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Novel optical oxygen sensing device: a thin film of a palladium porphyrin with a long alkyl chain on an alumina plate

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An optical oxygen sensor based on the phosphorescence quenching of a film of a palladium porphyrin containing a long alkyl chain [5-(1-carboxydecyl-4-pyridyl)-10,15,20-tritolylporphyrinato]palladium (PdPC10COOH), adsorbed onto an alumina plate has been developed. The phosphorescence intensity of the PdPC10COOH film decreased upon increasing the oxygen concentration, indicating that the film can be used as an optical oxygen sensing device based on phosphorescence quenching by oxygen. The ratio I_0/I_{100} as a measure of sensitivity of the sensing film ($I_0/I_{100} > 3.0$ indicates good sensitivity) is estimated to be 18.3, showing that the film is a highly sensitive device for oxygen. The film obeyed Stern–Volmer plots assuming a multi-site model and possessed good operational stability, reproducibility and a fast response. The response time is 26 s from deoxygenated to oxygenated conditions and 131 s for the reverse process.

Oxygen sensing techniques are applied to various fields, such as chemical and clinical analysis and environmental monitoring.[1–3] Several oxygen sensing systems have been established. The sensing systems are classified into a variety of categories, *i.e.* titration,[4] amperometry,[5] chemiluminescence[6] or thermoluminescence.[7] Among these, the most popular is amperometry using oxygen electrodes.[5] Such systems, however, are limited by the stability of the electrode surface and instabilities in the oxygen diffusion barrier, since they measure the rate of diffusion of oxygen to the cathode. Recently, a variety of devices and sensors based on photoluminescent quenching of organic dyes have been developed to measure oxygen pressure. Many optical oxygen sensors are composed of organic dyes, such as polycyclic aromatic hydrocarbons (pyrene and its derivatives, quinoline and phenanthrene)[8–14] and transition metal complexes (ruthenium,[15–20] osmium[21] or rhenium complexes[22]), immobilized in an oxygen permeable polymer (silicon polymer, polystyrene, *etc.*). As organic dyes interact with polymer molecules directly, the properties of the sensing films strongly depend on the properties of the polymer matrices. To overcome these problems chemisorbed films of organic compounds on metal oxide surfaces (Al_2O_3, Fe_2O_3, *etc.*) have been exploited.[23–25] Among a number of chemisorption film techniques, the use of compounds containing a carboxyl functional group is most prevalent in preparing chemisorption films of organic compounds on metal oxide surfaces. As the sensing dyes are arranged on the solid surface directly by using this technique, highly sensitive devices for oxygen sensing can be obtained. On the other hand, among luminescent dyes, palladium or platinum porphyrins display strong room-temperature phosphorescence with high quantum yields and long natural lifetimes under deoxygenated conditions.[26,27] Therefore, these compounds have been frequently utilized as oxygen sensitive dyes. Among porphyrins, [5-(1-carboxydecyl-4-pyridyl)-10,15,20-tritolylporphyrinato]palladium (PdPC10COOH, Fig. 1) is suitable for optical oxygen sensing using the chemisorption film technique, because of formation of a stable film on the surface on alumina *via* the carboxyl group of PdPC10COOH which forms a chemisorptive ester bond.

In this work we describe the fabrication of an adsorbed PdPC10COOH thin film on alumina as a phosphorescence probe for oxygen sensing and investigate the optical oxygen sensing properties of this film.

Experimental

Materials

All the reagents used were of analytical grade or the highest grade available. Alumina plate (TLC grade) was obtained from Merck Co. Ltd.

Synthesis of [5-(1-carboxydecyl-4-pyridyl)-10,15,20-tritolylporphyrinato]palladium (PdPC10COOH)

The starting material, 5-(4-pyridyl)-10,15,20-tritolylporphyrin (PyTP), was synthesized with refluxing pyrrole (0.149 mol), 4-pyridinecarbaldehyde (3.7×10^{-2} mol) and *p*-toluenecarbaldehyde (0.108 mol) in 300 ml of boiling propionic acid at 165 °C for 1 h. Purification was performed using silica gel column chromatography. 200 MHz ^{1}H NMR (Varian GEMINI-200) ($CDCl_3$): δ −2.9 to −2.7 (m, 2H), 2.7 (m, 9H), 7.7–7.8 (m, 9H), 8.1–8.3 (m, 8H), 8.7–9.1 (m, 10H). [5-(1-carboxydecyl-4-pyridyl)-10,15,20-tritolylporphyrinato]-

