

Stochastic Model of Photodynamics in Multichromophoric Conjugated Polymers

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A stochastic model of triplet exciton dynamics in multichromophoric conjugated polymers is presented and analyzed in detail, with a focus on the single molecule spectroscopy observables. The model deals with the evolution of a discrete statistical distribution of triplets in isolated polymer molecules. This approach should provide more accurate quantitative information on the dynamic processes involved, as compared to the previously used two-state model which assumes that a conjugated polymer cannot contain more than one triplet. In particular, it allows for determination of the triplet–triplet annihilation rate.

Introduction

Photodynamics of multichromophoric conjugated polymers (CP) has been under recent active investigation, in view of many promising applications of these materials in optoelectronic devices.^{1–17} The peculiar fluorescence kinetics observed in photoexcited CPs is understood in terms of singlet–triplet exciton interactions as well as interactions of excitons with polarons and/or charged chemical defects. While much is known about singlet excitons and the characteristic time scales of their reaction pathways, the information about triplet excitons has been difficult to obtain. The reason is in their nonemissive nature and lifetime orders of magnitude longer than that of singlets, which opens up additional relaxation channels, such as triplet–triplet annihilation and quenching by impurities.

In a series of recent papers, Barbara et al.^{7–10} have demonstrated the advantages of single molecule spectroscopy for the investigation of the triplet photodynamics in CPs. This technique can greatly minimize spectral and kinetic heterogeneity. To improve the signal-to-noise ratio in an emission transient, Barbara et al. have developed two experimental approaches based on fluorescence intensity autocorrelation analysis⁸ and, particularly fruitful, excitation intensity modulation.⁹ The triplet dynamics is measured indirectly, by monitoring the relaxation of singlet fluorescence toward equilibrium on a time scale much longer than the singlet radiative lifetime, in response to a wide rectangular laser pulse of about 0.5 ms duration. This methodology has allowed for a determination of the singlet–triplet quenching rate constant. Care had to be taken in sample preparation so as to diminish other quenching channels. The observed fluorescence intensity data have been analyzed with a two-state kinetic model. This model is an approximation of a more general multi-state kinetic model. The rationalization for the two-state model is as follows. Since singlets are short-lived, the CP molecule is expected to spend most of the time without any singlet. If the triplet–triplet annihilation rate is infinitely fast, the CP may contain either zero or one triplet. Hence, one has two states: (0, 0), no singlet, nor triplet and (0, 1), no singlet, one triplet.

Although the two-state model is consistent, has an advantage of simplicity, and, more importantly, describes the experimental data well, it offers no way to assess the validity of the

assumption of an infinitely fast triplet–triplet annihilation rate nor does it allow for a quantitative determination of the annihilation rate constant. In this paper, we present an extended stochastic model of photodynamics which has no limitation on the number of triplets per single CP molecule while still assuming that singlet excitons are short-lived. Our model is a multi-state kinetic model with (0, 0), (0, 1), (0, 2), and so forth, states in the notation of Barbara et al.

Perhaps the most fascinating feature of a single CP molecule fluorescence is blinking behavior.^{11–17} The duration of the dark periods in emission is ranging from milliseconds to minutes. Such long off states are usually attributed to polarons,¹⁴ charged chemical defects,¹¹ or triplet excitons^{15,18} which act as fluorescence quenchers. It is agreed that polymer conformation and the embedding medium play a very important role in the blinking behavior.^{12,13,17} In this paper, we will study singlet quenching by triplets as one of the various possible mechanisms for fluorescence blinking. Note that this mechanism can only account for fluorescence intermittency on the millisecond time scale.

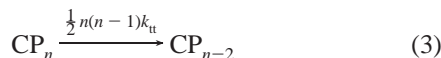
Photodynamic Models

A. Stochastic Multi-state Kinetic Model. Isolated molecules of CPs investigated by Barbara et al.^{7–10} are known to behave as multichromophoric systems due to a distribution of conjugated segments on the polymer chain. For example, there are ~50 effective chromophores for the F8BT molecules, poly(9,9'-dioctylfluorene cobenzothiadiazole). Each chromophore can be in either the ground state (S_0), the singlet excitonic state (S_1), or the triplet excitonic state (T_1). The population state of a whole CP molecule corresponds to each chromophore occupying S_0 , S_1 , or T_1 at a given time. The number of excitons continuously and spontaneously fluctuates. These fluctuations are well described by a set of first-order incoherent rate processes, which govern transitions between population states of the CP molecule. It is assumed that only the numbers of each type of electronic state define the population state, not their specific configuration in the polymer chain.⁸ This assumption implies locally homogeneous kinetics and a narrow distribution of site energies.

