

Oxygen Optical Gas Sensing by Reversible Fluorescence Quenching in Photo-Oxidized Poly(9,9-dioctylfluorene) Thin Films

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Received: July 2, 2009; Revised Manuscript Received: November 16, 2009

We investigated the fluorescence (FL) dependence on the environment oxygen content of poly(9,9-dioctylfluorene) (PF8) thin films. We show that the PF8 interactions with oxygen are not limited to the known irreversible photo-oxidation, resulting in the formation of Keto defects, but also reversible FL quenching is observed. This effect, which is stronger for the Keto defects than for the PF8, has been exploited for the realization of a prototype oxygen sensor based on FL quenching. The sensing sensitivity of Keto defects is comparable with the state of the art organic oxygen sensors based on phosphorescence quenching.

The development of new active materials for gas sensing received increasing attention in the last years for applications in several fields. In particular, oxygen sensors are extremely important due to their very wide range of applications, spanning from environmental analysis to medical monitoring of air and blood.¹ Different kinds of oxygen sensors have been developed to date, like amperometric,² chemiluminescent,³ and colorimetric⁴ sensors. In the past decade, the request for cheap, fast, and easily miniaturizable sensors increased the attention on optical gas sensors based on the oxygen induced photoluminescence quenching of the active material. Among the several luminescent materials, organic conjugated molecules present several properties required for a good active material for optical sensors, like low synthesis costs, possible production in large scale, easy deposition techniques, and wide chemical flexibility. For these reasons, several experiments on the oxygen dependence of the photoluminescence intensity of organic films have been performed, mainly exploiting phosphorescent oligomers, like Pt and Pd porphyrins, blended with an oxygen permeable organic matrix.⁵ In these systems, the oxygen presence causes a reversible quenching of the triplet excitons, thus leading to a reversible phosphorescence quenching.

On the contrary, the typically reported effect of the interaction with oxygen of photoirradiated organic fluorescent polymers is an irreversible photo-oxidation of the emitting molecules leading to the formation of nonradiative (like in polyphenylene-vinylenes^{6,7}) or radiative defects (like in polyfluorenes⁸).

In this paper, we investigate the dependence of the fluorescence (FL) spectra of poly(9,9-dioctylfluorene) (PF8) thin films on the environment atmosphere oxygen content. We show that in addition to the already known irreversible oxidation of PF8, resulting in irreversible quenching of the intrinsic blue PF8 FL due to the formation of luminescent Keto defects, also reversible FL quenching is present. This effect, which is stronger for the Keto defects emission than for the PF8 one, has been exploited to realize an optical oxygen sensor. The Keto defects sensor characteristic is consistent with a log-normal distribution of the Stern–Volmer constant K_{SV} , with $K_{SV} \approx 1500 \text{ M}^{-1}$ for oxygen contents lower than about 1 mM and $K_{SV} \approx 16 \text{ M}^{-1}$ for oxygen contents higher

than about 4 mM. The low oxygen concentration value of K_{SV} is comparable with the state of the art organic oxygen sensors based on phosphorescence quenching,⁹ thus suggesting possible future applications of conjugated polymers to oxygen optical sensors.

The samples, with a thickness of about 300 nm, were prepared by spin coating PF8 thin films from a 10^{-4} M chloroform solution on glass substrates. A He–Cd laser ($\lambda = 325 \text{ nm}$) has been used as the excitation source, with an excitation density of the order of 1 mW cm^{-2} . The samples have been fixed in a dynamic flow test chamber with four apertures: two of them were used for the gas inlet and outlet, respectively, while the others were connected with an excitation and a collection of optical fibers. The FL emission was detected with a 75 mm focal length spectrometer (Avantes MC2000) coupled with a 2048 pixels silicon charge coupled device. The spectral resolution was 4 nm.¹⁰ The desired gas concentration in the chamber was obtained by mixing different flows of dry air and N_2 through a bank of two mass flow controllers (Brooks Instrument 5850S). Each controller could operate in the flow range 2.5–50 mL/min with an accuracy of $\pm 0.2\%$. The total flow in the test chamber was fixed at 50 mL/min. Before each measurement, the tested samples were exposed for 20 min in dry air flux in order to get sample stabilization.

