

Optical oxygen sensing based on triplet-triplet decay of platinum octaethylporphyrin-polystyrene film using time-resolved spectroscopy by laser flash photolysis

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Abstract. Optical oxygen sensing system based on the quenching of the photoexcited triplet state of platinum octaethylporphyrin, PtOEP in polystyrene (PS) by means of time-resolved spectroscopy using laser flash photolysis has been developed. The decays of the triplet-triplet reflectance of PtOEP in PS consisted of two components (faster and slower lifetimes) in the absence and presence of oxygen. In both of faster and slower components, the lifetime decreases with increasing oxygen concentration and a Stern-Volmer plot of PtOEP-PS film exhibits linearity. However, k_q in faster component is larger than that of slower component, indicating that two different oxygen-accessible sites exist in PtOEP-PS film. The faster and slower components are attributed to oxygen-accessible sites on the surface and bulk of PtOEP film, respectively. The contribution of different oxygen-accessible sites in PtOEP-PS film for oxygen sensing is clarified by this technique.

Keywords. Platinum Octaethylporphyrin (PtOEP) – optical oxygen sensing – time-resolved spectroscopy – laser flash photolysis.

Determination of oxygen concentration is important in various fields of chemical, clinical analysis and environmental monitoring [1,2]. Recently, much attention has been paid to optical sensors based on the luminescence quenching of the indicator [3] such as polycyclic aromatic hydrocarbons [4-6], metalloporphyrins [7-9] and transition metal complexes [10-12], by oxygen, because of their high sensitivity and specificity. Many studies on optical sensing have explored the luminescence intensity change by oxygen. Although intensity measurements are simple, the observed intensity depends on the thickness of the sensing film, scattering light from background or the concentration of dye in the film. We reported the optical oxygen sensing system using luminescence intensity change of platinum octaethylporphyrin-polystyrene (PtOEP-PS) film by oxygen [8]. However, the oxygen sensing mechanism of PtOEP-PS film has not been clarified. On the other hand, lifetime measurements are concerned only with the rate of decrease of the light emission following a flash of excitation light and do not depend on the absolute intensity of the emitted light. The concept of using lifetime measurement of photoexcited triplet state of dye has proven to be attractive for optical oxygen sensing. It has important advantages for certain applications compared to the steady state luminescence quenching based methods [13]. As reported previously, the optical oxygen sensing system based on triplet-triplet absorption quenching of zinc porphyrin-polymer film by oxygen using time-resolved spectroscopy by laser flash photolysis has been

developed [14]. By using this method, the oxygen sensing mechanism of PtOEP-PS will be clarified.

In this letter, we describe the properties of optical oxygen sensing based on triplet-triplet absorption decay of PtOEP-PS film by oxygen using a time-resolved spectroscopy by laser flash photolysis.

Experimental

PtOEP (obtained from Porphyrin Products, Logan, UT, USA)-PS (average M.W. 280 000, GPC grade obtained from Aldrich, Milwaukee, WI) films were formed by casting mixture of 30-wt % PS in toluene and PtOEP onto non-luminescence glass slides. The concentration of PtOEP in PS was approximately 3.0×10^{-5} mol dm⁻³. The films were dried at room temperature and stored in dark prior to use. The PtOEP-PS film has a good photostability under laser irradiation. Laser flash photolysis was carried out using Nd-YAG OPO laser (Spectra Physics, pulse width 10 ns) at room temperature. The excitation wavelength was 535 nm, which is attributed to Q-band of PtOEP. The experimental setup for optical oxygen sensing using laser flash photolysis are reported previously [14]. The decay curves of photoexcited triplet state of PtOEP-PS film were obtained by averaging 256 single shots using a storage oscilloscope (SONY-Tektronix TDS360). Decay curves were analyzed without deconvolution by fitting with the following equation:

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$$R(t) = \sum A_n \exp(-t/\tau_n) \quad (1)$$

Where, $R(t)$ is time-resolved reflectance, τ is the lifetime of photoexcited triplet state. A_n is the fractional contributions to each lifetime components. The calculated values of $R_c(t)$ are then compared to the experimental $R(t)$ values and the goodness-of-fit is determined by minimization of the χ^2 function:

$$\chi^2 = \sum w_n [R(t) - R_c(t)]^2 \quad (2)$$

where, w_n is a statistical weighting factor that accounts for the uncertainty in each $R(t)$ value. When w_n accurately describes the uncertainty in $R(t)$, χ^2 and random distribution of residuals $[R_c(t) - R(t)]$ is equal to 1.0 and zero, respectively.

