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Oxygen-induced quenching of photoexcited states in polythiophene films

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Abstract

Oxygen causes reversible and irreversible detrimental effects to the performance of organic (opto-)electronic devices. In order to get some insight into the mechanisms of these effects, we investigated the kinetics of fluorescence quenching (FQ) in thin films ($d \approx 100$ nm–12 μm) of regioregular polyalkylthiophenes upon exposure to oxygen.

The kinetics of FQ consists of a fast component, which is fully reversible, as well as a slow component, which is partially irreversible. The fast reversible component leads to a loss of fluorescence intensity of approximately 2% at an oxygen partial pressure of 1 bar within milliseconds. It is independent of the intensity of the exciting light and is ascribed to collisional quenching of excited singlet states after oxygen diffusion into the bulk of the film. The diffusion coefficients of oxygen and singlet excitons were determined as $D(O_2) = 1.5(3) \times 10^{-7}$ cm^2 s^{-1} and $D(S_1) = 5 \times 10^{-4}$ cm^2 s^{-1}, respectively. The slow reversible component, whose amplitude depends on light intensity, occurs on a time-scale of minutes. It is assigned to the formation of charge-transfer complexes between excited singlet states of polythiophene and oxygen. Femtosecond pump-probe experiments show that effective quenching of excited singlet states by oxygen takes place on a picosecond time-scale, leading to the enhanced formation of charged states.

1. Introduction

Polythiophenes (PT) represent a class of materials intensively studied for organo-electronic applications. Using regioregular poly(3-hexylthiophene)s (RR-P3HT), stable organic field effect transistor (OFET) structures have been built that showed charge carrier mobilities exceeding 10^{-2} cm^2 V^{-1} s^{-1} [1,2]. These high mobilities derive from a highly ordered lamellar structure of the polymer strands, where ordered regions are in close contact with one another [3,4]. Molecular oxygen is known to be a strong electron acceptor leading to p-type conductivity of most organic semiconductors. The resulting enhanced bulk conductivity in the active P3HT layers of OFETs leads to a reversible decrease in the on/off-ratio of the devices [5]. Moreover, also irreversible photooxidation is found, leading to a complete bleaching of

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the active layer over time [6]. To explain reversible and irreversible oxygen effects on PT, the reversible formation of a charge-transfer (CT)-complex between molecular oxygen and the PT molecules has been invoked [7,8]. The existence of this metastable complex has been shown by its UV/Vis absorption band at the low energy edge of the P3HT absorption [7]. However, there is only little information on the transient nature of this CT complex. For a complete understanding of oxygen-induced effects in PT, knowledge is necessary on the formation and decay kinetics of the metastable states. This knowledge can only be gained in the time domain.

In this paper, the oxygen-induced quenching of excited states of RR-P3HT in thin films is investigated. Measurements of fluorescence quenching (FQ) as a function of oxygen sorption time yield diffusion coefficients for molecular oxygen and excited singlet states. Using femtosecond transient absorption (TA) spectroscopy of excited states it is shown that oxygen reversibly forms charged states within 1ps after pulsed irradiation, whereas the neutral excited states are strongly quenched.

2. Experimental

RR-P3HT was synthesized by Merck. The number molecular weight average of the polymer was $M_n = 36{,}500$. The material is characterized by a regioregularity of 96% and impurities of nickel (0.042%) and magnesium (0.3%). End groups are bromine. In order to reduce deterioration of the material during storage (which shows, e.g., in the formation of insoluble products due to cross-linking [6]), the material was kept under nitrogen at −27 °C. Thin films (100–200 nm) were produced by spin-coating from 2 wt.% chloroform solutions onto fused silica substrates. Thicker films (5–12 μm) were made by drop casting on fused silica windows; film thickness was measured by an alpha stepper. Thickness profiles across the spots irradiated by the fluorescence excitation light (spot diameter 1–3 mm) showed a surface roughness of up to 20% of the total thickness. Prior to measurement, the films were annealed in vacuum at 150 °C for 1 h.

Diffusion coefficients of oxygen were measured at $T = 293$ K in a custom-built setup according to the transient fluorescence method [9]. The cell consisted of a pressure chamber with two fused silica windows, one of which carried the PT film. Oxygen partial pressures from 10^{-5} mbar (high vacuum) to 11 bar were applied. The time constant for a jump in the oxygen partial pressure was estimated to $\Delta t(O_2) \approx 0.3$ s.

