# A Novel Optical Oxygen Sensing Based on Quenching of Photoexcited Triplet State of $C_{70}$ in Polystyrene Film by Oxygen Using Time-resolved Spectroscopy

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(Received November 10, 1998; CL-980854)

A novel optical oxygen sensor based on the quenching of triplet-triplet absorption of $C_{70}$ molecule by oxygen has been developed using time-resolved spectroscopy. The photoexcited triplet state of $C_{70}$ was quenched effectively by oxygen and large Stern-Volmer constant was obtained.

Measurement of oxygen concentration is very important in the various fields. The determination is usually carried out amperometrically using Clark-type electrodes. This system, however, is limited by the stability of the electrode surface and instabilities in the oxygen diffusion barrier. Recently, optical oxygen sensing methods based on luminescence quenching of an indicator by oxygen have gained much interest. Indicators for this sensor are luminescent and oxygen-quenchable organic dyes, such as polycyclic aromatic hydrocarbons,[1,2] metalloporphyrins [3-6] and transition metal complexes.[7,8] As most dyes have no oxygen-quenchable luminescence at room temperature, however, a number of oxygen-quenchable compounds is extremely limited. The excited triplet lifetime of such non-luminescent compounds is determined using triplet-triplet ($T_1$-$T_n$) absorption on a flash photolysis set-up. As reported previously, the system using $T_1$-$T_n$ absorption quenching of zinc porphyrin-doped film for measuring oxygen concentration.[9,10] This method extends a number of indicators available for oxygen sensor. One of the candidate indicators available for oxygen sensor is fullerenes ($C_{60}$, $C_{70}$ and so on). Fullerenes possess useful electronic and photochemical properties.[11-23] Among fullerenes, $C_{70}$ possesses long-lifetime of photoexcited triplet state and the triplet state is quenched by oxygen efficiently (quenching efficient is about 1.0).[11-13, 23] Thus, $C_{70}$ is attractive compound for optical oxygen sensor. In this letter we hope to describe the high sensitive oxygen sensor system based on $T_1$-$T_n$ absorption quenching of $C_{70}$-polystyrene film using time-resolved spectroscopy.

$C_{70}$ was obtained from Wako Chemicals and was purified by recrystalization with benzene. Polystyrene (PS, average M.W. 280 000, GPC grade) was purchased from Aldrich. The other materials were of the highest grade available. A quartz optical fiber (core/cladding diameter, 0.025 mm) was from DOLAN-JENNER Co. Laser flash photolysis was carried out by using Nd-YAG OPO laser (Spectra Physics, pulse width 10 ns) at room temperature. A xenon arc lamp as a monitoring light beam was coupled into one end of an optical fiber. The light reflected by oxygen sensing film was transmitted by the same fiber to a photomultiplier (Hamamatsu Photonics RE201). The transient spectra were stored in storage · oscilloscope (SONY-Tektronix TDS360). Different oxygen standards (in the range 0-100%) in a gas stream were produced by controlling the flow rates of oxygen and argon gases entering a mixing chamber. The oxygen concentration was estimated by dividing the oxygen flow rate by the sum of the total flow rate of mixed gases. The total pressure was maintained 760 Torr. The experimental details were described in the previous literature.[9] $C_{70}$-PS films were formed by casting of mixture of 30 wt% PS in toluene and $C_{70}$ onto glass slides. The concentration of $C_{70}$ in PS was approximately $3.0\times10^{-5}$ mol dm$^{-3}$. The films were dried at room temperature and stored in dark prior to use. The thickness of film was about 80 μm. The $C_{70}$-PS film has a good photostability under laser irradiation.

The absorption spectrum of $C_{70}$-PS film was similar than that of toluene solution, indicating that no electrical interaction between $C_{70}$ and PS at the ground state. The typical decays of the triplet state of $C_{70}$ excited at 532 nm with monitored at 860 nm under argon (a) and oxygen (b) are shown in Figure 1. The decays obeyed first order kinetics in the absence of oxygen. On the other hand, the absorption of the photoexcited triplet state of $C_{70}$ was disappeared in the oxygenated condition shown in Figure 1 (b). The lifetime of the photoexcited triplet state of $C_{70}$ under oxygen decreased, compared to that under argon, indicating that the effective quenching of excited triplet state of $C_{70}$ in PS film by oxygen occurred. This result shows $C_{70}$-PS film is effective oxygen sensing material.

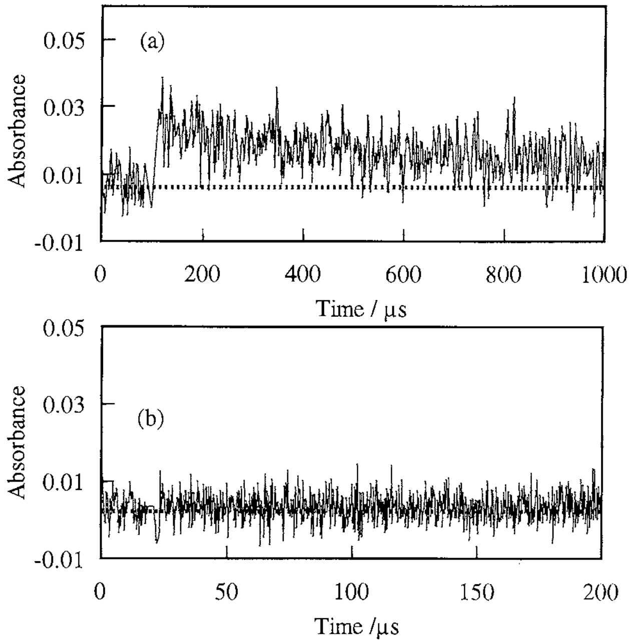

**Figure 1.** Typical decay of the photoexcited triplet state of $C_{70}$ in PS film, under argon (a) and oxygen (b). Excitation and monitored wavelength was 532 and 860 nm, respectively. The dotted line indicates the baseline.