Since the time scale of singlet decay is orders of magnitude different from that of triplet decay, we can separate the kinetics of triplet decay from that of singlet decay. The kinetics of triplet decay is described in terms of the number n of triplet excitons

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in the polymer chain, which is denoted by CP_n . The kinetic scheme is given by



Here, $k_{f,n}$ stands for the effective rate constant of triplet formation in a CP already containing n triplets

$$k_{f,n} = \frac{k_{exc}k_{isc}\tau_{fl}}{1 + k_{isc}\tau_{fl} + nk_q\tau_{fl}} \simeq \frac{k_{exc}k_{isc}\tau_{fl}}{1 + nk_q\tau_{fl}} \quad (4)$$

where $k_{exc} = I_{exc}\sigma$ is the excitation rate, k_{isc} is the intersystem crossing (ISC) rate, k_q is the singlet quenching rate by triplets, τ_{fl} is the singlet fluorescence lifetime, I_{exc} is the incident excitation intensity, and σ is the absorption cross section of the polymer molecule. Equation 4 implies that triplet formation proceeds through singlet excitation followed by ISC which competes with radiative decay and quenching. The rate of back reaction, eq 2, is governed by reverse ISC

$$k_b = k'_{isc} \quad (5)$$

k_{tt} is the first-order rate constant of triplet–triplet annihilation in a CP molecule with two triplets.

The above kinetic scheme corresponds to the following set of rate equations for the probability $P_n(t)$ to find n triplets in a CP molecule at time t

$$\begin{aligned} \frac{d}{dt}P_n(t) = & k_{f,n-1}P_{n-1}(t) - \left[k_{f,n} + nk_b + \frac{1}{2}n(n-1)k_{tt}\right]P_n(t) + \\ & k_b(n+1)P_{n+1}(t) + \frac{1}{2}(n+1)(n+2)k_{tt}P_{n+2}(t) \end{aligned} \quad (6)$$

In a typical experiment, one irradiates a single CP molecule with a repetitive sequence of rectangular excitation pulses of about 0.5 ms each.⁹ The pulse duration is chosen to be long enough so that the stationary stage is reached in the emission transient. Therefore, one can consider the kinetics under the condition of continuous irradiation, $I_{exc} = \text{const}$, with the initial condition for eq 6 given by

$$P_n(0) = \delta_{n,0} \quad (7)$$

where δ is the Kronecker delta. The quantity experimentally observed is the fluorescence intensity due to singlet excitons. If a CP molecule contains n triplets, then the quantum yield of fluorescence is given by $1/(1 + nk_q\tau_{fl})$. Therefore, the emission yield is given by

$$I(t) = I(0) \sum_{n=0}^{\infty} \frac{P_n(t)}{1 + nk_q\tau_{fl}} \quad (8)$$

where $I(0)$ is the emission intensity right after the laser pulse is turned on. The observed fluorescence intensity decays with time as the number of triplets in a CP molecule increases. At long times, the stationary stage is reached about the distribution of triplets. The corresponding long-time emission intensity, $I(\infty)$,