Fluorescence was excited and detected from the bottom side of the films, i.e., through the fused silica substrate (see inset in Fig. 1). For excitation, the films were irradiated with monochromatic light ($\lambda = 450$ nm) from a 150W Xenon light source/interference filter combination. Fluorescence light was collected at an angle of 30° with respect to the irradiating beam by a curved mirror and was focused onto a long pass filter/photomultiplier tube combination. The top side of the films was in contact with the gas phase. Since the penetration depth of light at $\lambda = 450$ nm is around 100 nm, whereas film thickness is at least 5 μm, only a thin sheet of P3HT near the substrate is reached by the

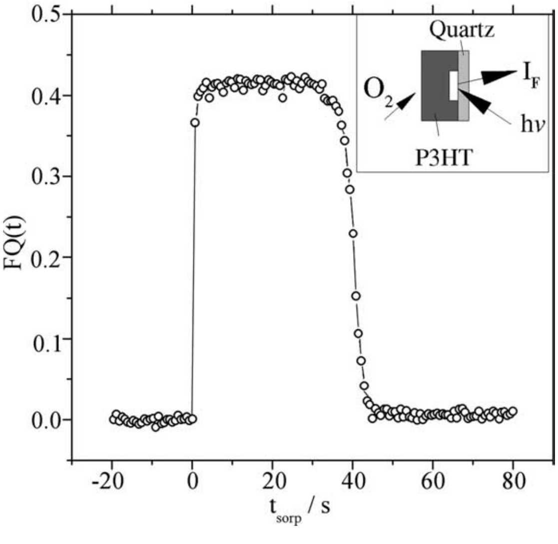

Fig. 1. Fluorescence quenching (defined according to Eq. (1)) in a P3HT film of thickness $d = 5$ μm as a function of oxygen sorption/evacuation time at a light intensity of $I = 7.4$ μW cm^{-2}. At $t_{sorp} = 0$ s, 11 bar of oxygen were applied, at $t = 30$ s, evacuation of oxygen started. The inset shows the measurement principle. The white rectangle near to the substrate gives the area where fluorescence originates.

exciting light. After admission of oxygen to the chamber, the gas diffuses into the film from the top side, eventually reaching the layer of excited P3HT at the bottom side. The time-dependence of oxygen concentration in the P3HT layer adjacent to the substrate is obtained by analytical expressions for diffusion in a plane sheet, inserting the film thickness measured by the alpha stepper [10].

If the P3HT layer illuminated by the exciting light is thin compared to the total film thickness, the molecular oxygen concentration in this layer is directly proportional to the observed FQ. This is a consequence of the Stern–Volmer equation, which relates FQ to quencher concentration for quenching processes which follow second order kinetics (see, e.g., [11]). Consequently the time-dependent FQ signal is given by

$$\mathrm{FQ}(t) \equiv F^0/F(t) - 1 = K_{\mathrm{SV}}[\mathrm{O_2}](t). \tag{1}$$

Herein, F^0 is the fluorescence intensity without oxygen, $F(t)$ is the fluorescence intensity in the presence of oxygen at the time t after the start of oxygen exposure, K_{SV} is the Stern–Volmer constant and $[\mathrm{O_2}](t)$ is the time-dependent oxygen concentration in the film region that is sampled by the exciting light. Fitting the experimental FQ curves to Eq. (1) yields the macroscopic mean of the diffusion coefficient of oxygen in the films, $D(\mathrm{O_2})$. The Stern–Volmer constant can be expressed by

$$K_{\mathrm{SV}} = k_{\mathrm{q}} \cdot \tau_0, \tag{2}$$

where k_{q} is the second order rate constant of the microscopic quenching process and τ_0 is the fluorescence lifetime in the absence of oxygen. The rate constant k_{q} is calculated from Eqs. (1) and (2), inserting τ_0, the fluorescence quenching FQ ($t \to \infty$) observed in equilibrium, and the equilibrium oxygen concentration $[\mathrm{O_2}]$ ($t \to \infty$).

Fluorescence decay curves were measured with the time correlated single photon counting method in a SPEX 112 fluorimeter, using a PICOQUANT diode laser ($\lambda = 392$ nm, pulse width 50 ps) for excitation, a photomultiplier tube for detection, and EG & G ORTEC components (preamplifier, discriminators, and time-to-amplitude converter) for signal processing.