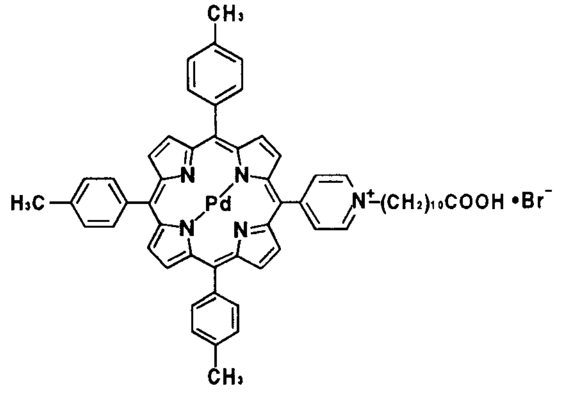

Fig. 1 Chemical structure of [5-(1-carboxydecyl-4-pyridyl)-10,15,20-tritolylporphyrinato]palladium (PdPC10COOH).

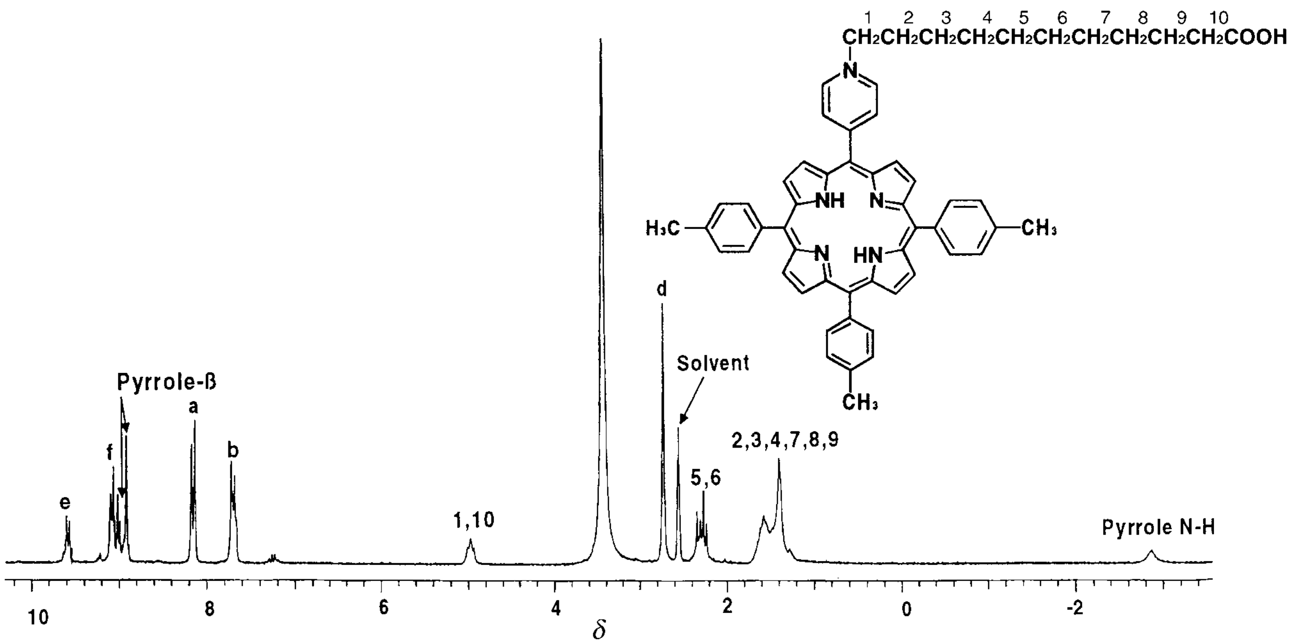

Fig. 2 200 MHz ^{1}H NMR spectra of PC10COOH in DMSO-d_6.

