levels, too small to reliably compare power exponents per level. For instance, for the molecule displayed in Figure 2a, only 17 blinking events were found in the highest intensity level, compared to 176 and 233 events in the intermediate and lowest levels, respectively. Thus, we analyze blinking events in 199 trimer molecules simultaneously and we separate all *on*- and *off*-times into those occurring in the highest intensity level (3 active PD units), intermediate intensity level (2 active units), and lowest intensity level (1 active unit). *Off*-states that were immediately followed by a level transition, that is, a photobleaching event, were removed from the data set. These “interlevel” *off*-states are terminated by partial photobleaching instead of back charge transfer to the trimer, and could thus change distributions for levels with 3 and 2 active units compared to the lowest intensity level. The resulting probability densities for *off*-times and *on*-times per level are given in Figure 3a and b, respectively. Clearly, all three distributions follow the same behavior, both for the *off*-states, as well as for the *on*-states. This is confirmed by the extracted power exponents listed in Table 1. Thus, we conclude that the blinking behavior of trimer molecules does not significantly change as a result of partial photobleaching and that, for example, intramolecular charge transfer does not play a significant role in the power-law blinking.

Next, we turn to the distributions of *on*- and *off*-states in single trimer molecule traces. For each molecule we retrieve a sequence of successive *on*-states and a similar sequence of *off*-states. An *on*-state with index  $i$  characterized by a number of detected photon counts  $\text{counts}(i)$  is followed by the *off*-state with index  $i$  of duration  $t_{\text{off}}(i)$ . In Figure 4a, we display the correlation graph between  $\text{counts}(i)$  and the corresponding *off*-state duration  $t_{\text{off}}(i)$  for the molecule shown in Figure 2a. Logarithmic axes are used because of the large range of the data. Correlations between *on*-states and subsequent *off*-states are negligibly small, which is confirmed by calculation of the corresponding linear correlation coefficients:  $R = 0.03$  and  $R_{\log} = 0.06$ , where  $R_{\log}$  corresponds to the correlation coefficient for log-log transformed data. Calculation of the correlation coefficient after logarithmic transformation puts relatively more weight to the shorter events, and thus, we will refer to  $R_{\log}$  as expressing short-time correlations. Correspondingly,  $R$  expresses long-time correlations. The absence of correlations between *on*- and *off*-states is in correspondence with results obtained by adding blinking events from all trimer molecules ( $R = -0.01$ ,  $R_{\log} = -0.09$ ).

Contrary to subsequent *on*- and *off*-states, correlations do appear for the same molecule when we plot successive *on*-states (Figure 4b) and successive *off*-states (Figure 4c). Between *on*-states  $i$  and  $i+1$  a linear correlation, indicative of a memory, is clearly present. Such a memory effect has been previously observed in the activity of single enzymes<sup>27</sup> and in the blinking of single quantum dots.<sup>20</sup> For the *on-on* correlation coefficients,



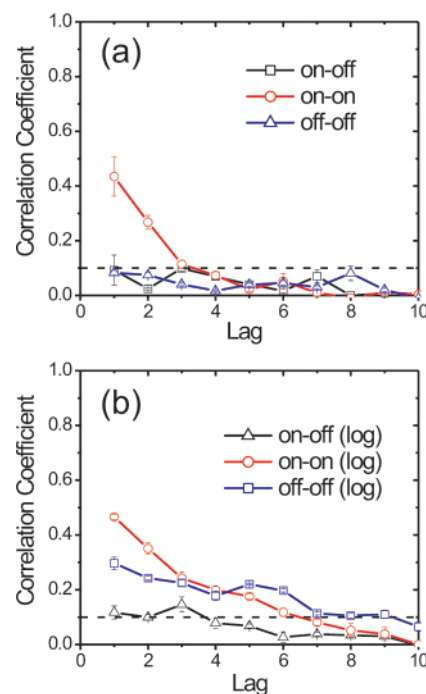


**Figure 4.** Correlation plots for the molecule shown in Figure 2. (a) *On*-time duration versus subsequent *off*-time duration, (b) *on*-time versus next *on*-time, (c) *off*-time versus next *off*-time. Correlations are absent between subsequent *on*- and *off*-events, but appear between successive *on*-times and weakly between successive *off*-times.

we find values of  $R = 0.44$  and  $R_{\log} = 0.60$ . For successive *off*-states, the correlation is less apparent, and we find correspondingly lower, but non-negligible, correlation coefficients:  $R = 0.16$  and  $R_{\log} = 0.29$ .