Femtosecond pump-probe spectroscopy was performed using a Ti-Sapphire Laser coupled to a regenerative amplifier. The frequency doubled pump beam had a wavelength of 390 nm at a pulse duration of 150 fs. The probe pulse was white light generated by a thin sapphire plate at a pulse duration of 150 fs. Typical pump pulse energies were $I_{\mathrm{p}} = 0.3\ \mathrm{mJ\,cm^{-2}}$. Details of the setup can be found elsewhere [12]. Unless otherwise stated, the pump-probe experiments started 1000 s after the begin of oxygen sorption. Since film thicknesses in this experiment were in the order of 100 nm, the oxygen concentration in the films had reached its equilibrium value within milliseconds. During oxygen sorption the sample was illuminated by the pump beam, so that also the slow photo-induced processes described below had reached their stationary states.

3. Results and discussion

3.1. Fluorescence quenching—an overview

In Fig. 1, the FQ trace of a P3HT film (thickness 5 μm) is shown as a function of sorption time at low light intensity. Upon admission of 11 bar of oxygen at $t = (0 \pm 0.3\ \mathrm{s})$, FQ reaches an equilibrium value of $\mathrm{FQ_{eq}} = 0.4$ within one second (time increment of data points is 0.7 s). Removal of oxygen at $t = (30 \pm 7\ \mathrm{s})$ leads to a complete recovery of the initial fluorescence, showing that this *fast* component of FQ is completely reversible. Repeating the same experiment with longer oxygen sorption times and higher light intensities (Fig. 2) shows that fast FQ is independent of light intensity. However, a slower FQ process is superimposed that becomes more prominent at higher light intensities and longer sorption times. Slow FQ is partially irreversible, the degree of irreversibility, $\mathrm{FQ_{irrev}}$, increasing with light intensity. We will now first discuss the fast FQ.

3.2. Fast reversible fluorescence quenching

Fig. 3 shows normalized time traces of FQ in thick films ($5\ \mu\mathrm{m} \leqslant d \leqslant 12\ \mu\mathrm{m}$) at a very low light intensity ($I = 3\ \mu\mathrm{W\,cm^{-2}}$) where only fast

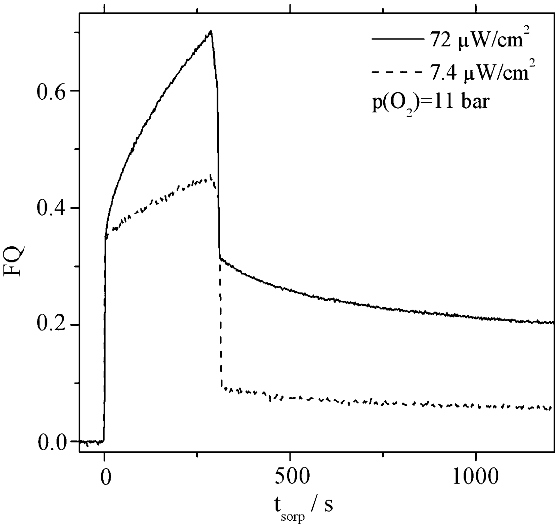

Fig. 2. Fluorescence quenching (defined according to Eq. (1)) in P3HT films (thickness $d = 5$ μm) as a function of oxygen sorption/evacuation time at two different light intensities, as indicated. At $t_{sorp} = 0$ s, 11 bar of oxygen were applied; at $t = 300$ s, evacuation of oxygen started.

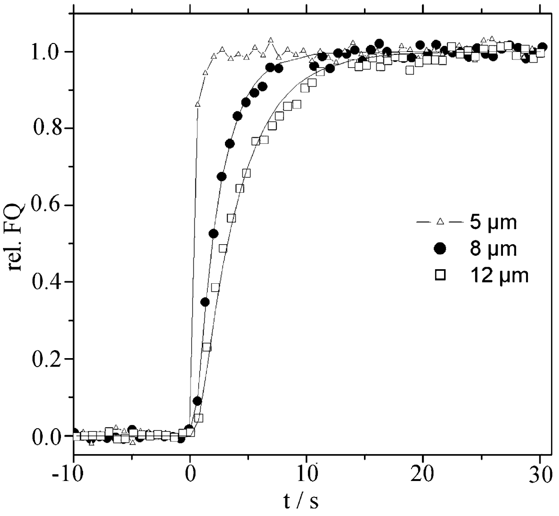

Fig. 3. Normalized fluorescence quenching in P3HT films at low light intensity as a function of oxygen sorption time at different film thicknesses. Symbols are data points, solid curves are numerical fits according to the model "diffusion in a plane sheet".