The sensor response curve has been determined by measuring the FL intensity every 3 s, both in the low wavelength range 410–438 nm in which the FL is fully due to intrinsic PF8 emission and in the high wavelength range 580–640 nm in which the FL is mainly due to Keto defects emission. The FL intensity has been measured, in both ranges, during consecutive O_2 ON and OFF phases of 10 and 45 min, respectively. The oxygen concentration of the sample atmosphere has been changed in the range 0.47–9.35 mM, corresponding to an oxygen volume content in the range 1–21%. In order to avoid artifacts due to the laser intensity fluctuations during the measurements, the FL intensity has been normalized by the laser intensity, that has been monitored during all of the measurements with a photodiode connected with a pico-ammeter.

The FL spectrum of the PF8 films immediately after the deposition (see Figure 1) shows the typical emission resonances of the PF8 β -phase, with the 0–0 line centered at about 439 nm, followed by the 0–1 and 0–2 vibronic replicas at about 466 and 498 nm, respectively.¹¹ This result indicates that initially the sample

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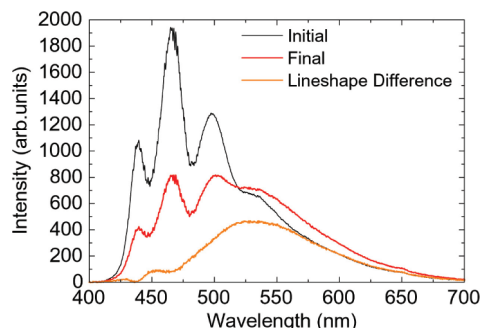


Figure 1. FL spectrum of the film before laser light exposure (black line), after 2 h of laser exposure in air (red line), and final Keto defects FL band (orange line).

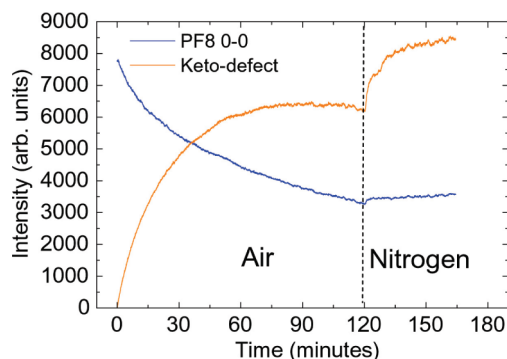


Figure 2. Time dependence of the Keto and PF8 0–0 line FL intensity during laser exposure in air for 2 h, followed by laser exposure in nitrogen.

is fully made by nonoxidized PF8 molecules. In order to investigate the effects of the interaction with oxygen in both the pristine PF8 and the photo-oxidized PF8, the first step of our experiment has been the photo-oxidation of the films by continuous laser exposure in air. The laser exposure in air results in a progressive exponential intensity decrease of the β -phase FL (see Figure 2) and in a simultaneous increase of the FL intensity in the 580–640 nm range. This effect is the typical signature of PF8 photo-oxidation leading to the formation of luminescent defects, commonly named Keto defects, with a FL emission centered at about 535 nm.⁸ This attribution is confirmed by the line shape of the difference between the final FL spectrum and the properly scaled initial FL, that is very close to the typical Keto defects emission band line shape (see Figure 1). Concerning the time dependence of the FL intensity of both the PF8 and the Keto defects FL, it is interesting to observe that while the PF8 FL continuously decreases, the Keto defects FL shows a formation in the first hour of laser exposure followed by a plateau, in which the FL intensity is stable within 5% of its maximum value for more than 1 h,¹² suggesting a constant number of emitting Keto defects. Once the constant Keto defect emission intensity regime has been reached, the sample atmosphere has been changed from dry air to nitrogen, observing a progressive and significant (about 40%) intensity increase of the Keto defects FL, which is completed in about 40 min. On the contrary, the PF8 FL shows a faster (about 2 min) but much weaker (about 4%) intensity recovery. This result clearly indicates that the presence of oxygen in the environment causes a partial quenching of the fluorescence of both species, that can be switched off by removing the oxygen. Such a reversible emission quenching has been observed in several phosphorescent molecules, and it has been ascribed to nonradiative exciton relaxation induced by collisions between the excited molecules and the oxygen ones.^{1,13}

In order to quantitatively investigate the FL quenching dependence on the oxygen content of the sample atmosphere,