Results and discussion

Figure 1 shows typical decays of the photoexcited triplet state of PtOEP (monitored at 470 nm, maximum of triplet-triplet absorption of PtOEP) under argon saturated (a) and oxygen saturated condition (b). The lifetimes of PtOEP in PS were calculated by fitting with the equation (1) and (2). When n is equal to 2, χ^2 value is close to 1.0 and best-fit curve is obtained under argon saturated ($\chi^2=1.09$) and oxygen saturated ($\chi^2=1.10$) conditions. Solid lines in figure 1 are best-fit curves using the equation (1) and (2) ($n=2$). Thus, the decays consisted of two components (shorter and

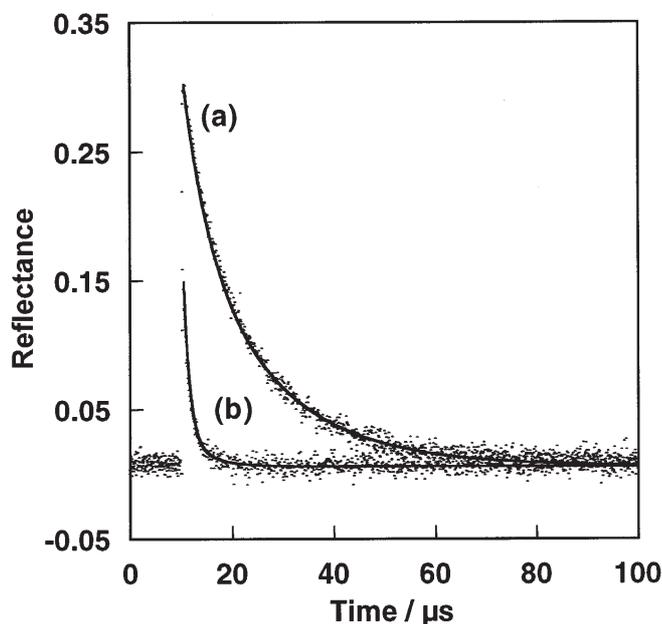


Fig. 1. Typical decay of the photoexcited triplet state of PtOEP-PS film after laser flash photolysis monitored at 470 nm. (a) argon saturated; (b) oxygen saturated condition. Excitation wavelength: 535 nm. The solid line indicates the best-fit curve by equation (1) and (2) ($n=2$).

longer lifetimes) under argon saturated and oxygen saturated conditions. The decay of the photoexcited triplet state of PtOEP under oxygen saturated condition was faster than that under argon saturated condition, indicates the effective quenching of the excited triplet state of PtOEP by oxygen.

Figure 2 (a) shows the lifetimes of photoexcited triplet state of PtOEP with oxygen concentration, calculated by fitting with the equation (1) and (2). The decays consisted of two components (shorter and longer lifetimes) under various oxygen concentration conditions. In all cases, the error of lifetime analyzed was within $\pm 0.2 \mu\text{s}$. In both faster (●) and slower (■) components, the lifetime decreases with

