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Optical Oxygen Pressure Sensing Based on Triplet–Triplet Quenching of Fullerene–Polystyrene Film Using Laser Flash Photolysis: Soccerballene C_{60} Versus Rugbyballene C_{70}

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An optical oxygen-sensing system based on the triplet lifetimes of fullerenes C_{60} and C_{70} in polystyrene (PS) under different oxygen pressures was developed using laser flash photolysis. The lifetime of the photoexcited triplet state of fullerene–PS film decreases with increasing oxygen pressure. The photoexcited triplet state of fullerene–PS film was effectively quenched by oxygen. The quenching rate constant of the photoexcited triplet state of C_{60} and C_{70} in PS film by oxygen, k_q, were estimated to be 6.6×10^2 and 1.4×10^3 $\text{Torr}^{-1}\,\text{s}^{-1}$, respectively (1 Torr = 133.322 Pa). The linearity of a Stern–Volmer plot of C_{60}–PS film ($r^2 = 0.999$) is superior to that of C_{70}–PS film ($r^2 = 0.992$). These results show that C_{60}– and C_{70}–PS films are highly sensitive for oxygen in the total oxygen pressure region and in the low oxygen pressure region, respectively.

Oxygen sensors are extensively used in various fields to determine the oxygen concentration.[1—3] The amperometric method using an oxygen electrode has been the most popular technique among various oxygen-sensing systems.[4] This system, however, is limited by the stability of the electrode surface and instabilities in the oxygen diffusion barrier. Recently, much attention has been given to optical oxygen-sensing methods based on the luminescence quenching of an indicator by oxygen. Indicators available for this sensor are luminescent and oxygen-quenchable organic dyes, such as polycyclic aromatic hydrocarbons (pyrene and its derivatives),[5—11] platinum and palladium porphyrins,[12—15] and transition-metal complexes.[16—23] Because the fluorescence lifetime of polycyclic aromatic hydrocarbons is fairly longer (ca. 100 ns), the fluorescence is quenched by oxygen.[24] On the other hand, the fluorescence of metalloporphyrins and transition-metal complexes is not quenched by oxygen, because of the short lifetime of the fluorescence.[25] Because most organic compounds have no phosphorescence at room temperature, however, the number of oxygen-quenchable compounds is extremely limited. Triplet–triplet absorption on a flash photolysis set-up allows us to decide the excited triplet lifetime of non-phosphorescent compounds. The photoexcited triplet state of an organic compound on the solid surface has been studied using diffuse reflectance laser flash photolysis.[26,27] As previously reported a system using triplet–triplet reflectance quenching of zinc porphyrin-doped film for measuring the oxygen concentration was developed.[28,29] This method extends the number of indicators available for oxygen sensor. One of the available candidate indicators is fullerene. Fullerene possesses useful electronic and photochemical properties.[30—41] The lifetime of the photoexcited triplet state of fullerenes is pretty long (ca. 500 μs). Especially, the photoexcited triplet state of fullerenes is quenched by oxygen efficiently.[30] The singlet oxygen is produced by the reaction of the photoexcited triplet state of fullerene with oxygen.[37]

Thus, fullerene is an attractive compound for an optical oxygen sensor based on laser flash photolysis. In this work we hope to describe the characterization of the quenching processes between the photoexcited triplet state of fullerenes (C_{60} and C_{70}) and the oxygen molecule in polystyrene (PS) film and a highly sensitive oxygen sensor system based on the triplet–triplet quenching of fullerene–PS film using laser flash photolysis.

Experimental

C_{60} and C_{70} were obtained from Tokyo Kasei Inc. and Wako Pure Chemicals, respectively. Fullerenes were purified by recrystallization with a toluene–benzene mixed solvent. Polystyrene (average M.W. 280000, GPC grade) was purchased from Aldrich. Non-luminescence glass slides were obtained from Mitsubishi Chemical Co., Ltd. The other reagents were of the highest grade available.

