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Photophysical and Photochemical Properties of Optical Oxygen Pressure Sensor of Platinum Porphyrin–Isobutylmethacrylate–Trifluoroethylmethacrylate Copolymer Film

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Oxygen sensing is finding application in chemical, clinical analysis and environmental monitoring,[1-3] and is classified titration,[4] amperometry,[5] chemiluminescence,[6] and thermoluminescence.[7] The most popular is amperometry using an oxygen electrode[5] in which the rate of diffusion of oxygen to the cathode is measured. This system has limited because of the stability of the electrode surface. Recently, a variety of devices and sensors based on photo-luminescence quenching of organic dyes, such as polycyclic aromatic hydrocarbons (pyrene and its derivatives, quinoline, and phenanthrene),[8-10] transition metal complexes (ruthenium,[11-13] osmium,[14] or rhenium-polypyridine complexes[15]), and metalloporphyrins,[16-18] immobilized in oxygen permeable polymer (silicon polymer, polystyrene, and so on) has been developed to measure oxygen pressure on the solid surface. Platinum and palladium porphyrins show no more than weak prompt fluorescence ($\Phi_F < 10^{-3}$) and phosphorescence yields Φ_P variable over the entire range from 10^{-4} to 1 at room temperature.[19-24] Phosphorescence lifetime τ_P is short, typically less than 3.0 ms.[19] Especially, platinum octaethylporphyrin (PtOEP) displays strong room-temperature phosphorescence with high quantum yield ($\Phi_P = 0.5$) and long lifetime (*ca.* 100 μs).[19] Some optical oxygen sensors based on phosphorescence quenching of PtOEP–polymer (polystyrene, silicone rubber, and so on) by oxygen have been developed.[25,26] Organic dyes interact with polymer molecules and thus optical sensing properties strongly depend on the properties of polymer matrices. Oxygen permeable polymers with lower diffusion barrier for oxygen and higher stability for photo-oxidation are desired. Fluoro-polymer film allows large permeability of oxygen.[27] C–F bond length is short (13.17 nm); bonding energy is large (116 kcal mol^{-1}), compared with C–H (99.5 kcal mol^{-1}) and electronegativity of fluorine is large, and thus polymers containing perfluoro-groups are stable forward photo-oxidation. Oxygen affinity is induced by large electronegativity of fluorine and oxygen permeability of the polymers containing perfluoro-group will be large.[28-32] Polymers containing perfluoro-group are suitable for the above requirements.

In this work, polymethacrylate containing perfluoro-group, poly(isobutylmethacrylate-*co*-trifluoroethylmethacrylate) as shown in Figure 1, was synthesized and applied to the matrix of optical oxygen sensing using PtOEP.

EXPERIMENTAL

Materials

Isobutylmethacrylate (IBM), trifluoroethylmethacrylate (TFEM) and polyisobutylmethacrylate (poly-IBM) were purchased from Wako Pure Chemicals Co., Ltd. and were distilled under reduced pressure to remove the inhibitor. Azobis(isobutyronitrile) (AIBN) was obtained from Tokyo Chemical Industry Co. Ltd. and was recrystallized from ethanol. PtOEP was purchased from Porphyrin Products. All other chemicals were obtained from Wako Pure Chemicals Co., Ltd.

Synthesis of Poly(isobutylmethacrylate-co-trifluoroethylmethacrylate) (Poly-IBM-co-TFEM)

Poly-IBM-*co*-TFEM was synthesized as follows. IBM (0.16 mol), TFEM (0.15 mol), and AIBN (25 mmol) were dissolved in 80 mL toluene. The reaction mixture was heated at 80°C for 5 h under nitrogen atmosphere. After the mixture was cooled to room temperature, the polymer was precipitated in methanol. The solid was collected by filtration, washed with methanol to remove unreacted monomer and finally dried in vacuum. The composition ratio of IBM and TFEM was determined using the molar absorption coefficients of IBM and TFEM at 270 nm. Molecular weight was determined by gel permeation chromatography (TSK HLC-802A TOYO SODA). IBM/TFEM = 1.2; GPC: $M_n = 33870$, $M_w = 58270$, and $M_w/M_n = 1.72$.

