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Platinum porphyrin embedded in poly(1-trimethylsilyl-1-propyne) film as an optical sensor for trace analysis of oxygen

Yutaka Amao,*[a] Keisuke Asai,[a] Ichiro Okura,[b] Hiromi Shinohara[c] and Hiroyuki Nishide[c]

[a] *Fluid Science Research Center, National Aerospace Laboratory, Jindaiji-higashi, Chofu, Tokyo 182-8522, Japan. E-mail: amao@nal.go.jp*
[b] *Department of Bioengineering, Tokyo Institute of Technology, Nagatsuta, Midori-ku, Yokohama 226-8501, Japan.*
[c] *Department of Polymer Chemistry, Waseda University, Tokyo 169-8555, Japan.*

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A highly gas permeable polymer, poly(1-trimethylsilyl-1-propyne) (poly(TMSP)), was applied as an optical oxygen sensing matrix using luminescence quenching of platinum octaethylporphyrin (PtOEP) by oxygen. PtOEP was homogeneously embedded in poly(TMSP) to give a mechanically tough film with a thickness of 10 μm. The luminescence intensity of PtOEP embedded in the poly(TMSP) film drastically decreased with an increase in oxygen concentration. The oxygen sensitivity of the film (I_0/I_{100}) was very high and estimated to be 225. The Stern–Volmer plot for the poly(TMSP) film-embedded PtOEP was obeyed at lower oxygen concentrations between 0 and 10% and the Stern–Volmer constant is estimated to be 5.7%$^{-1}$. The limit of oxygen detection was less than 0.3%. The response times of PtOEP embedded in the poly(TMSP) film are 3.6 s on going from argon to oxygen and 73.2 s on going from oxygen to argon, respectively. These results indicate that PtOEP embedded in the poly(TMSP) film is a novel optical sensing material for trace analysis of oxygen.

The determination of oxygen concentration is important in various fields of chemical and clinical analysis and environmental monitoring.[1–3] The sensing system for oxygen concentration is classified into titration,[4] amperometry,[5] chemiluminescence,[6] thermoluminescence[7] and colorimetry.[8] Among these systems, the most popular method is the amperometric method using an oxygen electrode,[5] in which the rate of oxygen diffusion to the cathode is measured. This system, however, is limited because of the stability of the electrode surface. Recently, a variety of devices and sensors based on luminescence quenching of organic dyes were developed to measure oxygen concentrations or partial pressures. Many studies on optical oxygen sensors have used organic dyes, such as polycyclic aromatic hydrocarbons (pyrene and its derivatives, quinoline and phenanthrene),[9–15] transition metal complexes (ruthenium,[16–21] osmium[22] or rhenium–polypyridine complexes[23]), and metalloporphyrins,[24,25] embedded in polymers (silicon polymer, polystyrene, *etc.*). Among these organic dyes, platinum and palladium porphyrins show strong phosphorescence at room temperature.[26] Platinum octaethylporphyrin (PtOEP), especially, displays strong room-temperature phosphorescence with a high quantum yield (Φ_P < 0.5) and a long lifetime (*ca.* 100 μs).[26] Some optical oxygen sensors based on the phosphorescence quenching of PtOEP have been developed by embedding it in polymer films.[27,28] As the organic dyes are surrounded with polymer molecules, the optical sensing performance strongly depends on the properties of polymer matrices. An oxygen permeable polymer with a low diffusion barrier for oxygen is desired. Poly(dimethylsiloxane)s have a high gas permeability but lack the mechanical strength in thin films. On the other hand, it has recently come to be known that the gas permeability of poly(1-trimethylsily-1-propyne) [poly(TMSP)] film is about 10 times larger than that of poly(dimethylsiloxane) film,[29,30] and provides a tough and thin film. Thus, a poly(TMSP) film is one of the candidates for the matrix of optical oxygen sensing.

In this communication, poly(TMSP) is, for the first time, applied as an optical oxygen sensing matrix based on the luminescence change of PtOEP and the excellent oxygen sensing property of PtOEP embedded in the poly(TMSP) film is reported.