Fullerene-doped PS films were prepared by casting a mixture of 30 wt% PS in toluene and fullerene onto non-luminescence glass slides. The concentration of fullerene in PS was approximately 3.0×10^{-5} $\text{mol}\,\text{dm}^{-3}$. The films were dried at room temperature and stored in dark prior to use.

The absorption spectra of fullerene in PS film and in toluene solution were measured using a Shimadzu Multi-spec 1500 spectrometer.

The experimental setup for an optical oxygen-sensing system using laser flash photolysis has been shown in our previous reports.[28,29] Laser flash photolysis was carried out using an OPO-Nd-YAG laser (Spectra Physics GCR-100, Spectra Physics MOPO-700, pulse width 10 ns) at room temperature. The laser power was ca. 40 mJ. A xenon arc lamp (Hamamatsu Photonics), used as a monitoring light beam, was coupled into one end of an optical fiber (Dolan–Jenner Co., Microopticscanner ELY 2724, core/cladding diameter, 0.025 mm). The light reflected by the oxygen-sensing film was transmitted by the same fiber to a monochromator (Spectra Physics, triple monochromator) and a photomultiplier (Hamamatsu Photonics R928). The transient spectra were stored in a storage oscilloscope (SONY-Tektronix TDS360). The optical changes are given as $\Delta R/R_0$, where R_0 is the reflectance of the sample in the absence of the laser and ΔR is the change produced by laser irradiation. 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 calculated by dividing the oxygen flow rate by the sum of the total flow rate of the mixed gases. The total pressure was maintained at 760 Torr.

Decay curves were obtained by averaging 256 single shots, which were analyzed without deconvolution by fitting with the following equation:

$$R(t) = \sum A_n \exp(-t/\tau_n). \tag{1}$$

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

$$\chi^2 = \sum w_n [R(t) - R_c(t)]^2, \tag{2}$$

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 the random distribution of residuals $[R_c(t) - R(t)]$ are equal to 1.0 and zero, respectively.

The stability of the sensing film against irradiation was measured by the change in the absorption spectrum before and after irradiation using a Nd-YAG laser or continuous irradiation using 100 mW-tungsten lamp against film.[42] Ultravisible light at less than 390 nm was removed using a cut-off filter (Toshiba L-39). The distance between the film and the lamp was 10 cm.

Results and Discussion

Figure 1 shows the absorption spectra of fullerenes C_{60} and C_{70} dispersed in PS films and in a toluene solution. In both cases, the shape of the spectrum in PS film is almost the same as in solution, indicating no interaction between the fullerenes and PS at the ground state.

Figure 2 shows the transient reflectance spectra of fullerene–PS films excited by light at 532 nm. The reflectance bands at 750 and 860 nm are attributed to the triplet–triplet reflectance of C_{60} and C_{70}, respectively. Figure 3 shows the typical decays of the triplet state of fullerene under argon (1) and oxygen (2) saturated conditions. The monitoring wavelength of C_{60} and C_{70} were 740 and 860 nm, respectively. When n is equal to 1, the χ^2 values are close to 1.0, and a best-fit curve is obtained in both the absence and presence of oxygen. The solid lines in Fig. 3 are the best fit using the Eq. 1 ($n = 1$). The decays in the absence and the presence of oxygen are followed by first-order kinetics. The photoexcited triplet state of fullerene decayed with increasing oxygen pressure, indicating that the excited triplet state of fullerene in PS film is effectively quenched by oxygen.

