Thenoyltrifluoroacetonato 1,10-Phenanthroline Europium (III) Complex Immobilized in Fluoropolymer Film as Optical Oxygen Sensing Material

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A new optical oxygen sensor based on the luminescence intensities of thenoyltrifluoroacetonato 1,10-phenanthroline europium (III) complex (Eu(TTA)$_3$phen) immobilized in poly(styrene-*co*-trifluoroethylmethacrylate) film was developed. The luminescence intensity of the Eu(TTA)$_3$phen film decreased with increasing the oxygen concentration. A Stern–Volmer plot of the Eu(TTA)$_3$phen film exhibited considerable linearity (r^2 = 0.996) and the Stern–Volmer quenching constant, K_{SV} is estimated to be 0.015 %$^{-1}$.

Recent years have seen a growing interest in optical oxygen sensors based on oxygen-induced changes in the luminescence intensity of organic dyes.[1–3] Many optical oxygen sensors are composed of organic dyes, such as polycyclic aromatic hydrocarbons (pyrene derivatives, quinoline and phenanthrene) [4–6], transition metal complexes (ruthenium, [7–10] osmium[11] or rhenium–polypyridine complexes[12]), and metalloporphyrins,[13–15] immobilized in an oxygen permeable polymer. The essential demands for the organic dyes are strong luminescence with high quantum yield and have long lifetime, are desirable probes for optical oxygen sensing materials. Recently, much attention has been given to the photochemical and photophysical properties of lanthanide complexes.[16] Europium (III) complexes display remarkably strong luminescence with high quantum yield and have long lifetime ($\tau < 300$ µs).[17] Thus, europium (III) complexes are attractive candidates as novel optical oxygen sensing materials. In addition of quantum yield and lifetime, oxygen permeability of the polymer matrix is a critical property. Polymers possessing high oxygen permeability are advantageous to the matrix of optical oxygen sensing systems. We have previously reported the development of highly oxygen sensitive optical sensor based on the phosphorescence intensity change of platinum octaethylporphyrin immobilized in styrene–trifluoroethyl methacrylate copolymer (poly-(styrene-*co*-TFEM)) film with high oxygen permeability.[18]

In this letter we describe a new optical oxygen sensing material, thenoyltrifluoroacetonato 1,10-phenanthroline europium (III) complex (Eu(TTA)$_3$phen; structure is shown in Figure 1) immobilized in a fluoropolymer (poly-(styrene-*co*-TFEM)) film, and its oxygen sensing properties.

Poly-(styrene-*co*-TFEM) was synthesized according to previous literature.[18] The Eu(TTA)$_3$phen immobilized in poly-(styrene-co-TFEM) film was formed by casting a mixture of 10 wt% poly-(styrene-*co*-TFEM) and Eu(TTA)$_3$phen in tetrahydrofuran (THF) onto 1.4 × 5.0 cm non-luminescent glass slides. The Eu(TTA)$_3$phen 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. The thickness of the films was determined by the use of a micron-sensitive calliper. The thickness of the prepared films was between 50 and 80 µm.

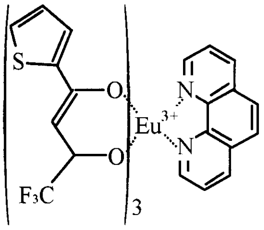

Figure 1. Chemical structure of thenoyltrifluoroacetonato 1,10-phenanthroline europium (III) (Eu(TTA)$_3$phen).

Oxygen sensing was carried out by using a spectrofluorophotometer with a 150 W Xenon lamp as the excitation light source. The sample film was 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).[18] All the experiments were carried out at room temperature. The oxygen sensing properties of Eu(TTA)$_3$phen films were characterized by 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. The K_{SV} value was obtained from a linear plot of (I_0/I) – 1 versus [O$_2$].

The absorption spectrum of Eu(TTA)$_3$phen film was almost identical to that in the THF solution. This result indicates that no electrical interaction occurred between Eu(TTA)$_3$phen and poly-(styrene-*co*-TFEM) in the ground state.

Eu(TTA)$_3$phen film showed strong luminescence at 612 nm. The excitation wavelength was 350 nm. The luminescence intensity of the film depended on the oxygen concentration. The intensity decreased with increasing the oxygen concentration as shown in Figure 2. The ratio I_0 / I_{100} is used as a measure of the film sensitivity, where I_0 and I_{100} represent the detected luminescence intensities from the film exposed to 100 % argon and 100 % oxygen, respectively. The I_0 / I_{100} value of Eu(TTA)$_3$phen film is estimated to be 1.91. This result indicates that the luminescence of Eu(TTA)$_3$phen in poly-(styrene-*co*-TFEM) film is quenched by oxygen, and that this film can

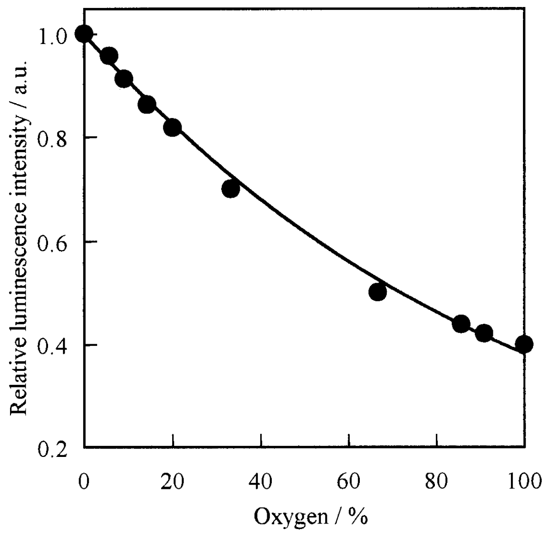

Figure 2. Oxygen-induced relative luminescence intensity change for Eu(TTA)$_3$phen immobilized in poly-(styrene-co-TFEM) film. Excitation and emission wavelengths are 350 and 612 nm, respectively.