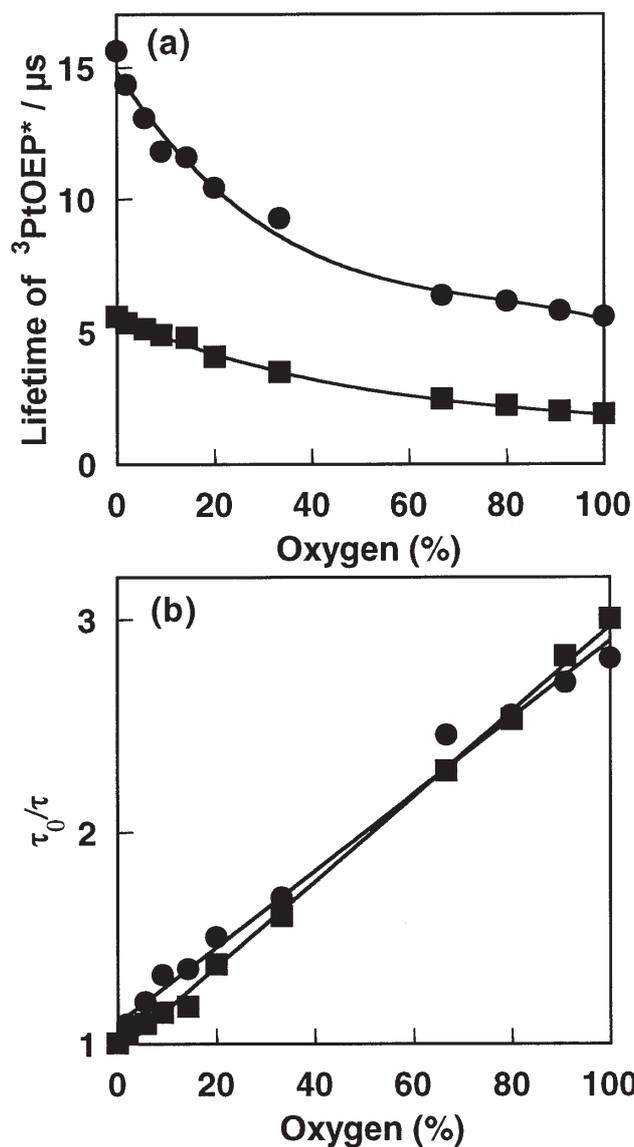


Fig. 2. Photoexcited triplet state of lifetime of PtOEP-PS film with oxygen concentrations (a) and Stern-Volmer plot (b). (●): faster component; (■): slower component. The lifetimes under various oxygen concentrations were calculated by equation (1) and (2).

increasing oxygen concentration. Figure 2(b) shows a Stern-Volmer plot ($\tau_0/\tau = K_{sv} [O_2] + 1$; where τ_0 and τ are lifetimes in the absence of oxygen and in various oxygen concentration, respectively. $[O_2]$ is the concentration of oxygen and K_{sv} is the Stern-Volmer quenching constant). K_{sv} was calculated from the slope of the straight line using least squares. K_{sv} of the faster (●) and slower (■) lifetime components are estimated to be 0.020 and 0.018 %⁻¹, respectively. The correlation factor, r^2 , as linearity index of plot, of the faster and slower lifetime components are estimated to be 0.990 and 0.997, respectively. However, K_{sv} strongly depends on τ_0 and quenching rate constant k_q ($K_{sv} = k_q\tau_0$). In faster and shorter components, the rate constant of quenching are estimated to be 4.0×10^3 and 1.3×10^3 %⁻¹ s⁻¹, respectively. K_{sv} and k_q values obtained are almost the same values using the luminescence lifetime [15]. These results indicate that two different oxygen-accessible sites exist in PtOEP-PS film. The faster and slower components are attributed to oxygen-accessible site on the surface and bulk of the PtOEP film, respectively. In the fractional contributions to each lifetime component, the contribution of the faster component is 1.40 times larger than that of the slower component, indicating that the sensing site on the surface is important for optical sensing. The sensing properties are strongly affected by the thickness of the film. In this system, however, K_{sv} seems to be little affected by the difference of the film thickness. This result indicates that the measurement system using triplet-triplet absorption decay is suitable to get the oxygen concentration on the surface. In this system, the limit of detection for oxygen on the surface was ca. 0.5 %.

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