Novel Oxygen Sensor Based on Quenching of Triplet-Triplet Absorption of Zinc Tetraphenylporphyrin

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A novel oxygen sensor based on the quenching of triplet-triplet absorption of zinc tetraphenylporphyrin (ZnTPP) molecules by oxygen has been developed. The excited triplet lifetime of ZnTPP-PS film decreases as increasing of oxygen concentration. This sensor showed linear Stern-Volmer plots and was capable of oxygen measurement.

Determination of oxygen concentration is important in various field of chemical, clinical analysis and environmental monitoring.[1-3] Recently, much interest has been gained to optical sensors based on the luminescence quenching of the indicator by oxygen because of their high sensitivity and specificity.[4-6] Indicators available for this sensor are luminescent and oxygen-quenchable organic dyes, such as polycyclic aromatic hydrocarbons and transition metal complexes. However, most organic compounds have no luminescence at room temperature and if so, the number of oxygen-quenchable compound is extremely limited. Triplet-triplet (T_1-T_n) absorption on a flash photolysis set-up allows us to decide the excited triplet lifetime of such nonluminescent compounds. This method extends the number of indicators available for oxygen sensor. In this study we have used T_1-T_n absorption quenching of zinc tetraphenylporphyrin (ZnTPP)-doped film for measuring oxygen concentration.

Tetraphenylporphyrin(TPP) was synthesized according to Adler's method.[7] ZnTPP was synthesized by refluxing TPP with about 10 equiv. of zinc acetate (Kanto Chemical Co., Inc.) in chloroform for 4 h. After evaporation of the solvent in vacuo, the product was washed with water several times, dried in vacuo and stored at room temperature. Polystyrene (average M.W. 280000, GPC grade) was purchased from Aldrich. A quartz optical fiber (core/cladding diameter, 0.025 mm) was from DOLAN-JENNER Co.

Figure 1 shows the sensor system for measuring oxygen. 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. The transient spectra were stored in storage oscilloscope (SONY-Tektronix TDS360). Different O_2

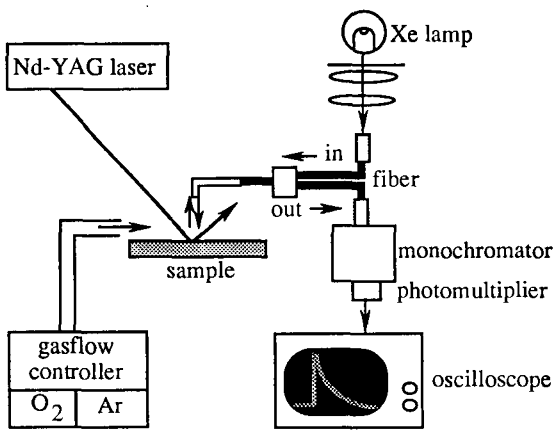

Figure 1. System for measuring of T1-Tn absorption of ZnTPP-PS film.

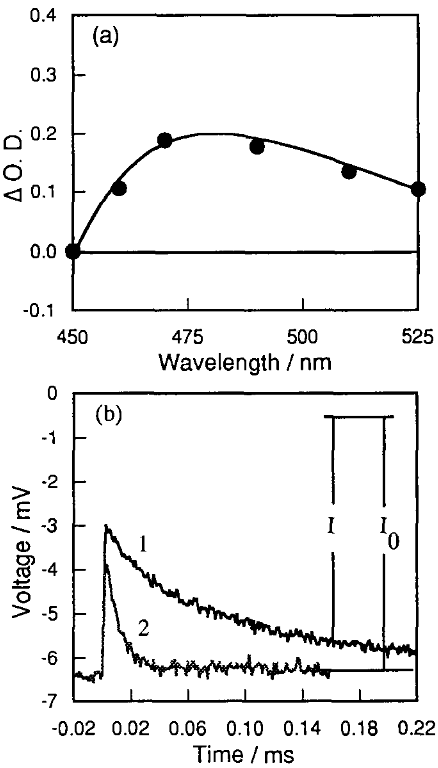

Figure 2. Transient absorption spetrum (a) and decay curve (b) of excited triplet ZnTPP in PS film, under argon (1) and oxygen (2). Note: Absorbance of excited triplet = log I_0 / I.

standards (in the range 0-100%) in a gas stream were produced by controlling the flow rates of O_2 and Ar gases entering a mixing chamber. The total pressure was maintained at 1 atm.