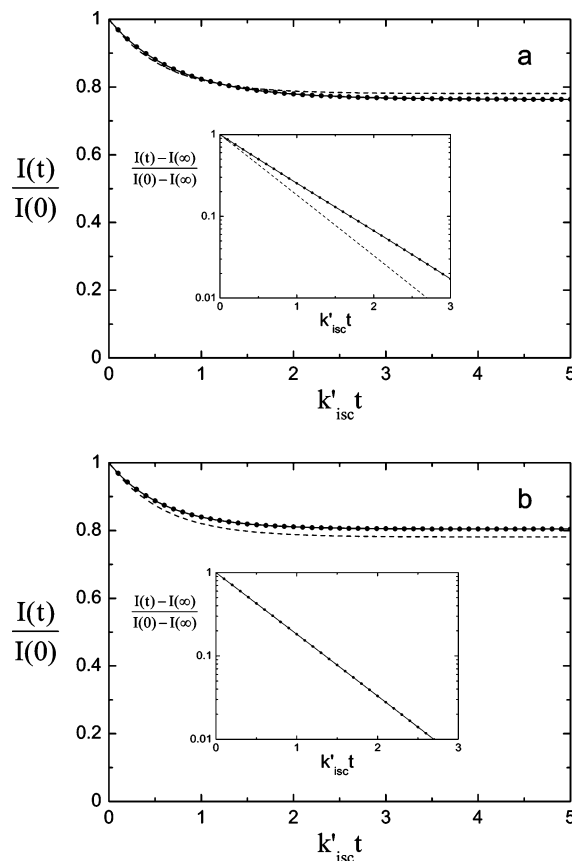


Figure 1. Fluorescence relaxation kinetics at low excitation intensity corresponding to $k_t^0/k'_{isc} = 0.52$, for (a) slow ($k_{tt}'/k'_{isc} = 0.025$) and (b) fast ($k_{tt}'/k'_{isc} = 250$) triplet–triplet annihilation. Other parameters were chosen to represent the F8BT molecule, as specified in the text. Solid lines and circles show numerical results for the multi-state model, and dashed lines are for the two-state model. The insets illustrate the exponentiality of the kinetics in a semilog scale.

is related to the contrast ratio, R , as defined by Barbara et al.

$$R = \frac{I(0)}{I(\infty)} - 1 \quad (9)$$

Equation 6 cannot be solved analytically. Numerical analysis will be presented in the next section. A useful analytical result can be obtained, however, under the assumption of the constant forward rate, $k_{f,n} \approx k_{f,0} = k_t^0$. This implies inefficient singlet quenching by triplets. In this limit, eq 6 reduces to a system of differential equations well-known in the emulsion polymerization theory.^{19,20} Although a general time-dependent solution is not available, the stationary solution can be obtained as follows

$$P_n(\infty) = \frac{2^{(\beta-1-3n)/2} \alpha^n I_{\beta-1+n}(\alpha/\sqrt{2})}{n! I_{\beta-1}(\alpha)} \quad (10)$$

where $\alpha = 4(k_t^0/k_{tt})^{1/2}$, $\beta = 2k_b/k_{tt}$, and $I_p(x)$ denotes the modified Bessel function of the first kind.

B. Two-State Model. In the limit of infinitely fast triplet–triplet annihilation, a given CP molecule will contain only zero or one triplet exciton. This corresponds to a kinetic scheme of Barbara et al.⁹



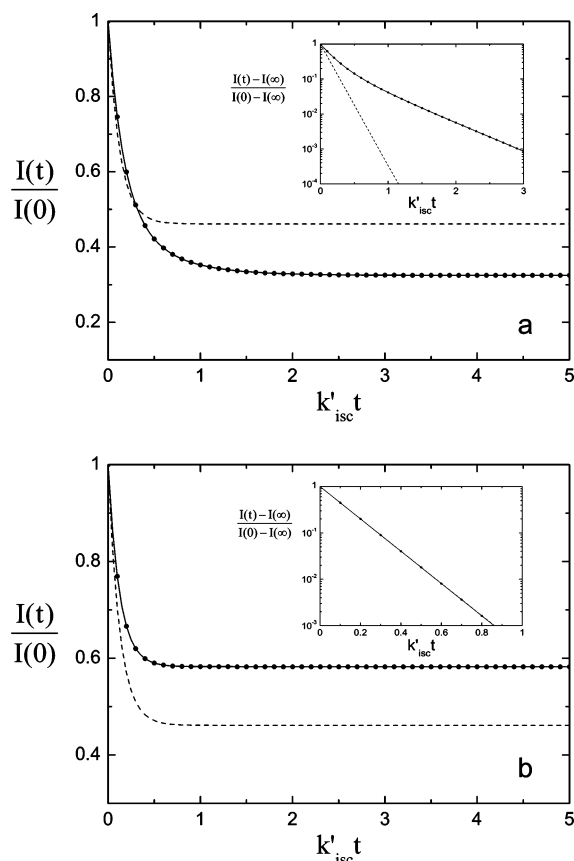


Figure 2. Same as Figure 1 for high excitation intensity corresponding to $k_f^0/k'_{isc} = 5.2$.