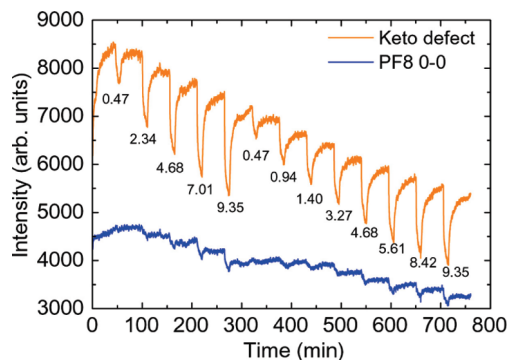


Figure 3. Response curve of the Keto defects and PF8 to different O₂ contents (in mM) (the PF8 intensity has been multiplied by 1.4 for clarity).

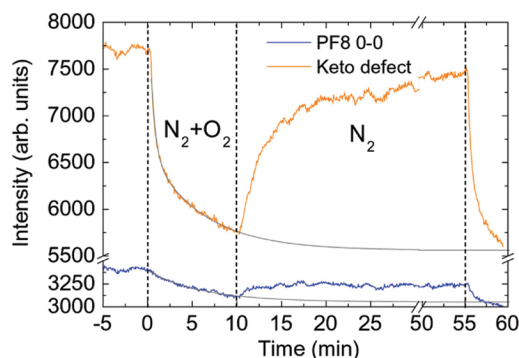


Figure 4. Details of the Keto defects FL and PF8 0–0 response curve to 8.42 mM O₂. The gray lines are the best fit curves.

we measured the FL intensity during laser exposures with oxygen content in the range 0.47–9.35 mM, corresponding to a volume content in the range 1–21%. The obtained results (see Figure 3) show that each laser exposure in the presence of the air–nitrogen mixture leads to a FL quenching of both emitting species, which increases with the oxygen content of the atmosphere. By looking at the intensity reduction after 10 min of exposure in the presence of oxygen, our measurements show that the PF8 FL quenching increases up to about 10%, but it is poorly reversible, as only less than one-half of the intensity reduction is recovered after the oxygen removal, indicating that the main oxygen effect on the pristine PF8 molecules is an irreversible FL quenching. On the contrary, the Keto defects FL quenching increases up to about 44% and more than 80% of this FL reduction is recovered at all of the investigated oxygen contents when oxygen is removed. The FL recovery in nitrogen is completed in about 40 min for both species. Together with the reversible FL quenching, an overall decrease of the FL intensity is observed during the measurements, as shown by the decrease of the steady state FL intensity in nitrogen of about 35% for both species after 12 h of continuous laser exposure that, anyway, does not affect the value of the relative FL quenching. Concerning the FL quenching time dynamics, the observed PF8 FL quenching can be reproduced (see Figure 4) at all of the investigated oxygen contents by a monoexponential decay with a nonzero limit value I_{on} with a time constant of 6.0 ± 0.3 min. The Keto defect FL quenching dynamics is instead biexponential with a fast decay time of 25 ± 1 s and a slow decay time of 7.2 ± 0.8 min.

The evidence of strong and reversible FL quenching observed for the Keto defects shows the basic properties of an active material for optical oxygen sensors based on FL quenching. In order to quantify the sensitivity of the Keto defects FL for

oxygen detection, we determined, for all of the explored oxygen contents, the ratio between the FL intensity immediately before the O₂ ON phases I_{off} and the plateau value during the O₂ ON phases I_{on} . We remember that in the simplest case of a single quenched species with a well-defined quenching efficiency a linear increase of the quenching ratio $I_{\text{off}}/I_{\text{on}}$ with the oxygen concentration [O₂] is expected, according to the Stern–Volmer relation:

$$\frac{I_{\text{off}}}{I_{\text{on}}} = 1 + K_{\text{SV}}[\text{O}_2] \quad (1)$$

where the Stern–Volmer constant K_{SV} represents the sensor sensitivity.