Figure 2 shows the photoexcited triplet lifetimes of $C_{70}$ in

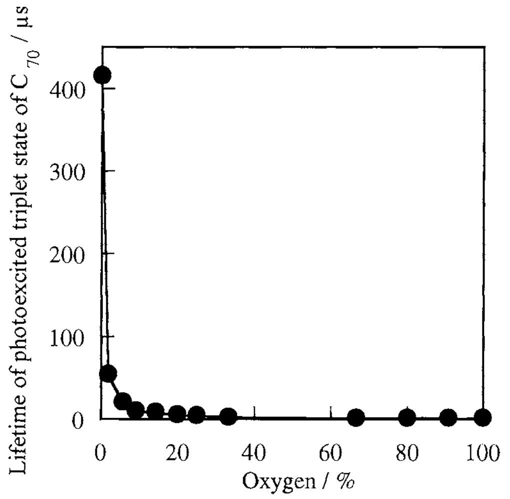

**Figure 2.** Quenching of the photoexcited triplet state of $C_{70}$ in PS film by oxygen.

PS with oxygen concentration. The photoexcited triplet lifetimes of $C_{70}$ were estimated by the first order kinetics ($C = \exp(-kt)$; where $C$ is the concentration of photoexcited triplet state of $C_{70}$, $k$ is the rate constant for the decay of photoexcited triplet state, equal to the inverse of the lifetime, $\tau$). The lifetime decreases with increasing oxygen concentration. Figure 3 shows a Stern-Volmer relationship between the photoexcited triplet state of $C_{70}$ in PS film and oxygen concentration ($\tau_0/\tau - 1 = K_{sv}[O_2]$, $K_{sv} = k_q\tau_0$; where $\tau_0$ and $\tau$ are triplet lifetimes in the absence and in the presence of oxygen, respectively. $[O_2]$ is the concentration of oxygen and $K_{sv}$ is the Stern-Volmer quenching constant. $k_q$ is the bimolecular quenching constant by oxygen.). A Stern-Volmer plot of $C_{70}$ exhibits linearity ($r^2$=0.992) and $K_{sv}$ is estimated to be 4.31 $\%^{-1}$. The quenching rate constant, $k_q$ is estimated to be 1.1 $\times 10^4$ $\%^{-1}$ $s^{-1}$. In the system using zinc tetraphenylporphyrin (ZnTPP), on the other hand, $K_{sv}$ was estimated to be 0.124 $\%^{-1}$.[9] Especially, $C_{70}$ film indicates high sensitivity for oxygen at a low concentration. The limit of detection for oxygen concentration was improved up to about 0.5%. These results show the $C_{70}$-PS film is novel oxygen sensor, compared with the other dye compounds.

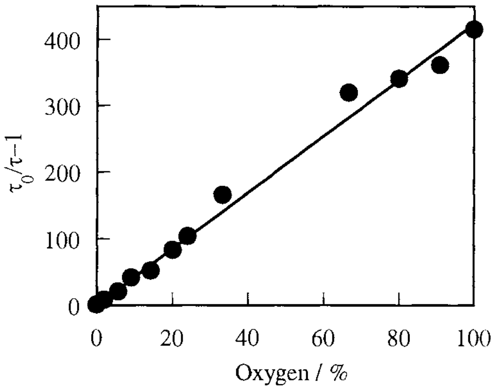

**Figure 3.** Stern-Volmer relationship between the lifetime of photoexcited triplet state of $C_{70}$ in PS film and oxygen concentration.

Next let us focus on the sensing properties of $C_{70}$-PS film for oxygen. In general, the sensing properties are strongly affected by the thickness of film. A thinner film needs less time for the oxygen inside of the film to reach equilibrium with the outside environment. In this system, however, $K_{SV}$ seems to be little affected by differences in the film thickness. This result indicates that this system is able to measure the oxygen concentration on the surface. The photostability of sensing film is important factor to apply for optical sensor. To characterize the photostability of $C_{70}$-PS film, the absorption spectrum of $C_{70}$-PS film was measured after laser irradiation. No spectrum change was observed, indicating that the $C_{70}$-PS film has a good photostability under laser irradiation.

In this study, the photoexcited triplet lifetimes of $C_{70}$ in PS under different oxygen pressure conditions were measured by T-T absorption method using time-resolved spectroscopy. The photoexcited triplet state of $C_{70}$ in PS was quenched effectively by oxygen and large Stern-Volmer constant was obtained. A high sensitive oxygen sensor based on the quenching of triplet-triplet absorption of $C_{70}$ molecules by oxygen has been developed.

This work was partially supported by the Grant-in Aid for Scientific Research on Priority-Areas-Research from the Ministry of Education, Science, Sports, and Culture of Japan (No.10145211).

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