Here, the triplet formation process (eq 11) is the same as before, while the back reaction is supplemented by an additional channel, the disappearance of the triplet already present in the CP molecule by triplet-triplet annihilation with a newly formed triplet. Since triplet-triplet annihilation is assumed to be infinitely fast, the rate of the additional channel is given by the rate of formation of a new triplet. Therefore, k'_b is given by

$$k'_b = k'_{isc} + \frac{k_{exc} k_{isc} \tau_{fl}}{1 + k_q \tau_{fl}} \quad (13)$$

More precisely speaking, the two-state model is expected to work when k_{tt} is much larger than both k'_{isc} and $k_{f,1}$. The latter condition implies relatively low excitation intensity.

Schemes 11 and 12 allow for a simple analytical solution of the corresponding system of rate equations. The following exponential relaxation kinetics is predicted

$$\frac{I(t)}{I(0)} = \frac{R e^{-t/\tau} + 1}{R + 1} \quad (14)$$

where τ is the relaxation time

$$\tau = (k_f^0 + k'_b)^{-1} \quad (15)$$

and R is the contrast ratio

$$R = \left(\frac{k'_b}{k_f^0} + \frac{1}{k_q \tau_{fl}} + \frac{k'_b}{k_f^0 k_q \tau_{fl}} \right)^{-1} \quad (16)$$

According to Barbara et al., experimentally observed fluores-

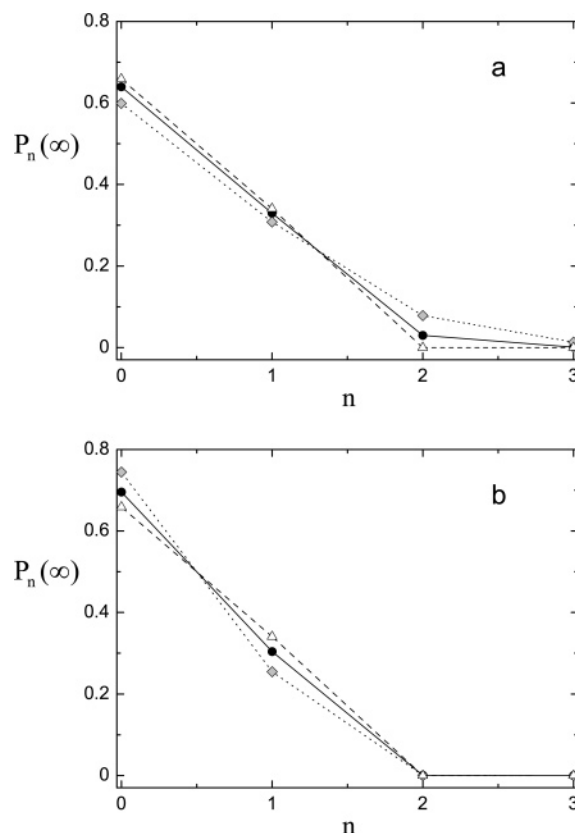


Figure 3. Stationary distribution of triplets in a CP molecule at low excitation intensity corresponding to $k_f^0/k'_{isc} = 0.52$, for (a) slow ($k_{tt}/k'_{isc} = 0.025$) and (b) fast ($k_{tt}/k'_{isc} = 250$) triplet-triplet annihilation. Other parameters were chosen to represent the F8BT molecule, as specified in the text. Numerical results are given for the multi-state model (circles), eq 10 (diamonds), and the two-state model (triangles).

cence decay kinetics are in good agreement with the general functional form of eq 14.

Numerical Results and Discussion

To compare the predictions of the two-state model vs the multi-state model, we choose a typical set of parameter values corresponding to one of the CP molecules studied by Barbara et al., namely, the F8BT molecule.⁸ Thus, we set $k_{isc} = 7 \times 10^6 \text{ s}^{-1}$, $k'_{isc} = 2 \times 10^3 \text{ s}^{-1}$, $k_q = 6 \times 10^8 \text{ s}^{-1}$, and $\tau_{fl} = 3 \times 10^{-9} \text{ s}$. We consider two limits of triplet-triplet annihilation: fast ($k_{tt} \gg k'_{isc}$) and slow ($k_{tt} \ll k'_{isc}$). In the fast annihilation limit, the kinetics is saturated with respect to k_{tt} in a sense that any further increase in k_{tt} beyond the chosen value of $k_{tt}/k'_{isc} = 250$ does not lead to any significant change in the fluorescence relaxation kinetics. The results for the intermediate regime of triplet-triplet annihilation ($k_{tt} \sim k'_{isc}$) are not presented, as they can be readily inferred by comparing the above two limits. Regarding the excitation intensity, we consider relatively high and low limits here as well. We define the excitation intensity via a dimensionless parameter $k_f^0/k'_{isc} = k_{exc} k_{isc} \tau_{fl}/k'_{isc}$, proportional to I_{exc} . Whether or not the excitation intensity is high or low for a given set of other parameters can be judged by the value of the contrast ratio or, in our preference, by the ratio of $I(\infty)/I(0)$. The low excitation intensity limit corresponds to $I(\infty)/I(0) \approx 0.8$. Lower intensities are of marginal interest. The high-intensity limit corresponds to $I(\infty)/I(0) \approx 0.5$, roughly speaking, the deepest fluorescence relaxation level observed in experiments by Barbara et al.⁹