In our samples, the $I_{\text{off}}/I_{\text{on}}$ dependence on the oxygen content (see Figure 3) shows a nonlinear quenching increase, with a slope progressively decreasing with the oxygen concentration from about 1500 M⁻¹ for [O₂] ≤ 1 mM down to about 16 M⁻¹ for [O₂] ≥ 4 mM. Several models have been proposed to explain the nonlinear Stern–Volmer plot in oxygen sensors, like the presence of two or more types of quenching sites within the active medium,¹⁴ of a single type of quenched species with K_{SV} distributed with a truncated Gaussian distribution,¹⁵ or with a log-normal distribution.¹⁶ In particular, the K_{SV} log-normally distributed model has been adopted with success to heterogeneous active films with a distribution of FL lifetime, including organic molecules.^{16,17} We then assumed a Gaussian distribution of $\ln(K_{\text{SV}}/\bar{K})$ with standard deviation ρ . The best fit curve (see Figure 3) excellently reproduces the data for $\bar{K} = 12 \text{ M}^{-1}$ and $\rho = 5.5$. The distribution of K_{SV} (see inset of Figure 3) shows that K_{SV} increases up to about 3000 M⁻¹ within one standard deviation of $\ln(K_{\text{SV}}/\bar{K})$. For the sake of comparison, we observe that this value is comparable with the highest values reported for phosphorescent organic oxygen sensors,⁹ which is of the order of 1200 M⁻¹. The broad distribution of K_{SV} results in the strongly nonlinear Stern–Volmer plot, in which the molecules with $K_{\text{SV}} \geq 1500 \text{ M}^{-1}$ determine the sensor performances up to [O₂] ≈ 1 mM, while the molecules with lower K_{SV} determine the sensor response at higher oxygen contents.

In conclusion, we investigated the FL dependence on the oxygen content of the environment of PF8 thin films. We show that the interactions of photoexcited PF8 with oxygen include not only the well-known irreversible photo-oxidation, resulting in blue FL quenching and in the formation of Keto defects, but also reversible FL quenching, which has been exploited for the realization of a prototype oxygen sensor based on FL quenching. The Keto defects sensors show a nonlinear response to the oxygen concentration increase, consistent with a distribution of K_{SV} . The best fit distribution of K_{SV} indicates that the sensing sensitivity of Keto defects is comparable with the organic oxygen sensors based on phosphorescence quenching. These results open the way for applications of conjugated polymers to oxygen sensors based on fluorescence quenching. We observe that, despite the promising results in terms of sensing sensitivity, our samples also show irreversible degradation of the fluorescence, leading to an overall decrease of the FL intensity of about 35% after 12 h of continuous laser exposure. Even if this degradation does not affect the relative FL quenching values, which is exploited for the quantification of the oxygen content of the atmosphere, it is clear that the fluorescence irreversible quenching in the presence of oxygen has to be reduced, in order to allow a sensor lifetime adequate for applications. Even if the possible strategies to improve the lifetime

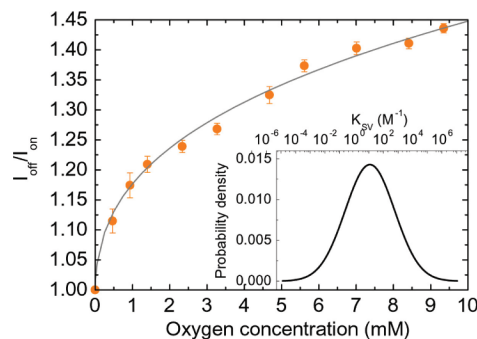


Figure 5. Stern–Volmer FL intensity quenching plot for the Keto defects FL (full dots). The gray line is the best fit curve. Inset: best fit distributions of the Stern–Volmer constants for the Keto defects.

surely include the development of properly functionalized molecules with higher photostability in air, we observe that the actual lifetime is strongly affected by the details of the experiment that we performed. First of all, the actual lifetime is limited by the necessity to continuously probe the FL intensity, in order to study the time dynamics of the quenching. Anyway, as the time scale of the FL quenching and recovery is of the order of tens of minutes, the simple use of optical excitation of the sample every few minutes, instead of continuous, should allow a strong lifetime extension (for example, the probing of the FL intensity every 15 min would extend the lifetime by about 300 times). Finally, the improvement of the collection geometry that currently exploits an optical fiber coupled to a spectrograph, by decreasing the exposure time necessary to obtain a good FL signal, could lead our films not so far from the typical lifetimes required for commercial applications.

Acknowledgment. We wish to thank Mauro Lomascolo, Arianna Cretí, and Marco Alemanno for useful discussions and Flavio Casino for valuable technical assistance.

References and Notes

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