Preparation of Oxygen Sensing Film

PtOEP-polymer film was formed by casting a mixture of 30 wt% polymer (poly-IBM-*co*-TFEM or poly-IBM) and PtOEP in toluene onto non-luminescent glass

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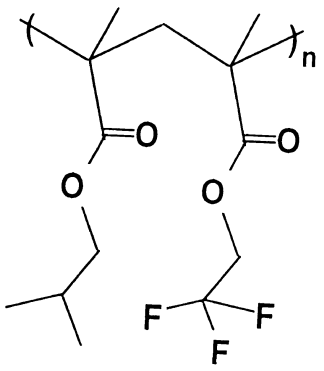

Figure 1. Chemical structure of polymethacrylate containing perfluoro-group, poly(isobutylmethacrylate-*co*-trifluoroethylmethacrylate) (poly-IBM-*co*-TFEM).

slides. PtOEP concentration in the film was approximately 2.9×10^{-5} mol dm^{-3}. The films were dried at room temperature and stored in the dark prior to use. Film thickness was determined by a micron-sensitive caliper.

Spectroscopic Measurement

Absorption spectrum of PtOEP-polymer film was recorded using a Shimadzu U-2400PC spectrometer. Steady state phosphorescence spectra and excitation spectra were measured using a Shimadzu F-5300PC spectrofluorophotometer with a 150 W Xenon lamp as the visible excitation light source. Excitation and emission bandpasses were 5.0 nm. All samples were excited at 535 nm attributed to the Q-band of PtOEP, the wavelength producing maximum phosphorescence intensity at 646 nm.

Oxygen Sensing System

Oxygen sensing was carried out using a spectrofluorophotometer with a 150 W Xenon lamp as the visible excitation light source. Sample film was mounted at 45° angle in the quartz cell to minimize light scatter 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 the mixing chamber. Total pressure was maintained at 760 Torr.[25,26] PtOEP–poly-IBM film was used as a reference. All experiments were carried out at room temperature.

RESULTS AND DISCUSSION

Photophysical Properties of PtOEP-Polymer Films

Absorption spectra of PtOEP in poly-IBM and in poly-IBM-*co*-TFEM films were almost the same as in solution (absorption maxima = 534, 501, and 378 nm in the polymer; 535, 500, and 377 nm in toluene solution; data are not shown). This indicates no electrical interaction between PtOEP and polymer at the ground state.

Phosphorescence spectra of PtOEP–poly-IBM-*co*-TFEM film under deoxygenated, ambient, and oxygenated conditions are shown in Figure 2, indicating quenching of the phosphorescence by oxygen. In the case of PtOEP–poly-IBM film as reference, quenching of the

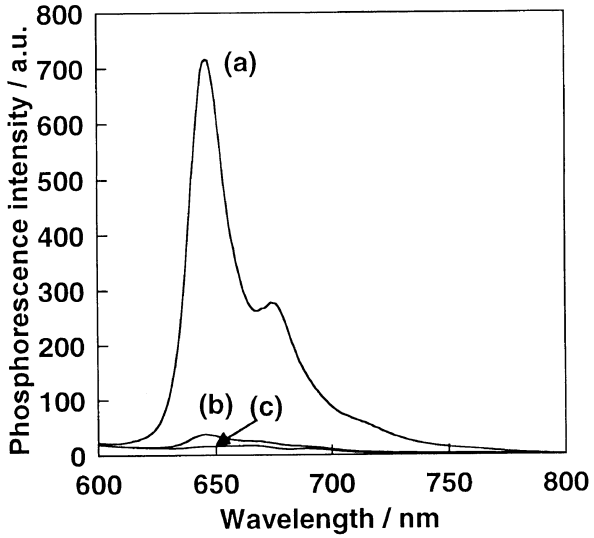

Figure 2. Phosphorescence spectrum change of PtOEP–poly-IBM-*co*-TFEM film at various oxygen pressures. Excitation wavelength was 535 nm. (a) deoxygenated, (b) ambient, and (c) oxygenated conditions.

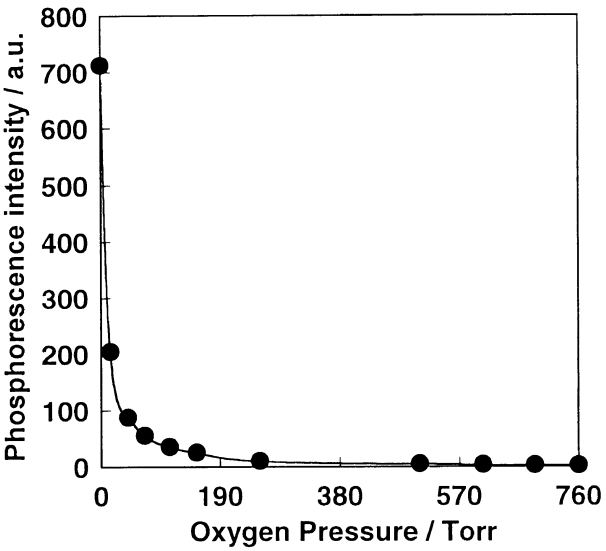

Figure 3. Relative phosphorescence intensity changes of PtOEP–poly-IBM-*co*-TFEM film at various oxygen pressures. Excitation and emission wavelength was 535 and 646 nm, respectively.