Figures 1 and 2 show the calculated fluorescence relaxation kinetics. The insets focus on the exponentiality of the decay

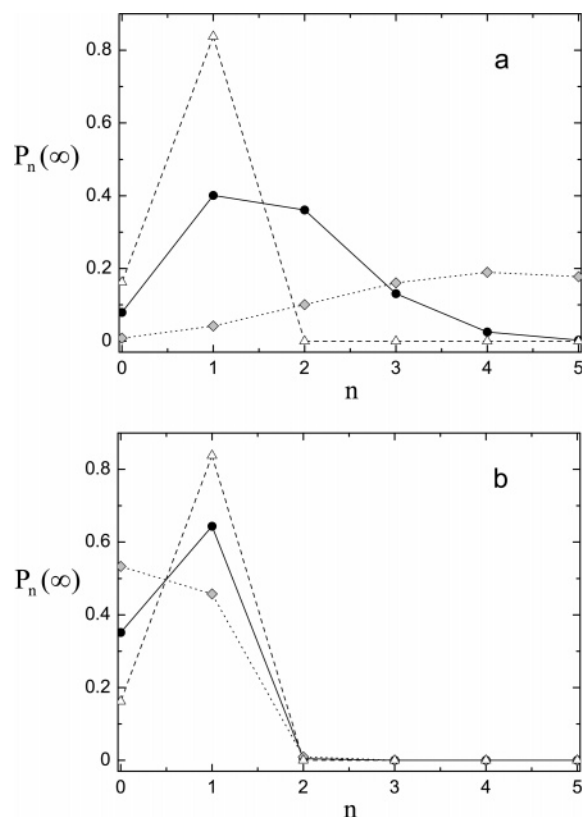


Figure 4. Same as Figure 3 for high excitation intensity corresponding to $k_t^0/k'_{isc} = 5.2$.

kinetics by plotting the normalized intensity, $[I(t) - I(\infty)]/[I(0) - I(\infty)]$, in a semilog scale. At low excitation intensities (Figure 1), the relaxation curves obtained from the multi-state model are similar to those from the two-state model. This is reasonable because at low excitation intensities populations at $n > 2$ are not so important. If we look at Figure 1 more carefully, we see that in the fast triplet–triplet annihilation limit (b), the kinetics is exponential with the characteristic relaxation time τ well predicted by the two-state model. When the triplet–triplet annihilation is slow (a), we still see exponential kinetics but with a somewhat different relaxation rate. At high excitation intensities (Figure 2), the relaxation curves obtained from the multi-state model are quite different than those from the two-state model, especially in the long-time limit. In the fast triplet–triplet annihilation limit (b), the kinetics is exponential with the relaxation time well predicted by the two-state model. In the slow triplet–triplet annihilation limit (a), the kinetics exhibits an initial nonexponential stage, then becomes exponential but with a largely different relaxation rate than that predicted by the two-state model.

Figures 3 and 4 show the stationary distribution of triplets. Only a small fraction of CP molecules is occupied by two triplets when the excitation intensity is low (Figure 3) and the agreement between the models is good. For high excitation intensity and rapid triplet–triplet annihilation (Figure 4b), double triplet occupancy is also hardly seen but the discrepancy between the models for single triplet occupancy is substantial. As expected, maximum deviation is observed for high excitation intensity and slow triplet–triplet annihilation (Figure 4a) where multiple occupancy of a CP molecule by triplets is significant. It is interesting to note that the exact occupancies are between the corresponding occupancies given by the approximate expression of eq 10 and those given by the two-state model approximation. Equation 10 is expected to work progressively worse as $k_q\tau_{fl}$ is