Experimental

Materials

PtOEP was obtained from Porphyrin Products (Logan, UT, USA). Polystyrene (average MW 280 000, GPC grade) and poly(DMS) (average MW 95 000, GPC grade) were purchased from Aldrich (Milwaukee, WI, USA). Poly(TMSP) was synthesized according to the literature method.[31] 1-Trimethylsilyl-1-propyne (Chisso Co. Ltd.) (10 ml, 68 mmol) and $TaCl_5$ (0.5 g, 1.4 mmol) as the catalyst were dissolved in toluene (30 ml) and warmed at 80 °C for 2 h under nitrogen. The reaction mixture was poured into methanol, the precipitated polymer being dissolved in toluene. The polymer was reprecipitated from the toluene solution into methanol. The obtained polymer was further purified by chromatography on polystyrene gel with toluene eluent (white powder, yield 86%). Molecular weight, polydispersity ratio, and glass transition temperature of the polymer were 8.2×10^5, 2.3 and > 200 °C, determined by gel permeation chromatography with tetrahydrofuran as the solvent and polystyrene as the standard and differential scanning calorimetry, respectively.

Preparation of oxygen sensing film

PtOEP embedded in the poly(TMSP) film was formed by casting the mixture of 5 wt.% poly(TMSP) and PtOEP in toluene onto 1.4×5.0 cm non-luminescent glass slides. The PtOEP concentration in the film was approximately 2.9×10^{-5} mol dm^{-3}. As references, PtOEP embedded in polystyrene film and in poly(DMS) were prepared. The films were dried at room temperature and stored in the dark prior to use. The thickness of the films was determined by use of a micron-sensitive caliper. The thickness of the film prepared was 10 μm.

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Spectroscopic measurements

The absorption spectrum of PtOEP embedded in the poly(TMSP) film was recorded using a Shimadzu (Tokyo, Japan) UV-2400PC spectrometer. Steady state luminescence spectra and excitation spectra of the films were measured using a Shimadzu (Tokyo, Japan) RF-5300PC spectrofluorophotometer with a 150 W Xenon lamp as a visible excitation light source. The excitation and emission bandpasses were 5.0 nm.

Oxygen sensing properties of PtOEP embedded in the poly(TMSP) film

Oxygen sensing was carried out using a spectrofluorophotometer with a 150 W xenon lamp as a visible light excitation source. The sample films were mounted at a 45° angle in the quartz cell to minimize light scattering from the sample and substrate. 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 total pressure was maintained at 760 Torr (1 Torr = 133.322 Pa).[27,28] All the experiments were carried out at room temperature. The oxygen sensing properties of PtOEP embedded in the poly(TMSP) film were characterized by the I_0/I_{100} value , where I_0 and I_{100} represent the detected luminescence intensities from a film exposed to 100% argon and 100% oxygen, respectively, and the Stern–Volmer quenching constant, $K_{SV,}$ obtained from the following equation.

$$I_0/I = 1 + K_{SV}[O_2]$$

where I_0 , I and $[O_2]$ are the luminescence intensities in the absence and presence of oxygen and oxygen concentration, respectively. K_{SV} was obtained from a linear plot of (I_0/I)-1 *versus* $[O_2]$.

Results and discussion

Spectroscopic properties of PtOEP embedded in the poly(TMSP) film

The absorption spectrum of PtOEP in the poly(TMSP) film was almost the same as in a solution (absorption maxima = 534, 501 and 378 nm in the poly(TMSP) film; 535, 500, and 377 nm in toluene solution). This denies any electrical interaction between PtOEP and poly(TMSP) in the ground state.

Luminescence spectrum change of PtOEP embedded in the poly(TMSP) film by oxygen

The film luminesced with a strong red color (646 nm). The luminescence spectral change of PtOEP in the poly(TMSP) film is shown in Fig. 1. The excitation wavelength was 535 nm, attributed to Q-band of PtOEP. The luminescence intensity of the film decreased with an increase of oxygen concentration as shown in Fig. 2. This indicates that the luminescence of PtOEP in the poly(TMSP) was quenched by oxygen. These results suggest that this film can be used as an optical oxygen sensing device based on luminescence quenching by oxygen. The ratio I_0/I_{100} has been used as an indicator of the sensitivity of the sensing film; a sensor having a ratio I_0/I_{100} more than 3.0 is a suitable oxygen sensing device.[32] The I_0/I_{100} values of PtOEP embedded in the poly(TMSP), polystyrene and poly(DMS) films were 225, 4.5 and 5.5, respectively. This result indicates that PtOEP embedded in the poly(TMSP) film is a potential candidate for a highly sensitive device for oxygen. Next, let us focus on the limit of oxygen detection of PtOEP embedded in the poly(TMSP) film. The $I_0/I_{0.3}$ values of PtOEP embedded in the poly(TMSP), polystyrene and poly(DMS) films are estimated to be 0.358, 0.996 and 0.990, respectively. For PtOEP embedded in the poly(TMSP), the luminescence intensity was drastically changed by the oxygen concentrations, and the limit of oxygen detection was less than 0.3%. This result indicates that PtOEP embedded in the poly(TMSP) film is especially useful for sensing a small amount of oxygen.