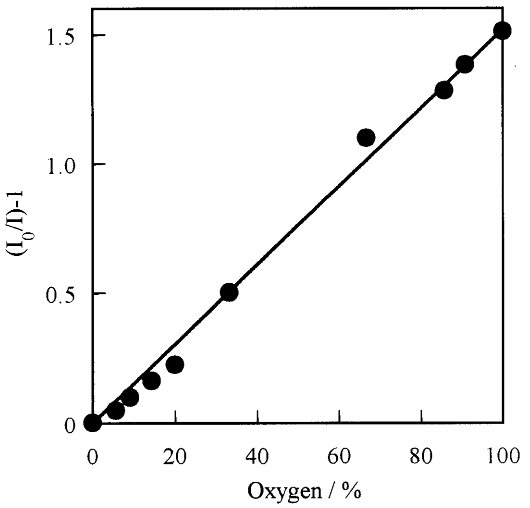

Figure 3. Stern-Volmer plot of Eu(TTA)$_3$phen immobilized in poly-(styrene-co-TFEM) film.

thus be used as an optical oxygen sensing device by employing its oxygen-induced luminescence quenching ability as an indicator of oxygen concentration.

Figure 3 shows a Stern–Volmer plot for the Eu(TTA)$_3$phen film. The plot exhibits considerable linearity supported by the correlation factor, r^2, estimated to be 0.996 by the least squares method. The K_{SV} value of the Eu(TTA)$_3$phen film is estimated to be 0.015 %$^{-1}$.

An operational stability test was conducted by reading the luminescence intensity signal while oxygenated and deoxygenated gases were switched for 300 s. The response times of the Eu(TTA)$_3$phen film were 6.7 s for switching from argon to oxygen, and 7.0 s for switching from oxygen to argon. The signal changes were fully reversible and hysterisis was not observed during the measurements. In general, oxygen sensing systems using dye immobilized 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 the Eu(TTA)$_3$phen film, however, K_{SV} was little affected by differences of 50 and 80 μm in the film thickness. An important factor for application of the Eu(TTA)$_3$phen film as an optical oxygen sensing material, is its photostability. To characterize the photostability of the Eu(TTA)$_3$phen film, the absorption spectrum of the film was measured after continuous irradiation using a 150 W tungsten lamp on the film for 12 h. No spectrum change was observed, indicating that the Eu(TTA)$_3$phen film is stable against irradiation.

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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 T. Ishiji, and M. Kaneko, *Analyst*, **120**, 1633 (1995).
5 A. Sharma and O. S. Wolfbeis, *Appl. Spect.*, **42**, 1009 (1988).
6 E. D. Lee, T. C. Werner, and R. Seitz, *Anal. Chem.*, **59**, 279 (1987).
7 W. Xu, R. Schmidt, M. Whaley, J. N. Demas, B. A. DeGraff, E. K. Karikari, and B. L. Farmer, *Anal. Chem.*, **67**, 3172 (1995).
8 P. Hartmann, M. J. P. Leiner, and M. E. Lippitsch, *Anal. Chem.*, **67**, 88 (1995).
9 E. Singer, G. L. Duveneck, M. Ehrat, and M. Widmer, *Sens. Actuators, A*, **41–42**, 542 (1994).
10 X. M. Li and H. Y. Wong, *Anal. Chim. Acta*, **262**, 27 (1992).
11 W. Y. Xu, K. A. Kneas, J. N. Demas, and B. A. DeGraff, *Anal. Chem.*, **68**, 2605 (1996).
12 L. Sacksteder, J. N. Demas, and B. A. DeGraff, *Anal. Chem.*, **65**, 3480 (1993).
13 D. B. Papkovsky, G. V. Ponomarev, W. Trettnak, and P. O'Leary, *Anal. Chem.*, **67,** 4112 (1995).
14 J. Vanderkooi, G. Maniara, J. Green, and D. F. Wilson, *J. Biol. Chem.*, **262**, 5476 (1987).
15 A. Mills, and A. Lepre, *Anal. Chem.*, **69**, 4653 (1997).
16 G. F. de Sá, O. L. Malta, C. de Mello Donegá, A. M. Simas, R. L. Longo, P. A. Santa-Cruz, and Jr. da Silva, *Coord. Chem. Rev.*, **196**, 165 (2000).
17 G. Vicentini, L. B. Zinner, J. Zukerman-Schpector, and K. Zinner, *Coord. Chem. Rev.*, **196**, 353 (2000).
18 Y. Amao, K. Asai, T. Miyashita, and I. Okura *Chem. Lett.*, **1999**, 1031.