reversible FQ is observed. It is found that the time needed to reach the equilibrium FQ increases with film thickness. This suggests that macroscopic diffusion of molecular oxygen from the film surface to the substrate is the reason for the measured FQ kinetics. The experimental curves are fitted to Eq. (1). The resulting fitting curves shown in Fig. 3 fit the data very well. A value of $D(O_2) \approx 1.5(3) \times 10^{-7}$ cm^2 s^{-1} is obtained as the diffusion coefficient of oxygen for all film thicknesses, which shows that there is a good correlation between the mechanically determined film thickness and the actual diffusion path length. The quality of the fits obtained with only one diffusion coefficient also shows that the distribution of diffusion coefficients in the films is rather narrow. This value is ten times larger than that obtained by the pressure gradient method for free standing P3HT films ($D = 1.2 \times 10^{-8}$ cm^2 s^{-1}) [7]. A possible explanation for this discrepancy is the finding from small angle X-ray scattering that drop casting of P3HT produces partially crystalline films, consisting of nanocrystallites with diameters of about 10 nm, which are embedded in an amorphous matrix [3]. Diffusion coefficients of oxygen in amorphous regions of polymers are much larger than those in crystalline regions, mainly due to reduced order and enhanced mobility of the alkyl side-chains in amorphous regions [13]. As crystallinity and side-chain mobility are strongly dependent on preparation conditions, oxygen mobilities may vary over a broad range. Fig. 4 shows that at low irradiation intensity FQ in films which are in equilibrium with oxygen depends linearly on oxygen partial pressure. The data points were taken after an oxygen saturation time of 30 s, see Fig. 3. The linear dependence shows that the requisites for Stern–Volmer FQ are met, i.e., P3HT excited singlet states are quenched by collisions with molecular oxygen in a second order process, and that no significant swelling of the polymer occurs at high oxygen pressures. The dynamic nature of the quenching process is also demonstrated by the decrease of the fluorescence decay time from $\tau_0 = 340$ ps for the films in vacuum to $\tau_q = 200$ ps under 11 bar of oxygen. Converting oxygen partial pressures into oxygen concentrations in the films using the literature value [6] for the solubility constant of molecular oxygen in P3HT, $k_h \approx 0.22$ v/v, a Stern–Volmer slope of $k_q\tau_0 = 6.7$ M^{-1} is obtained. From this slope $k_q = 1.9 \times 10^{10}$ M^{-1} s^{-1}

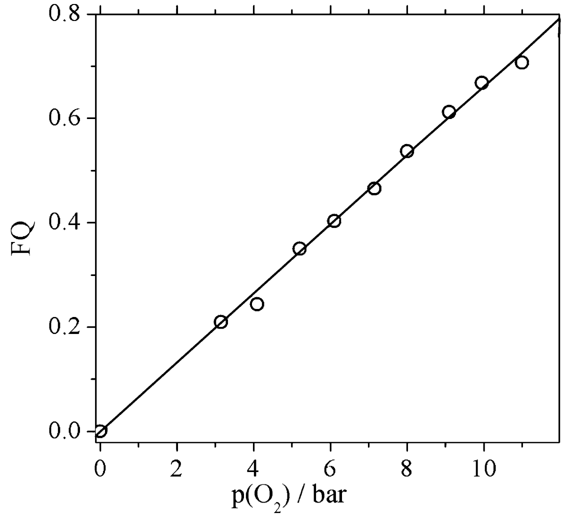

Fig. 4. Fluorescence quenching of a P3HT film (thickness $d = 12$ μm) at equilibrium with the gas phase (at $t_{\text{sorp}} = 30$ s) at low light intensity ($I = 7$ μW cm^{-2}) as a function of oxygen pressure (symbols). Solid lines are linear regressions passing through the origin.