phosphorescence by oxygen was observed. The phosphorescence spectra of PtOEP–poly-IBM-*co*-TFEM and PtOEP–poly-IBM films showed no red (or blue)-shift and no differences in peak shape compared to that of toluene solution (646 nm in both instances). Phosphorescence maxima intensity increased strongly on going from oxygenated to ambient and deoxygenated conditions. The intensity of PtOEP–poly-IBM-*co*-TFEM film decreased with increase oxygen pressure as shown in Figure 3. This indicates that the phosphorescence intensity of PtOEP in poly-IBM-*co*-TFEM strongly depends on oxygen pressure and this film can be used for optical oxygen sensing based on phosphorescence quenching by oxygen. I_0/I_{100} is used as sensitivity of sensing film, where I_0 and I_{100} represent detected phosphorescence intensity from film exposed to 100% argon and 100% oxygen, respectively. A sensor with I_0/I_{100} more than 3.0 is suitable for oxygen sensing.[33] I_0/I_{100} of poly-IBM-*co*-TFEM and poly-IBM film was

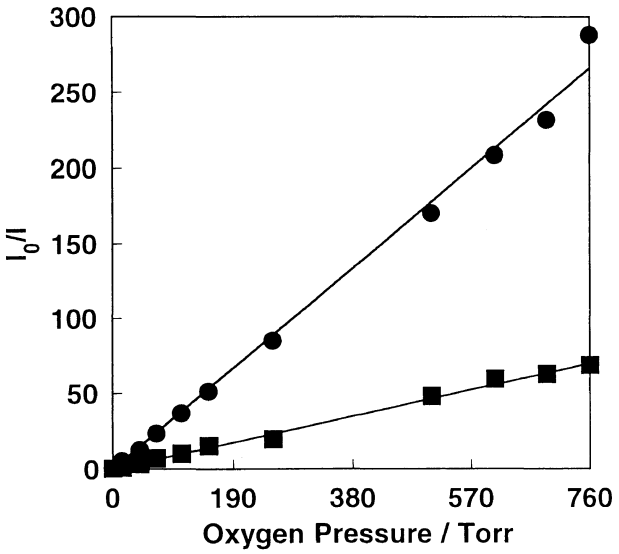

Figure 4. Stern–Volmer plot for PtOEP in poly-IBM-*co*-TFEM (●) and in poly-IBM (■). Excitation and emission wavelengths were 535 and 646 nm, respectively.

288 and 69.3, respectively. This indicates that PtOEP–poly-IBM-*co*-TFEM film is a highly sensitive device for oxygen.

Oxygen Sensing Properties of PtOEP-Polymer Film

Phosphorescence intensity from PtOEP in polymer film is quenched by oxygen according to the Stern-Volmer equation ($I_0/I=1+K_{SV}pO_2$; where I_0 and I are phosphorescence intensity in the absence and presence of oxygen, respectively; K_{SV} is the Stern–Volmer quenching constant. pO_2 is oxygen pressure). Figure 4 shows Stern–Volmer plots of PtOEP–poly-IBM-*co*-TFEM and PtOEP–poly-IBM films. K_{SV} of poly-IBM-*co*-TFEM and poly-IBM films were obtained by least squares as 0.091 and 0.38 $Torr^{-1}$, respectively. In both polymers, the plots exhibit considerable linearity (correlation factor, $r^2=0.994$ for poly-IBM-*co*-TFEM film and 0.996 for poly-IBM film, respectively).

These polymers differ in the size and rigidity of side functional groups. In the case of poly-IBM-*co*-TFEM, interfacial intermolecular force between the gaseous phase and surface on polymer film is lower than that of poly-IBM, and oxygen affinity is induced by the large electronegativity of fluorine.[28-32] Thus, large oxygen permeability of poly-IBM-*co*-TFEM is induced by lower surface free energy and larger electronegativity of fluorine. A highly sensitive optical sensor was developed using poly-IBM-*co*-TFEM as polymer matrix.