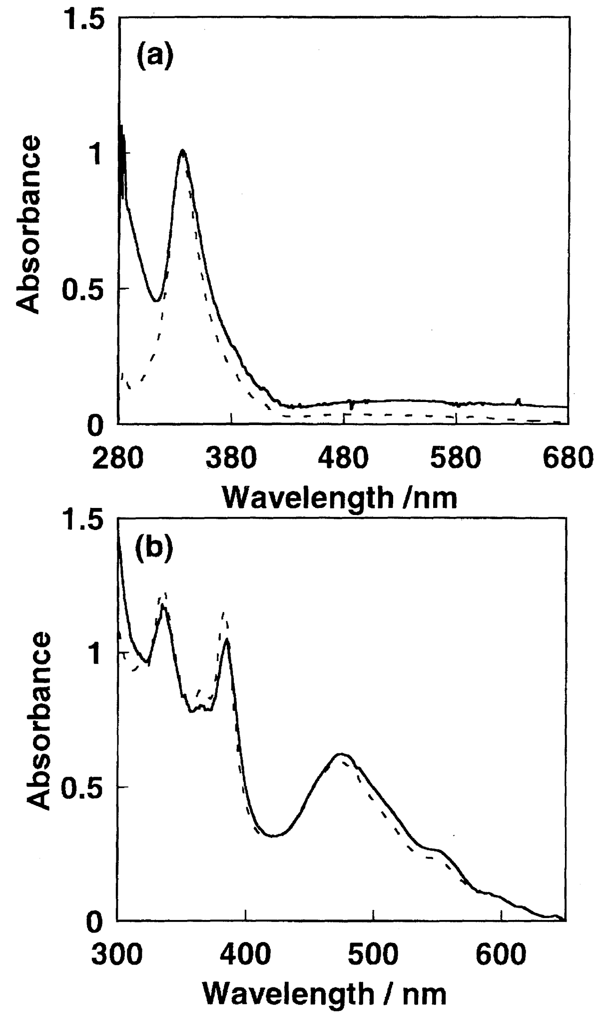

Fig. 1. Absorption spectra of (a) C_{60} and (b) C_{70} in PS film (solid line) and in toluene solution (dotted line).

Figure 4 shows the photoexcited triplet lifetimes of fullerene in PS film with oxygen pressure. The triplet lifetimes of fullerene in PS film were calculated by the fitting of decays using Eq. 1 in Experimental Section. The decays are followed by first-order kinetics in the total oxygen pressure region. The lifetime decreases with increasing oxygen pressure. The lifetimes of the photoexcited triplet state of fullerene in PS under deoxygenated, air-saturated, and oxygenated conditions are summarized in Table 1. The lifetime of the photoexcited triplet state of C_{70} is about four times longer than that of C_{60} under the deoxygenated condition. It has been reported that the photophysical properties of C_{70} resemble those of C_{60}, but differ in some respects. The lifetime of the photoexcited triplet state of C_{70} in benzonitrile is about four-times longer than that of C_{60}.[32,33] On the other hand, the lifetimes of C_{60} are longer than those of C_{70} under air-saturated and oxygenated conditions. A highly sensitive oxygen sensor has been developed using compounds having a long lifetime of the photoexcited triplet state under the deoxygenated condition and efficient quenching of the