ZnTPP-doped PS films (ZnTPP-PS) were formed by casting of mixture of 30 wt% polystyrene (PS) in toluene and ZnTPP onto glass slides. The concentration of ZnTPP in PS was approximately 2.9×10^{-5} M. The films were dried at room temperature and stored in dark prior to use. The ZnTPP-PS film has a good photostability under laser illumination.

Figure 2(a) shows the transient absorption spectra of ZnTPP-PS film excited at 550 nm. The band at 470 nm is attributed to the T_1-T_n absorption. Figure 2(b) is the time profiles of the triplet state of ZnTPP (monitored at 470 nm) under argon(1) and oxygen(2). The decays in the absence and the presence of oxygen were followed by first order kinetics. The faster decay under oxygen, compared to that under argon, indicates that the excited triplet state of ZnTPP is quenched by oxygen. This result indicates the application to an oxygen sensor.

In the reaction conditions the decays of the T_1-T_n absorption of ZnTPP obeyed first order kinetics. Figure 3(a) shows the photoexcited triplet lifetimes of ZnTPP with oxygen concentration. The triplet lifetimes of ZnTPP were calculated by the first order plot. The lifetime decreases with increasing oxygen concentration. Figure 3(b) shows a Stern-Volmer plot ($t_0/t - 1 = K_{sv} [O_2]$; where t_0 and t are triplet lifetimes in the absence and presence of oxygen, respectively. $[O_2]$ is the concentration of oxygen and K_{sv} is the Stern-Volmer quenching constant). A Stern-Volmer plot of ZnTPP exhibits considerable linearity (r=0.988) and a good reproducibility.

In this study, the triplet lifetimes of ZnTPP under different O_2 pressure conditions were measured by T-T absorption method. The excited triplet lifetimes were quenched effectively by oxygen and this response were reproducible. This relationship shows that ZnTPP is available as a material for oxygen sensor. The studying of the applicability of other nonluminescent compounds to measure O_2 concentrations using O_2 quenching of T-T absorption method is now in progress.

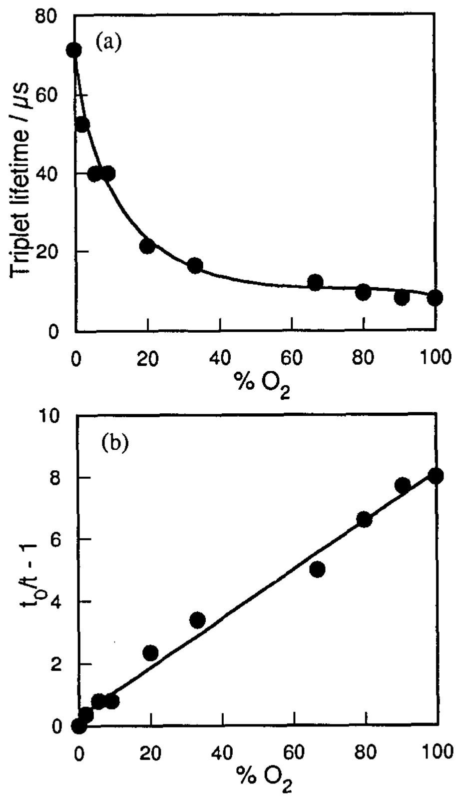

Figure 3. Quenchingof the lifetime of ZnTPP by oxygen (a) and a Stern-Volmer plot (b).

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