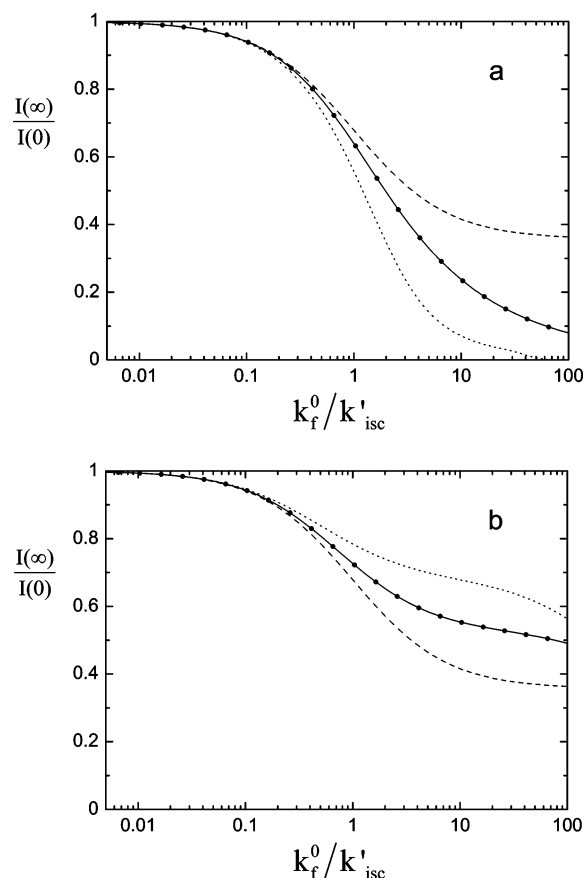


Figure 5. Normalized stationary fluorescence intensity as a function of excitation power (via k_f^0/k'_{isc}) for (a) slow ($k_t/k'_{isc} = 0.025$) and (b) fast ($k_t/k'_{isc} = 250$) triplet–triplet annihilation. Other parameters were chosen to represent the F8BT molecule, as specified in the text. Numerical results are given for the multi-state model (solid lines and circles), the constant forward rate approximation (dotted lines), and the two-state model (dashed lines).

increased. Figure 5 shows the normalized stationary fluorescence intensity as a function of k_f^0/k'_{isc} (i.e., the excitation power). The models agree well only for $k_f^0/k'_{isc} < 1$, that is, for low excitation intensities. Again, the two-state approximation and the constant forward rate approximation (eq 10 substituted into eq 8) provide lower and upper bounds for the “exact” solution. As we have already mentioned, experimentally, the excitation power is chosen so that the stationary fluorescence level is at least 20% lower than the initial fluorescence level. Therefore, the effect of a finite triplet–triplet annihilation rate is always important as far as the stationary fluorescence intensity is concerned.

We have also performed numerical analysis using parameter values corresponding to yet another typical CP molecule, poly-[2-methoxy-5-(2'-ethylhexyloxy)-*p*-phenylene vinylene] (MEH-PPV): $k_{isc} = 6 \times 10^7 \text{ s}^{-1}$, $k'_{isc} = 5 \times 10^3 \text{ s}^{-1}$, $k_q = 10^{10} \text{ s}^{-1}$, and $\tau_{fl} = 2 \times 10^{-10} \text{ s}$ (as extracted from ref 8). The results were very similar to those presented for F8BT, which is in part due to the fact that two significant dimensionless parameters of the model, $k_q\tau_{fl}$ and $k_{isc}\tau_{fl}$, and the corresponding quantum yields of intersystem crossing are close for MEH-PPV and F8BT.

Figure 6 illustrates the “real-time” fluctuations in the number of triplets in a single CP molecule after the laser is turned on and the corresponding fluorescence blinking trajectories obtained by Monte Carlo simulation on the basis of the multi-state kinetic scheme, eqs 1–3. The characteristic time scale of this numerical