palladium (PdPC10COOH) was prepared as follows. PyTP (2.9×10^{-4} mol) was quaternized using a 10-fold excess of 11-bromoundecanecarboxylic acid (2.9×10^{-3} mol) in toluene at 110 °C for 48 h to obtain 5-(1-carboxydecyl-4-pyridyl)-10,15,20-tritolylporphyrin (PC10COOH). ^{1}H NMR ($CDCl_3$): δ −2.9 to −2.7 (m, 2H), 1.2–1.7 (q, 12H), 2.2–2.4 (q, 4H), 2.7 (m, 9H), 4.9–5.1 (t, 4H), 7.7–7.8 (m, 9H), 8.1–8.3 (m, 8H), 8.7–9.1 (m, 10H). PC10COOH (1.2×10^{-4} mol) and a 10-fold excess of palladium chloride (1.2×10^{-3} mol) were refluxed in DMF solution at 120 °C for 24 h to obtain PdPC10COOH. The progress of the reaction and its completion were monitored using UV–VIS spectroscopy. Purification of PdPC10COOH was conducted by repeated precipitation and recrystallization from DMF–water (1 : 10).

Preparation of the PdPC10COOH film

A PdPC10COOH film was prepared by dipping an alumina plate into 0.1 mmol dm^{-3} PdPC10COOH in DMF soution at room temperature for 24 h. After dipping the plate was washed with water and ethanol several times. PdPC10COOH adsorbed onto alumina physically was removed by ultrasonication and the film dried *in vacuo* overnight.

Spectroscopic measurements

Absorption spectra of a PdPC10COOH solution were recorded using a Shimadzu Multispec-1500 spectrometer. Steady state phosphorescence spectra and excitation spectra of the films were measured using a Hitachi model F-4010 fluorescence spectrometer with a 150 W xenon lamp as the visible excitation light source. Excitation and emission bandpasses were 5.0 nm.

Oxygen sensing system

The oxygen sensing system was developed using a fluorescence spectrometer and gas flow meter. Sample films were mounted at a 45° angle in a quartz cell to minimize light scattering from the sample and substrate. Different oxygen concentrations (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. All experiments were carried out at room temperature.

Results and discussion

Preparation of PdPC10COOH

The structure of PdPC10COOH was elucidated by ^{1}H NMR spectroscopy. The ^{1}H NMR spectrum of PC10COOH is shown in Fig. 2 and signal assignments are given. During the synthesis of PdPC10COOH, initial peaks at 421 (Soret band), 520, 552, 590 and 650 nm (Q-band) of PC10COOH were shifted and replaced by new peaks at 418 (Soret band), 530 and 562 nm (Q-band) in DMF solution as shown in Fig. 3.

Excitation spectrum of the PdPC10COOH film

The excitation spectrum of the PdPC10COOH film monitored at 708 nm under deoxygenated conditions is shown in Fig. 3 which showed absorption maxima at 418, 523 and 556 nm. The shape and peaks of the spectrum were almost the same as the absorption spectrum of PdPC10COOH in DMF solution. In general, broadening of absorption and excitation spectrum occurs as a consequence of aggregation or stacking between porphyrin molecules in the solid state and in crystals. However, no broadening of the excitation spectrum was observed in the film indicating the absence of aggregation or stacking between PdPC10COOH molecules in the film.

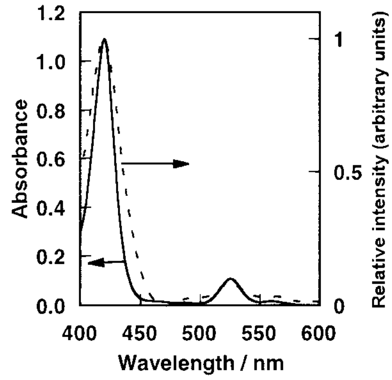

Fig. 3 Absorption spectrum of PdPC10COOH in DMF solution. The dashed line is the excitation spectrum of the PdPC10COOH film under deoxygenated condition monitored at 708 nm.