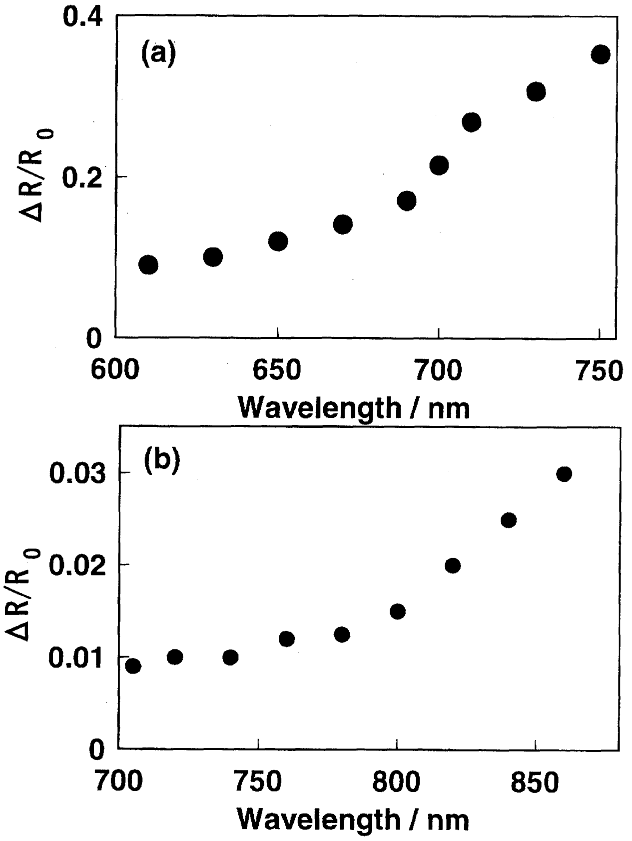

Fig. 2. Transient reflectance spectrum of the photoexcited triplet state of (a) C_{60} and (b) C_{70} in PS film under argon-saturated condition. Excitation wavelength is 532 nm.

photoexcited triplet state by oxygen. C_{70} is an attractive compound for an optical oxygen sensor. To determine the oxygen pressure, the Stern–Volmer relationship between the photoexcited triplet state of fullerene in PS and the oxygen pressure was examined. Figure 5 shows a Stern–Volmer plot for fullerene–PS film ($\tau_0/\tau - 1 = K_{sv}\,pO_2$, where τ_0 and τ are the triplet lifetimes in the absence and presence of oxygen, respectively; K_{sv} is the Stern–Volmer quenching constant; pO_2 is the oxygen pressure). K_{sv} are estimated to be 0.065 and 0.57 Torr^{-1} for C_{60} and C_{70}, respectively, and the quenching rate constant of photoexcited triplet state of C_{60} and C_{70} in PS film by oxygen, k_q ($K_{sv} = k_q\tau_0$) are estimated to be 6.6×10^2 and 1.4×10^3 $\mathrm{Torr}^{-1}\,\mathrm{s}^{-1}$, respectively. A Stern–Volmer plot of C_{70}–PS film exhibits considerable linearity in the low oxygen pressure region. In the case of an optical oxygen sensor based on the phosphorescence change of platinum tetrakis(pentafluorophenyl)porphyrin (PtTFPP)–PS film by oxygen, for example, K_{sv} is estimated to be 0.0038 Torr^{-1}.[14] On the other hand, K_{sv} is estimated to be 0.010 Torr^{-1} using an optical oxygen sensor based on the quenching of the photoexcited triplet state of zinc tetraphenylporphyrin (ZnTPP)–PS film by oxygen using time-resolved spectroscopy by laser flash photolysis.[28,29] This result indicates that a highly sensitive optical oxygen sensor of fullerene–PS film using time-resolved