is calculated, inserting $\tau_0 = 340$ ps for the fluorescence lifetime in the absence of oxygen. Under the assumption of a diffusion-controlled reaction with Smoluchowski boundary condition, the total diffusion coefficient D is calculated using

$$D = D(S_1) + D(O_2) = k_q/(4 \cdot \pi \cdot N_A R), \tag{3}$$

where $D(S_1)$ and $D(O_2)$ are the diffusion coefficients for excited singlet states and molecular oxygen, respectively, N_A is Avogadro's constant, and R is the reaction radius. Letting $R = 500$ pm, we obtain $D \approx 5 \times 10^{-4}$ cm^2 s^{-1} as the total diffusion coefficient. Since $D(O_2) \ll D$, D reflects the diffusion coefficient for singlet excitons. Efficient FQ despite short lifetime of the excited states in P3HT films is therefore explained by a high mobility of the singlet excitons. Due to the exciton diffusion length of about 4 nm, excitations in nanocrystallites are quenched effectively, even if no oxygen is present within the crystallites at the instant of quenching. Finally, it should be noted that the value obtained for D represents a lower limit due to the assumptions made. If not every encounter leads to quenching (Smoluchovsky condition not met), the diffusion coefficient is even higher. The same applies if the reaction radius is smaller.

3.3. Slow fluorescence quenching

For the investigation of fast FQ in the previous section very low light levels ($I < 10$ μW cm^{-2}) were used. Under these conditions FQ is only observed while molecular oxygen is present in the films. For higher light levels a slower component of FQ appears, which is only partly reversible (Fig. 2). The extent of slow FQ, both reversible and irreversible, increases with intensity and duration of illumination. Also the relative contribution of the irreversible component to slow FQ depends on light intensity and/or duration of illumination. In contrast to fast FQ, the reversible component of slow FQ persists for several minutes after the removal of dissolved molecular oxygen. This suggests that slow FQ involves metastable oxygen species which are formed in a photoreaction. These photoproducts partly undergo irreversible follow-up reactions [5,6], whose products act as quenching centers and thus cause the irreversible component of slow FQ. This quenching process is very efficient due to the high mobility of the singlet excitons. While after irradiation of the film for 600 s the initial ground state absorbance of A $(t = 0) = 1.2$ at $\lambda = 520$ nm has decreased by only 0.6%, the concomitant irreversible decrease of fluorescence intensity amounts to 21%.

A good candidate for the metastable species involved in FQ is the CT complex formed between P3HT and oxygen, which was detected by Abdou and Holdcroft by its CT absorption band [6]. Their results were corroborated by our own studies of time-resolved photoconductivity in oligothiophene films [8]. Upon irradiation into the main absorption band of oxygen containing oligothiophene films the metastable CT complex was formed in a photoreaction over several minutes. As the CT complex acts as a precursor for charge carrier generation, the formation of the CT complex was accompanied by the increase of photoconductivity. After storage of the films in the dark for several days, irradation into the main absorption band resulted in fast reestablishment of the photoconductivity level which had been observed immediately before light-off, due to charge carrier generation by quenching of mobile excited singlet states on encounter with the CT complex.

Both these earlier findings and the results of the present FQ studies are readily explained by the existence of a metastable species, probably a CT complex, which is produced in a photoreaction. Photoconductivity studies on P3HT films are currently under way in order to further test the applicability of this model for polythiophenes.

3.4. Ultrafast quenching of excited states: femtosecond pump-probe measurements

Photo-induced absorption of P3HT films has been studied extensively. It has been shown that upon pulsed excitation, neutral singlet excitons, absorbing around 870 nm, and charged states, absorbing around 650 nm, are formed [14]. In Fig. 5, time traces of differential transmission with and without oxygen are presented (please note that the time axis in this graph is pump-probe delay t_{pp} and should not be confused with the time axis used in the previous paragraph, were it was oxygen sorption time t_{sorp}). Under 1 bar of oxygen approximately one third of the singlet excited states is quenched during the first five picoseconds. For the charged state, the picture is more complex: during the first picoseconds after the excitation pulse, an increase of the concentration of charged states is found under oxygen. However, also the decay of the charged states is enhanced under oxygen, which leads to a crossing of the curves with and without oxygen after around 10 ps. Applying vacuum after oxygen sorption reproduces almost exactly the time trace before oxygen sorption, showing that the measured kinetics are nearly completely reversible.