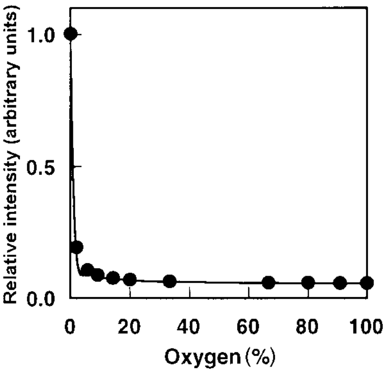

Fig. 4 Relative phosphorescence intensity changes of the PdPC10COOH film under various oxygen concentrations. The excitation and emission wavelengths were 418 and 708 nm, respectively.

Phosphorescence spectrum of the PdPC10COOH film

The PdPC10COOH film showed strong phosphorescence at 708 nm when excited at wavelengths attributed to the Soret or Q bands. The phosphorescence intensity of the film depended on the oxygen concentration with an intensity decrease upon increasing the oxygen concentration (Fig. 4). This result indicates that the phosphorescence of PdPC10COOH was quenched by oxygen. Most notably the emission peak at *ca.* 708 nm diminished in the presence of oxygen, showing that this film can be used as an optical oxygen sensing device based on phosphorescence quenching by oxygen. The ratio I_0/I_{100} is used as a measure of the sensitivity of the film, where I_0 and I_{100} represent the detected phosphorescence intensities from a film exposed to 100% argon and 100% oxygen, respectively. In general, the ratio I_0/I_{100} should be >3.0 for a good sensitive oxygen sensing device.[28,29] The I_0/I_{100} value of this film is estimated to be 18.3 (by comparison, for a palladium porphyrin ketone–polystyrene film, I_0/I_{100} is estimated to be *ca.* 4.0[30]), indicating that the PdPC10COOH film is a highly sensitive device towards oxygen.

Stern–Volmer relationship for the PdPC10COOH film

Fig. 5 shows a plot of the phosphorescence of the PdPC10COOH film as a function of oxygen concentration (Stern–Volmer plot, $I_0/I=1+K_{SV}[O_2]$; where I_0 and I are the phosphorescence intensities in the absence and in the presence of oxygen, respectively; K_{SV} is the Stern–Volmer quenching constant). At low concentrations of oxygen, the intensities from the photoexcited PdPC10COOH molecules in the film are quenched by oxygen according to the Stern–Volmer equation as well as in the homogeneous system. At higher concentrations, on the other hand, Stern–Volmer plots of phosphorescence quenching of the sensor are nonlinear, because of the simultaneous presence of static and dynamic quenching. Demas *et al.* reported a multisite model for a sensing film with different oxygen-accessible sites.[31] In this model, the sensor molecule can exist in different sites each with their own characteristic quenching constant. As the observed phosphorescence intensity is a sum of emission from different oxygen-accessible sites, the Stern–Volmer relationship is modified [eqn. (1)].

$$I_0/I=\left[\sum_1^n (f_n/(1+K_{SVn}[O_2]))\right]^{-1} \qquad (1)$$

In this equation f_n are the fractional contributions from sites of different oxygen accessibility where K_{SVn} are the quenching constants for the different sites. The solid line in Fig. 5 shows the best fit using above equation for $n=2$. Thus, there are two types of oxygen accessible sites in the sensing film; one is readily accessible to oxygen ($K_{sv1}=3.00\%^{-1}$, $f_1=0.977$; dynamic quenching site) and the other is less accessible to oxygen ($K_{sv2}=0.0060\%^{-1}$, $f_2=0.023$; static quenching site). The inset in Fig. 5 shows the Stern–Volmer plot for each of these oxygen sensing sites. The value of K_{sv2} is very low ($0.0060\%^{-1}$) and provides a low contribution ($f_2=0.023$) compared to K_{sv1}, indicating that the oxygen inaccessible site is a static quenching site of the PdPC10COOH film.

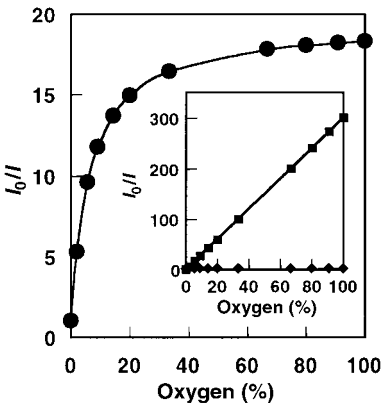

Fig. 5 Stern–Volmer plot for the PdPC10COOH film. The inset shows the Stern–Volmer plot for each different oxygen sensing site of the PdPC10COOH film. (■): Oxygen accessible site (K_{SV1}), (◆) oxygen inaccessible site (K_{SV2}).