The presence of a memory in the power-law distributed set of *on*-times is confirmed by analysis of the entire data set of 199 blinking trimer molecules. In total, we observed 1096 pairs of successive blinking events in this data set (applying a uniform binning, and thus minimum  $t_{\text{off}}$  of 25 ms). For the *on*-states, we find  $R = 0.33$ , and for the *off*-states  $R = 0.01$ . To acquire more insight into long-time and short-time memory and to probe the extent of the memory, further analysis was carried out at the single-molecule level. In the data set, we have 9 molecules for which a threshold could be applied to the intensity trace after binning at 1 ms and that displayed sufficient blinking events for a single-molecule statistical analysis. The number of blinking events in these molecules ranged from 71 to 655. These molecules reveal a distribution of correlation values. For the *on*-states,  $R > 0.40$  for 7 of 9 molecules, while the other two molecules show no correlations ( $R < 0.1$ ). The threshold  $R = 0.1$  for assigning memory or not was determined by calculation of  $R$  and  $R_{\log}$  for uncorrelated experimental data, which gave values ranging from slightly negative to 0.1. For all 9 molecules,  $R_{\log}$  for the *on*-states is usually high, with at least  $R_{\log} > 0.1$ . For the *off*-states, 4 molecules show sign of weak correlation ( $R = 0.10$ – $0.30$ ), like the molecule in Figure 4, whereas the other 5 molecules have  $R < 0.10$ . The values of  $R_{\log}$  for the *off*-states vary between 0.1 and 0.7 for 8 molecules with one molecule with  $R_{\log} < 0.1$ . Thus, we conclude that the duration of successive *on*-states is clearly correlated, with the degree of correlation varying from molecule to molecule. For the *off*-states, correlations are absent or only weakly present, again with variations from molecule to molecule.

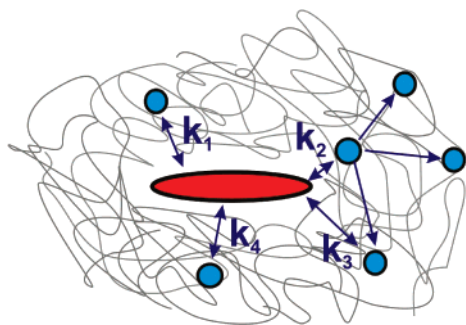
The extent of the memory was assessed by calculating auto- and cross-correlation functions for both the series of *on*- and *off*-states in each single-molecule trace. These correlation functions are expressed as a function of the lag  $\Delta i$ , or distance in index, between *on*- or *off*-states in their respective series. For  $\Delta i = 1$ , this gives the same result as the linear correlation



**Figure 5.** (a) Extent of memory probed by calculating autocorrelation (*on*–*on* and *off*–*off*) and cross-correlation (*on*–*off*) functions averaged over 9 single trimer molecules that displayed between 71 and 655 blinking events. The lag denotes the extent, expressed in index difference  $\Delta i$ , over which correlations are calculated. Error margins indicate the variance of the underlying single-molecule distribution. (b) Same result for the logarithmically transformed series of *on*- and *off*-states, probing a short-time memory, that is, between relatively short-lived events. Dashed lines indicate the threshold for assigning memory as explained in the text. *On*-time correlations appear over a limited number of successive blinking events. *Off*-time correlations are weak and predominantly (in (b) only) present over shorter time scales.

coefficients for successive events calculated above. Figure 5 displays the result of averaging each of the nine correlation functions. Like for the correlation coefficients  $R$  and  $R_{\log}$ , we distinguish between long-time memory, calculated from the untransformed data, and short-time memory calculated after logarithmic transformation. The corresponding correlation functions are given in Figure 5a and b, respectively. In Figure 5a, the correlations between successive *on*-states again clearly appear and it can be seen that this memory only lasts over 3 events on average. For the *off*-states as well as for *on*–*off* cross-correlations, memory is clearly absent. Examining the short-time correlations (Figure 5b), a weak correlation appears in the sequence of *off*-states as well. Furthermore, the extent of memory increases to about 6–7 blinking events for the shorter time-scales.