The effects of the composition ratio of IBM to TFEM and degree of polymerization on oxygen sensing are now being studied.

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REFERENCES

1. C. Prininger, I. Klimant, and O.S. Wolfbeis, *Anal. Chem.*, **66**, 1841 (1994).
2. R. C. Martin, S. F. Malin, D. J. Bartnil, A. M. Schilling, and S. C. Furlong, *Proc. SPIE.*, **2131**, 426 (1994).
3. M. J. Atkinson, F. I. M. Thomas, N. Larson, E. Terrill, K. Morita, and C. C. Lium, *Deep-Sea Res. I.* **42**, 761 (1995).
4. D. A. Skoog, D. M. West, and F.J. Holler, "Fundamentals of Analytical Chemistry," Saunders, Philadelphia, 1988, p 344.
5. L. C. Clark, *Trans. Am. Artif. Intern. Organs.*, **2**, 41 (1956).
6. T. M. Freeman and W. R. Seitz, *Anal. Chem.*, **53**, 98 (1981).
7. H. D. Hendricks, US Patent, 3 709 663 (1973).
8. T. Ishiji and M. Kaneko, *Analyst*, **120**, 1633 (1995).
9. A. Sharma and O. S. Wolfbeis, *Appl. Spect.*, **42**, 1009 (1988).
10. H. W. Kroneis and H. J. Marsoner, *Sens. Actuators*, **4**, 587 (1983).
11. W. Xu, R. Schmidt, M. Whaley, J. N. Demas, B. A. DeGraff, E. K. Karikari, and B. L. Farmer, *Anal. Chem.*, **67**, 3172 (1995).
12. E. R. Carraway, J. N. Demas, B. A. DeGraff, and J. R. Bacon, *Anal. Chem.*, **63**, 332 (1991).
13. J. R. Bacon and J. N. Demas, *Anal. Chem.*, **59**, 2780 (1987).
14. W. Y. Xu, K. A. Kneas, J. N. Demas, and B. A. DeGraff, *Anal. Chem.*, **68**, 2605 (1996).
15. L. Sacksteder, J. N. Demas, and B. A. DeGraff, *Anal. Chem.*, **65**, 3480 (1993).
16. D. B. Papkovsky, G. V. Ponomarev, W. Trettnak, and P. O'Leary, *Anal. Chem.*, **67**, 4112 (1995).
17. J. Vanderkooi, G. Maniara, J. Green, and D. F. Wilson, *J. Biol. Chem.*, **262**, 5476 (1987).
18. A. Mills and A. Lepre, *Anal. Chem.*, **69**, 4653 (1997).
19. K. Kalyanasundaram, "Photochemistry of Polypyridine and Porphyrin Complexes," Academic Press, New York, N.Y., 1992, p 500.
20. D. Eastwood and M. Gouterman, *J. Mol. Spectrosc.*, **35**, 359 (1970).
21. S. J. Lander and R. S. Becker, *J. Chem. Phys.*, **43**, 3344 (1965).
22. A. T. Gradyushko, V. A. Mashenkow, K. N. Solov'ev, and A.N. Sevchenko, *Sov. Phys. Dokl.*, **13**, 869 (1969).
23. J. B. Allison and R. S. Becker, *J. Chem. Phys.*, **32**, 1410 (1960).
24. R. S. Becker and J. B. Allison, *J. Phys. Chem.*, **67**, 262 (1963).
25. S-K. Lee and I. Okura, *Anal. Sci.*, **13**, 535 (1997).
26. S-K. Lee and I. Okura, *Spectrochim. Acta A*, **54**, 91 (1998).
27. N. Yi-Yan, R. M. Felder, and W. J. Koros, *J. Appl. Polym. Sci.*, **25**, 1755 (1980).
28. W. A. Zisma, *Advance in Chem. Series*, **43**, 1 (1964).
29. A. G. Pittman, "Fuluoropolymers," Wiley-Intersceince, New York, N.Y., 1972, p 446.
30. E. Wicke and E. U. Frank, *Angew. Chem.*, **66**, 701 (1954).
31. K. G. Denbigh, *Trans. Faraday Soc.*, **36**, 936 (1940).
32. A. Y. Kupryazhkin and E. V. Popof, *Vysokomol. Soedin., Ser. B*, **21**, 287 (1976).
33. B. D. MacCraith, C. M. McDonagh, G. O'Keeffe, E. T. Keyes, J. G. Vos, B. O'Kelly, and J. F. McGilp, *Analyst*, **118**, 385 (1993).