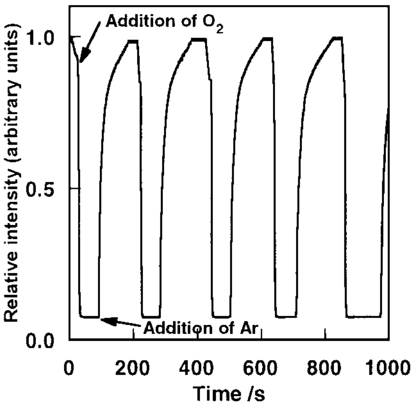

Fig. 6 Response time, relative phosphorescence intensity changes and reproducibility for the PdPC10COOH film on switching between 100% argon (1) and 100% oxygen (2). The excitation and emission wavelengths were 418 and 708 nm, respectively.

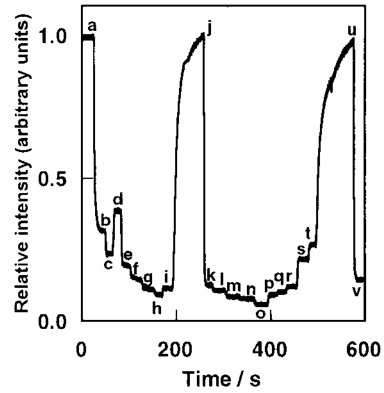

Fig. 7 Dynamic response of the PdPC10COOH film when oxygen concentrations were changed randomly. (a) 0, (b) 0.8, (c) 1.22, (d) 0.60, (e) 1.75, (f) 2.90, (g) 4.10, (h) 7.90, (i) 4.22, (j) 0, (k) 3.34, (l) 4.80, (m) 7.90, (n) 10.8, (o) 100, (p) 6.26, (q) 4.66, (r) 3.72, (s) 1.54, (t) 1.05, (u) 0, (v) 2.9% oxygen. The excitation and emission wavelengths were 418 and 708 nm, respectively.

Response time and reproducibility of the PdPC10COOH film

Fig. 6 shows a typical response of the sensor when switching between fully oxygenated and fully deoxygenated atmospheres. The response times of the sensor are 36 s on switching from argon to oxygen and 148 s on switching from oxygen to argon (*cf.* 65 s on switching from argon to oxygen and 200 s on switching from oxygen to argon for a palladium coproporphyrin–silicon rubber system[32]). The PdPC10COOH film thus shows a fast response. The signal changes were fully reversible and hysteresis was not observed. The dynamic response of the PdPC10COOH film to various oxygen concentrations is shown in Fig. 7. When different decreasing oxygen concentrations are supplied, the signal becomes lower and finally reaches its lowest level at 100% oxygen. When an increasing oxygen concentration is supplied, the signal increases and reaches the initial signal level of 0% oxygen. This test was repeated and signal changes were monitored with random increasing and decreasing oxygen concentrations. The resulting signal changes were fully reversible and no hysteresis was observed. Since no decomposition was observed upon irradiation for 4 h, it appears that the film is also stable to irradiation. In summary, the sensing film possesses good reproducibility and a fast response time.

Conclusion

An optical oxygen sensor has been prepared using a PdPC10COOH thin film on an alumina plate. The ratio I_0/I_{100}, a measurement of sensitivity of the PdPC10COOH film is estimated to be 18.3, showing that this film is highly sensitive towards oxygen. This sensing film showed good linearity according to a two-site model (more and less accessible to oxygen) Stern–Volmer plot *vs.* O_2 concentration and possesses good operational stability, reproducibility and a fast response. These results show that PdPC10COOH thin films can be developed for sensitive oxygen sensing devices.