Several models have been proposed to explain the observed power-law blinking in single-emitters.<sup>15–18</sup> Taking into account electron or hole tunneling from the emitter to a static distribution of charge acceptors in the local environment as the mechanism for charge separation, the broad range of *off*-times observed in a power-law distribution can be explained.<sup>15,18,28</sup> Furthermore, the tunneling model is consistent with the observation of only weak temperature dependence of *off*-state population and depopulation kinetics in both quantum dots<sup>1</sup> and organic molecules.<sup>19</sup> However, the static tunneling model fails to explain the observed power-law distribution of *on*-state durations.<sup>1,15</sup> Dynamical rearrangements in the local environment of the emitter, could, in combination with charge tunneling, provide an explanation for the *on*-state power-law behavior.<sup>15,17</sup> As we will discuss below, the observation of correlations in a single-



**Figure 6.** Schematic indication of a polymer-embedded trimer molecule surrounded by four charge acceptors with charge-transfer rates  $k_1$ – $k_4$ . For simplicity, forward and backward charge-transfer rates are assumed equal. For charge tunneling,  $k_1$ – $k_4$  are strongly (exponentially) distance-dependent, and small environmental rearrangements may lead to large variations in their magnitude. The forward charge tunneling rate, equal to  $\Sigma k_i$ , may correspondingly fluctuate over orders of magnitude in time. After forward charge tunneling, the carrier can diffuse in the matrix, or as indicated for acceptor 2, the charge may hop to nearby acceptors other than the dye molecule, thus losing *on*–*off* and *off*–*off* correlations.

molecule sequence of *on*-times demonstrated above, provides evidence for this picture.

In Figure 6, a sketch of a trimer molecule in the polymer matrix is given, which, to clarify our discussion, we will first consider in a static picture. In the local polymer environment, a few charge acceptors are present, which may be acceptor groups associated with the polymer matrix, solutes or impurities in the matrix, and surface states at the glass/polymer interface. The probability for charge separation to any one of these acceptors is given by a specific transfer rate,  $k$ , which for charge tunneling is a function of the emitter-acceptor distance and the height of the energy barrier between donor and acceptor level. The distance dependence of tunneling rates is exponential, which leads to strong, orders of magnitude, variations in transfer rates for small, nanometer-scale differences in emitter-acceptor distances. Thus, the order of magnitude of the four charge-transfer rates  $k_1$ – $k_4$  indicated in Figure 6 may differ considerably. The rate for forward tunneling, that is, charge ejection from the emitter to one of the acceptors, is however simply the sum over individual rates  $k_t = k_1 + k_2 + k_3 + k_4$ , leading to a single-exponential distribution. This rate is governing the *on*-state durations. For the back-transfer rate, determining the *off*-state duration, this situation is different and the full survival time distribution of each of the acceptor has to be taken into account. This leads to an overall distribution spanning the full range of orders of magnitude given by  $k_1$ – $k_4$ , which in turn gives rise to the observed power-law *off*-time distribution.<sup>1,15,28</sup> Thus, while the static tunneling model could provide an explanation for power-law *off*-times, it fails to explain the observed power-law distribution of *on*-times.

Environmental rearrangements, such as motions of the polymer backbone and diffusion of solutes, will change the instantaneous spatial distribution of charge acceptors. Nanometer-scale variations in the position of one or several of the acceptors lead to strong variations of the corresponding individual rates due to the exponential distance dependence of tunneling rates. This in turn may drastically change the average forward transfer rate  $k_t$  and thus lead to *on*-time distributions varying orders of magnitude in size over time-scales typical to environmental dynamics. Rearrangements in the polymer matrix may take place, at room temperature, on the scale of tens of milliseconds.<sup>29</sup> Triplet population and depopulation rates for organic dye molecules in PMMA were found to vary on the

scale of several hundreds of milliseconds due to environmental changes.<sup>30</sup> These time scales are much smaller than the time window necessary to statistically determine blinking dynamics due to charge separation and can thus explain the observed power-law distributed *on*-time durations. For the variations in triplet kinetics in PMMA it was observed that sampling the entire range of possible rates requires at minimum 10 s,<sup>30</sup> a time-scale comparable to the largest *on*-times observed in our system. With the present dynamic range of our experiment, which is limited by photobleaching, we cannot distinguish whether the *on*-times distribution is cut at or beyond this time-scale due to the expected averaging out of the environmental fluctuations.