Stern–Volmer relationship for PtOEP embedded in the poly(TMSP) film

Fig. 3 shows the Stern–Volmer plots for PtOEP embedded in the poly(TMSP), polystyrene and poly(DMS) films. For PtOEP embedded in the poly(TMSP) film, the plot exhibited considerable linearity in the low oxygen concentration range between 0 and 10%, although this was not the case at a higher oxygen concentration. This result suggested that the luminescence of PtOEP was almost fully quenched at the oxygen concentration of *ca* 10%. The K_{SV} of PtOEP embedded in the poly (TMSP) film was estimated to be $5.7\%^{-1}$ in the oxygen concentration range between 0 and 10%, which was much higher than those of the polystyrene film ($0.13\%^{-1}$) and the poly(DMS) film ($0.20\%^{-1}$). This result indicates that PtOEP embedded in the poly (TMSP) film was a more sensitive device for oxygen. Oxygen permeability coefficients of poly(TMSP), polystyrene and poly(DMS) films at 30 °C were reported to be 7700, 2.63 and 760 barrer (1 barrer = 1×10^{-10} cm^3(STP) cm cm^{-2} s

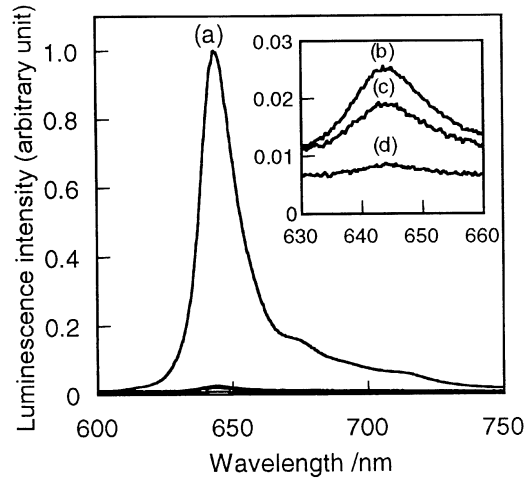

Fig. 1 Luminescence spectrum of PtOEP embedded in the poly(TMSP) film: (a) 0%; (b) 5.7%; (c) 10% and (d) 100% oxygen. The excitation wavelength was 535.0 nm.

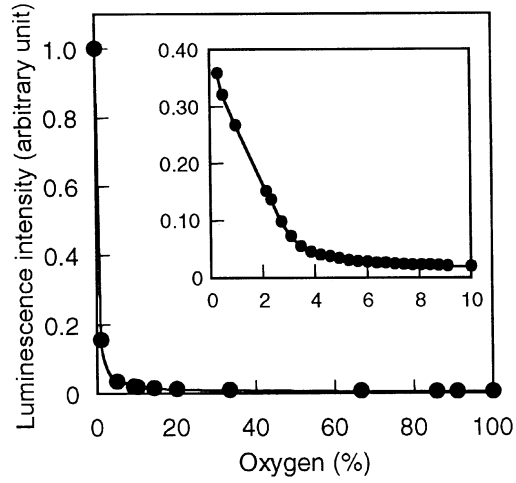

Fig. 2 Relative luminescence intensity changes of PtOEP embedded in the poly(TMSP) film under various oxygen concentrations. The excitation and emission wavelengths were 535.0 and 646.0 nm, respectively. The inset shows the intensity changes in the oxygen concentration range between 0.3 and 10%.

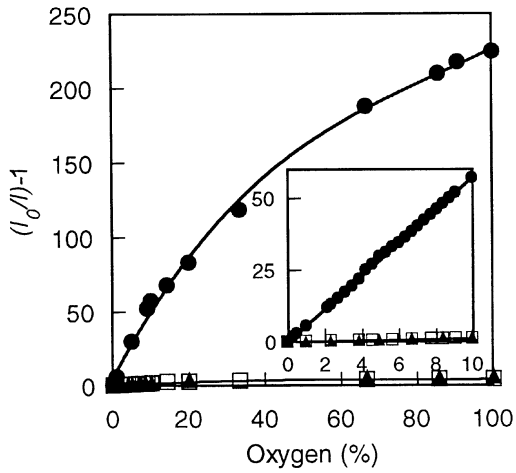

Fig. 3 Stern–Volmer plots for PtOEP embedded in the poly(TMSP) (●), polystyrene (□) and poly(DMS) (▲) films. The excitation and emission wavelength was 535.0 and 646.0 nm, respectively.