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References

1 C. Prininger, I. Klimant and O. S. Wolfbeis, *Anal. Chem.*, 1994, **66**, 1841.
2 R. C. Martin, S. F. Malin, D. J. Bartnil, A. M. Schilling and S. C. Furlong, *Proc. SPIE*, 1994, **2131**, 426.
3 M. J. Atkinson, F. I. M. Thomas, N. Larson, E. Terrill, K. Morita and C. C. Lium, *Deep-Sea Res. I*, 1995, **42**, 761.
4 D. A. Skoog, D. M. West and F. J. Holler, *Fundamentals of Analytical Chemistry*, Saunders, Philadelphia, PA, 1988, p. 344.
5 L. C. Clark, *Trans. Am. Artif. Intern. Organs.*, 1956, **2**, 41.
6 T. M. Freeman and W. R. Seitz, *Anal. Chem.*, 1981, **53**, 98.
7 H. D. Hendricks, *US Pat.*, 3 709 663, 1973.
8 T. Ishiji and M. Kaneko, *Analyst*, 1995, **120**, 1633.
9 A. Sharma and O. S. Wolfbeis, *Appl. Spectrosc.*, 1988, **42**, 1009.
10 E. D. Lee, T. C. Werner and R. Seitz, *Anal. Chem.*, 1987, **59**, 279.
11 S. M. Ramasamy and R. J. Hurubise, *Anal. Chim. Acta*, 1983, **152**, 83.
12 H. W. Kroneis and H. J. Marsoner, *Sens. Actuators*, 1983, **4**, 587.
13 W. Xu, R. Schmidt, M. Whaley, J. N. Demas, B. A. DeGraff, E. K. Karikari and B. L. Farmer, *Anal. Chem.*, 1995, **67**, 3172.
14 J. Olmsted, *Chem. Phys. Lett.*, 1974, **26**, 33.
15 P. Hartmann, M. J. P. Leiner and M. E. Lippitsch, *Anal. Chem.*, 1995, **67**, 88.
16 M. G. Sasso, F. H. Quina and E. J. H. Bechera, *Anal. Biochem.*, 1986, **156**, 239.
17 E. Singer, G. L. Duveneck, M. Ehrat and M. Widmer, *Sens. Actuators A*, 1994, **41–42**, 542.
18 E. R. Carraway, J. N. Demas, B. A. DeGraff and J. R. Bacon, *Anal. Chem.*, 1991, **63**, 332.
19 J. R. Bacon and J. N. Demas, *Anal. Chem.*, 1987, **59**, 2780.
20 X. M. Li and H. Y. Wong, *Anal. Chim. Acta*, 1992, **262**, 27.
21 W. Y. Xu, K. A. Kneas, J. N. Demas and B. A. DeGraff, *Anal. Chem.*, 1996, **68**, 2605.
22 L. Sacksteder, J. N. Demas and B. A. DeGraff, *Anal. Chem.*, 1993, **65**, 3480.
23 R. G. Nuzzo, F. A. Fusco and D. L. Allara, *J. Am. Chem. Soc.*, 1987, **109**, 2358.
24 M. D. Porter, T. B. Bright, D. L. Allara and C. E. D. Chidsey, *J. Am. Chem. Soc.*, 1987, **109**, 3559.
25 P. E. Laibinis and G. M. Whitesides, *J. Am. Chem. Soc.*, 1992, **114**, 1990.
26 K. Kalyanasundaram, *Photochemistry of Polypyridine and Porphyrin Complexes*, Academic Press, New York, 1992.
27 D. Eastwood and M. Gouterman, *J. Mol. Spectrosc.*, 1970, **35**, 359.
28 D. B. Papkovsky, G. V. Ponomarev, W. Trettnak and P. O'Leary, *Anal. Chem.*, 1995, **67**, 4112.
29 S.-K. Lee and I. Okura, *Anal. Commun.*, 1997, **34**, 185.
30 B. D. MacCraith, C. M. McDonagh, G. O'Keeffe, E. T. Keyes, J. G. Vos, B. O'Kelly and J. F. McGilp, *Analyst*, 1993, **118**, 385.
31 J. N. Demas, B. A. DeGraff and W. Xu, *Anal. Chem.*, 1995, **67**, 1377.
32 P. M. Gewehr and D. T. Delpy, *Med. Biol. Eng. Comput.*, 1993, **31**, 11.

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