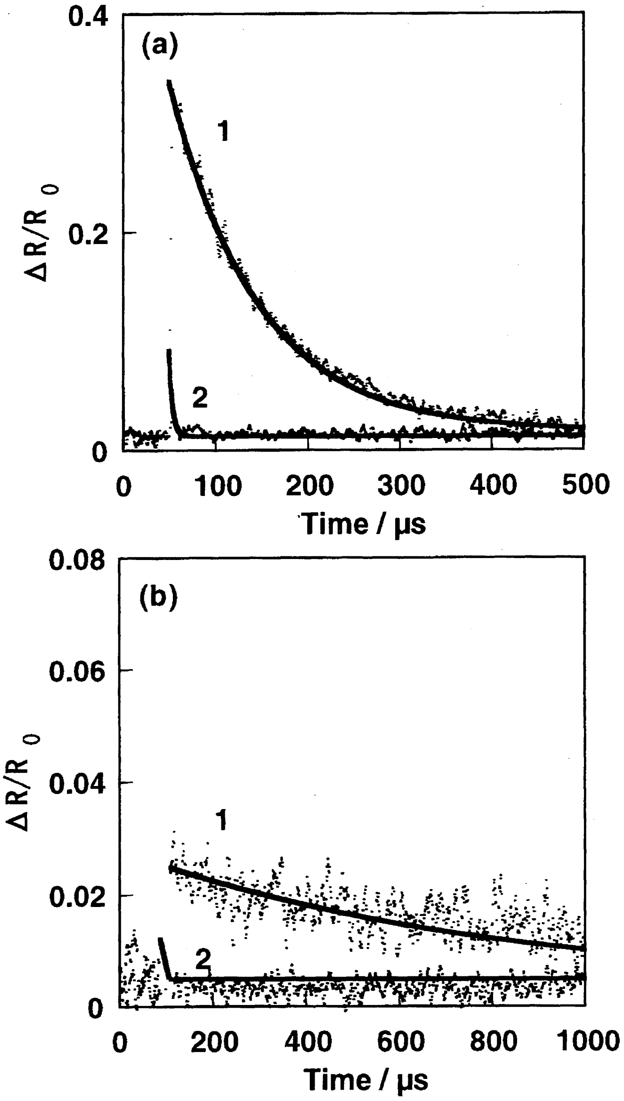

Fig. 3. Typical decay of the photoexcited triplet state of (a) C_{60} and (b) C_{70} –PS film after laser flash under various oxygen pressures; (1) argon- and (2) oxygen-saturated conditions. Excitation wavelength is 532 nm. Monitoring wavelengths of C_{60} and C_{70} are 740 and 860 nm, respectively. The solid line indicates the best-fit curve by Eq. 1 ($n = 1$).

Table 1. Lifetimes of the Photoexcited Triplet State of C_{60} and C_{70} in PS Film under Deoxygenated, Air-Saturated, and Oxygenated Condition

Compounds	$\tau_{\mathrm{argon}}/\mu\mathrm{s}$ (χ^2)	$\tau_{\mathrm{air}}/\mu\mathrm{s}$ (χ^2)	$\tau_{\mathrm{oxygen}}/\mu\mathrm{s}$ (χ^2)
C_{60}	98.4 (1.11)	9.01 (1.13)	1.98 (1.16)
C_{70}	414 (1.21)	4.13 (1.25)	< 1.0 (—)

Excitation wavelength: 532 nm. χ^2 is calculated using Eq. 2.