Thus the pump-probe experiment reveals one of the mechanisms of reversible oxygen-induced fluorescence quenching: singlet excitons are quenched by oxygen under the formation of charged states. The remarkably fast rate of this process is due to the high mobility of the singlet excitons and the high concentration of molecular oxygen in the films of $[O_2] = 6 \times 10^{18}$ cm^{-3} at an oxygen pressure of $p = 1$ bar [6], which corresponds to a mean distance of about 5.5 nm between oxygen molecules.

3.5. Femtosecond time traces as function of sorption time

Fig. 6 shows time traces of singlet exciton absorption, measured at different times after the start of oxygen sorption/evacuation. In order to visualize the extent of oxygen-induced quenching of excited singlet states, the singlet exciton signal after 5 ps is plotted versus oxygen sorption time. Oxygen-induced quenching increases slowly after the beginning of oxygen sorption to reach a steady state value after about 1000 s. Upon evacuation partial recovery of the singlet exciton absorption is obtained after approximately 1000 s. The

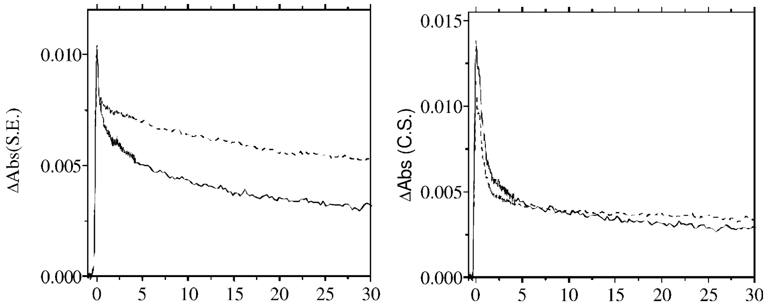

Fig. 5. Decay traces of differential absorption Δ Abs in P3HT films (thickness $d = 150$ nm) after excitation at 390 nm under high vacuum (dashed lines) and under 1 bar of oxygen (solid lines). (a) differential absorption at 870 nm (singlet exciton absorption, SE); (b) differential absorption at 650 nm (charged state, CS).

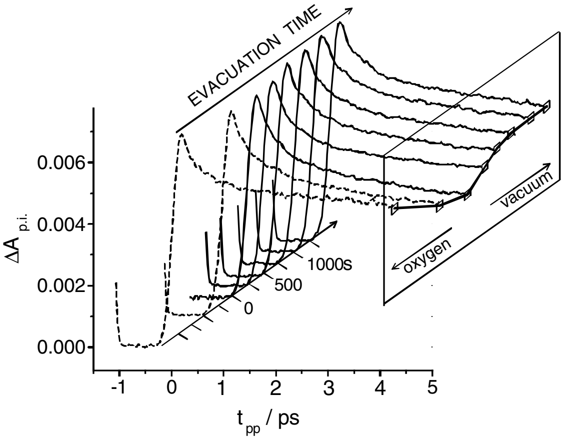

Fig. 6. Decay traces of differential absorption Δ Abs (SE) at 840 nm in P3HT films of thickness $d = 150$ nm after excitation at 390 nm under oxygen (dashed curves) and in high vaccum (solid curves). The third axis vanishing in the paper plain gives the evacuation time.

development of ultrafast singlet exciton quenching with oxygen sorption time follows the same kinetics as slow FQ at high light intensities. Due to the high-intensity illumination of the sample during the pump-probe experiment the slow FQ component is so strong that it masks the fast component. This suggests that the metastable states, which have been proposed above as the species responsible for slow FQ and recovery are also involved in the ultrafast quenching of singlet states.

4. Summary

We have presented an analysis on oxygen-induced quenching of excited states in P3HT films. Fluorescence quenching consists of a fast component, which is fully reversible and a slow component, which is only partly reversible. Fast reversible FQ is due to macroscopic diffusion of oxygen into the bulk of the films. The oxygen pressure dependence of FQ follows Stern–Volmer kinetics, so that diffusion coefficients for oxygen and singlet states have been obtained independently. Slow FQ is strongly light intensity dependent. It is due to photo-induced formation of metastable species which are assigned to a charge-transfer complex between molecular oxygen and conjugated polythiophene segments. Ultrafast pump-probe experiments show that quenching is at least partially due to electron transfer from the excited polylhiophene to oxygen. The role of the metastable CT complex in the ultrafast quenching of excited states is demonstrated.

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