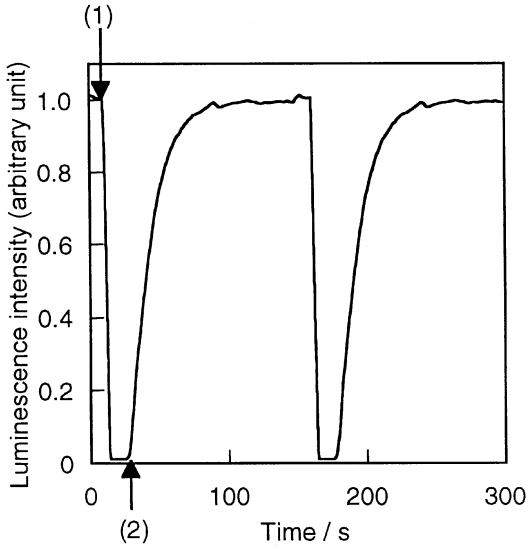

Fig. 4 Response time and relative intensity change for PtOEP embedded in the poly(TMSP) film on switching between 100% argon (1) and 100% oxygen (2) for 300 s. The excitation and emission wavelengths were 535.0 and 646.0 nm, respectively.

cmHg), respectively.[30,32–35] The oxygen permeability of poly(TMSP) is higher than those of polystyrene and poly(DMS). Such enormously high permeability has been successfully applied to, for example, a film matrix for cobalt porphyrin-mediated oxygen transport.[36] Thus, a more sensitive optical sensor results from using poly(TMSP) as a polymer matrix.

Operational stability and response time of PtOEP embedded in the poly(TMSP) film

Fig. 4 shows an operational stability test conducted by reading the intensity signal from PtOEP embedded in a poly(TMSP) film when oxygenated and deoxygenated gases were switched for 300 s. The response times of the film are 3.6 s on going from argon to oxygen, and 73.2 s on going from oxygen to argon, respectively (for PtOEP embedded in polystyrene and in the poly(DMS) films, 35.0 and 10.0 s on going from argon to oxygen and 100 and 82.0 s on going from oxygen to argon, respectively). By using poly(TMSP) as the polymer matrix, a fast response time was obtained. The signal changes were fully reversible and measurement hysteresis was not observed. In general, oxygen sensing systems using dye embedded in polymer film are strongly affected by the thickness of the film. A thinner film requires less time for endogenous oxygen migration to reach equilibrium with the external environment. For PtOEP embedded in the poly(TMSP) film, however, K_{SV} was little affected by differences of 10 and 50 μm in the film thickness. An important factor for application of the PtOEP embedded in the poly(TMSP) film as an optical oxygen sensing material is its photostability. To characterize the photostability of the PtOEP embedded in the poly(TMSP) film, the absorption spectrum of the film was measured after continuous irradiation using a 150 W tungsten lamp on the film for 12 h. After irradiation for 12 h, a 3.0% decrease of initial absorption intensity of PtOEP at 378 nm was observed, indicating that the PtOEP embedded in the poly(TMSP) film is stable against irradiation.

Conclusions

In this communication, PtOEP embedded in the highly gas permeable polymer, poly(TMSP) film, is reported. The I_0/I_{100} value of PtOEP in the poly(TMSP) film is estimated to be 225 and a large Stern–Volmer constant (K_{SV} = 5.7%$^{-1}$) is obtained compared with the PtOEP embedded in polystyrene film. Especially, the luminescence intensity of PtOEP embedded in the poly(TMSP) film was drastically changed by the oxygen concentration. The limit of oxygen detection of PtOEP embedded in the poly(TMSP) film was less than 0.3%. This result indicates that PtOEP embedded in the poly(TMSP) film is a useful sensing device for a trace analysis of oxygen. As the oxygen permeability of the poly(TMSP) is not lost at a lower temperature, about −196 °C, the oxygen sensing performance of PtOEP embedded in the poly(TMSP) film at cryogenic temperature (around the liquefaction temperature of oxygen, −183 °C) is now being studied.

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