Given a typical dynamical time scale for changes in the *on*-state depopulation rate of hundreds of milliseconds as mentioned above, the observation of correlations between successive *on*-states supports the notion of a dynamical electron tunneling model. Moreover, the fact that the extent of *on*-state memory increases from on average 3–7 events when comparing long-time (Figure 5a) to short-time (Figure 5b) correlations, also points to underlying environmental dynamics. An important point to note is the difference between *on*-state durations and *off*-state durations. Although the *on*-state behavior is always governed by the instantaneous local distribution of charge acceptors, in the *off*-state, the charge carrier may diffuse or alternatively the charge may tunnel to other nearby acceptors, as indicated in Figure 6. In accordance with the dynamical charge tunneling model, cross-correlations between *on*- and *off*-times as well as correlations between successive *off*-times are absent. The weak log–log correlation observed for the *off*-times supports the notion of a low amount of nearby dynamic charge acceptors that varies both in time and from molecule to molecule. Successive back-transfer events may be drawn from a momentarily nearly single or stretched exponential distribution, giving rise to the weak short-time correlations for a subset of molecules. Equivalently, the temporary presence of solutes like O<sub>2</sub>, which can enhance the back-transfer rate,<sup>19</sup> may give rise to weak correlations between short *off*-times.

The influence of the local environment on the power-law distributed blinking kinetics has so far been mostly discussed and demonstrated in terms of static, dielectric properties, both for systems of quantum dots<sup>31</sup> and of organic molecules.<sup>4</sup> Environmental dynamics has been considered as being at least partly responsible for the observed power-law behavior,<sup>17</sup> but a dynamic charge tunneling model is furthermore consistent with the weak temperature dependence of *off*-state population and depopulation kinetics observed in bulk measurements of rhodamine 6G molecules in a polymer matrix.<sup>19</sup> Recently, Stefani et al. have observed short-lived correlations between successive *on*- and successive *off*-events in the blinking of uncapped quantum dots.<sup>20</sup> For core–shell quantum dots however, charge trapping in the shell or at the shell surface may lead to complicated emission dynamics and the occurrence of multiple *on*-states.<sup>13,18</sup> Our results now demonstrate that, for a system of polymer-embedded organic perylene diimide molecules displaying power-law distributed blinking, dynamic effects underlie the power-law distribution of *on*-events and are only weakly present in the distribution of *off*-events. Thus, for two-state *on*–*off* blinking, power-law statistics in both *on*- and *off*-time distributions may be modeled by taking into account charge tunneling to a dynamic distribution of charge acceptors in the environment of the emitter. Obviously, the dependence on the local distribution of charge acceptors and their dynamics can give rise to stretched exponential or even monoexponential behavior depending on the matrix and its treatment, in line with

recent observations.<sup>32</sup> Finally, we want to note that while the occurrence of power-law statistics itself is insensitive to temperature due to the tunneling mechanism, the occurrence and extent of *on-on* and *off-off* correlations can be expected temperature dependent.

## Conclusions

In conclusion, we have demonstrated the existence of a memory effect in the power-law distributed blinking of single molecules. The memory is present in the duration of successive *on*-times and spans on average three blinking events. Between successive *off*-times, the memory is much weaker and only present between relatively short-lived events. These results reveal that power-law blinking is the result of charge tunneling to a limited number of dynamic charge acceptors in the local environment. Nanoscale environmental dynamics lead to the power-law distribution of *on*-times and the observed memory. The weak, short-time memory observed for the *off*-times indicates a low number of acceptors which varies in time and from molecule to molecule. Apart from organic molecules, this finding is directly relevant for similar systems displaying power-law blinking, like semiconductor quantum dots and nanocrystals, fluorescent proteins, and conjugated polymers. Exploitation of the optical or charge-transfer properties of these systems in nanotechnology applications thus requires a careful, nanoscale control over the local environment to avoid the extremely long-lived waiting times associated with power-law blinking.

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