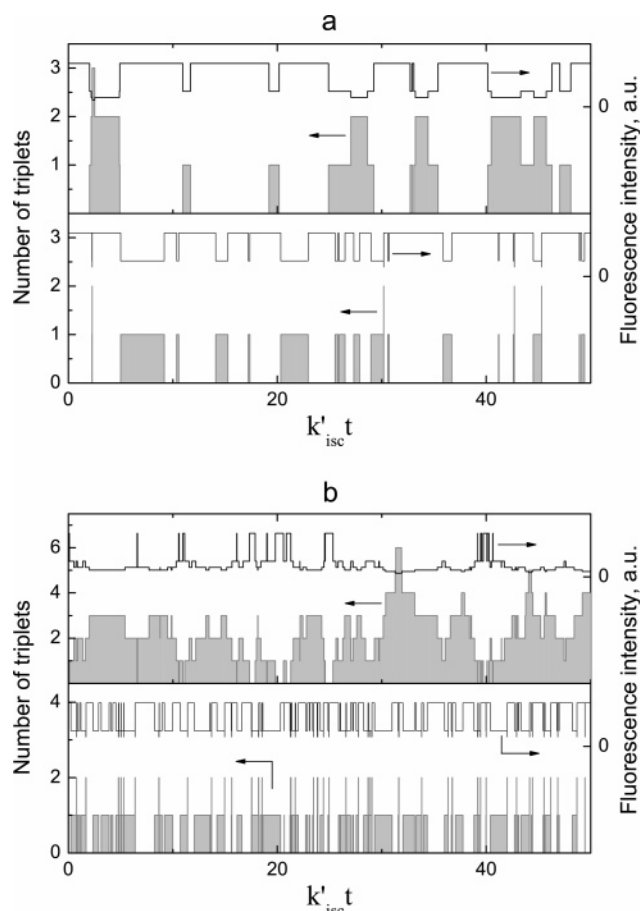


Figure 6. Fluctuations in the number of triplets in a single CP molecule (grey filled) and the corresponding fluorescence blinking trajectories (solid lines) for (a) low ($k_f^0/k'_{isc} = 0.52$) and (b) high ($k_f^0/k'_{isc} = 5.2$) excitation intensities, within the multi-state model. The top subpanel in each panel illustrates the results for slow triplet–triplet annihilation, $k_{tt}/k'_{isc} = 0.025$, while the bottom subpanel is for fast triplet–triplet annihilation, $k_{tt}/k'_{isc} = 250$. Other parameters were chosen to represent the F8BT molecule, as specified in the text.

experiment indicates that these are essentially stationary fluctuations. The amplitude of fluctuations in the occupancy is basically determined by the triplet–triplet annihilation rate, while their frequency is sensitive to the excitation intensity. Figure 6 indicates that one can distinguish between zero and nonzero occupancies from the observed singlet fluorescence intensity. However, it is difficult to distinguish from the fluorescence intensity between different nonzero occupancies. In addition, fluorescence intensities from nonzero occupancies can be easily mixed up with background noise. On the other hand, the experimental technique of Barbara et al.,⁹ although measuring only statistically averaged singlet fluorescence, has proven to be rather sensitive to higher occupancy numbers in the distribution of triplets. We also note that singlet quenching by triplets can only account for fluorescence intermittency on the millisecond time scale. Experimentally observed longer blinking time scales,^{11–17} up to minutes, can be attributed to quenching by polarons¹⁴ or charged chemical defects.^{15,18}

Concluding Remarks

We have presented a stochastic multi-state model of photo-dynamics in isolated CPs. This is not a novel approach. Similar models arise in a variety of fields, particularly when it comes to the description of the excited-state relaxation dynamics in a finite system with a limited number of excitations. Examples

are triplet–triplet annihilation in micelles^{20,21} and electron–hole recombination in nanoparticles²² or nanotubes.²³ We believe that the power of the experimental technique developed by Barbara et al.⁹ for probing triplet photodynamics in CPs by measuring singlet fluorescence relaxation is not fully exploited if the data is analyzed on the basis of the two-state model. The multi-state model approach should provide more accurate quantitative information on the kinetic processes involved. In particular, it allows for the determination of the triplet–triplet annihilation rate which is not directly included in the two-state model. The triplet–triplet annihilation rate depends on the system size and the triplet diffusion coefficient. For larger systems and/or for those systems where, for some reason, the diffusion is slow, triplet–triplet annihilation will also be slow thus making the multi-state analysis especially important. Even if the triplet–triplet annihilation rate is relatively fast, the probability of finding two triplets in a single CP molecule is not negligible at high excitation intensities which has a pronounced effect on the contrast ratio. We have shown that, at least for MEH-PPV and F8BT molecules, experimentally significant excitation intensities are indeed sufficiently high so that the effect of a finite triplet–triplet annihilation rate should be observable.

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