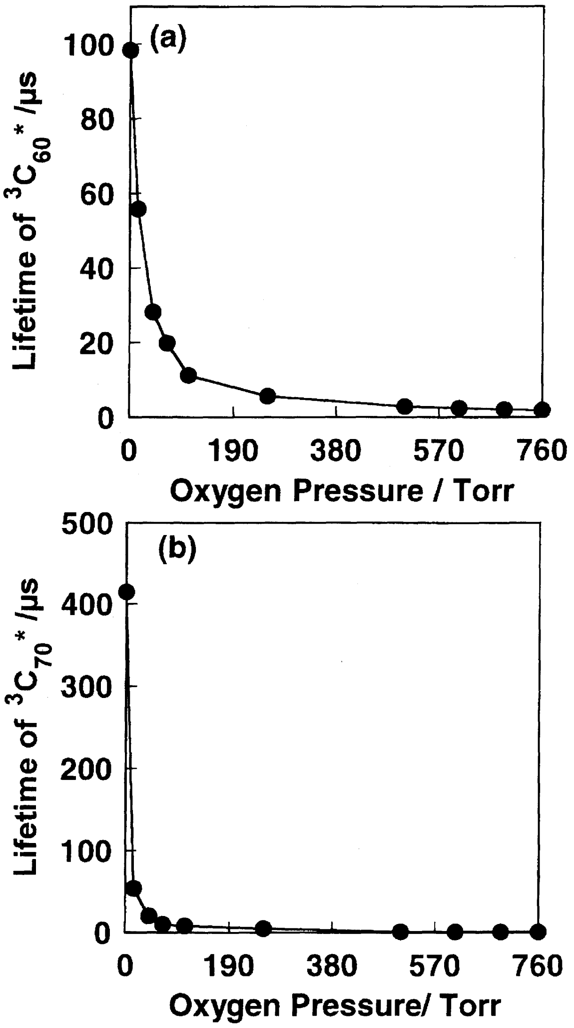

Fig. 4. Lifetime change of photoexcited triplet state of (a) C_{60} and (b) C_{70} –PS film by oxygen.

spectroscopy by laser flash photolysis has been developed. Because large K_{sv} and k_q are obtained using C_{70}–PS film, the linearity of a Stern–Volmer plot of C_{60}–PS film ($r^2 = 0.999$) is superior to that of C_{70}–PS film ($r^2 = 0.992$). These results show that the C_{60}– and C_{70}–PS films are a highly sensitive for oxygen in the total oxygen pressure region and in the low oxygen pressure region, respectively.

The sensing properties are strongly affected by the thickness of fullerene–PS film. From the relationship between K_{sv} and the film thickness (10—80 μm), K_{sv} seems to be little affected by the film thickness. This result indicates that the oxygen-sensing properties are not affected by the film thickness because of rapid oxygen diffusion in the film.

The photostability of the sensing film is an important factor to apply for optical sensors. To characterize the photostability of fullerene–PS film, the absorption spectrum of fullerene–PS film was measured after laser irradiation. No spectrum change was observed after irradiation. In the case of continuous irradiation against film using visible light (100 mW- tungsten lamp), no absorption spectrum change was also observed. These results indicate that fullerene–PS films have a good photostability. On the other hand, no change in the reflectance intensity and lifetime of the photoexcited triplet state of fullerene in PS were observed in five repeated experiments using the same film. These results indicate that fullerene is a superior optical oxygen-sensing device.

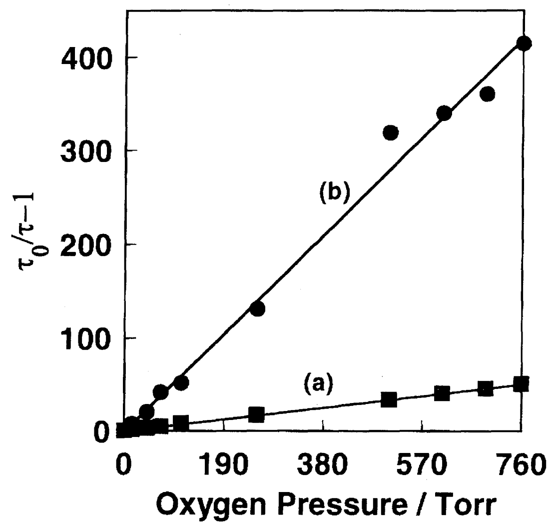

Fig. 5. Stern–Volmer relationship for triplet state of (a) C_{60} and (b) C_{70}–PS film.

Conclusion

The triplet lifetimes of fullerenes (C_{60} and C_{70}) under different oxygen pressure conditions were measured by diffuse reflectance laser flash photolysis. The photoexcited triplet states of fullerenes were effectively quenched by oxygen. Because large K_{sv} and k_q are obtained using C_{70}–PS film, the linearity of a Stern–Volmer plot of C_{60}–PS film ($r^2 = 0.999$) is superior to that of C_{70}–PS film ($r^2 = 0.992$). C_{60}– and C_{70}–PS films are highly sensitive to oxygen in the total oxygen pressure region and in the low oxygen pressure region, respectively. Because fullerene–PS films have good stability for irradiation, they are superior optical oxygen-sensing films. The system using fullerene is a novel oxygen sensor, and will probably open new applications in research fields concerning optical sensing techniques.

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