Headline Articles

Optical Oxygen Sensing Based on the Luminescence Quenching of Europium(III) Complex Immobilized in Fluoropolymer Film

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New optical oxygen sensors based on the luminescence intensities of four different europium(III) complexes, ((1, 10-phenanthroline)tris(thenoyltrifluoroacetonato)europium(III) complex ([Eu(tta)$_3$phen]), tris(thenoyltrifluoroacetonato)-europium(III) dihydrate ([Eu(tta)$_3$]·2H$_2$O), tris(1,1,1-trifluoro-5,5-dimethyl-2,4-hexanedionato)europium(III) complex ([Eu-(pta)$_3$]·2H$_2$O) and tris(1,1,1,2,2,3,3-heptafluoro-7,7-dimethyl-4,6-octanedionato)europium(III) complex ([Eu(fod)$_3$]·2H$_2$O)) immobilized in poly(styrene-*co*-2,2,2-trifluoroethyl methacrylate) (poly-(styrene-*co*-TFEM)) films were developed. The luminescence intensity of the europium(III) complex films decreased with increasing the oxygen concentration. Stern–Volmer plots of the europium(III) complex films exhibited considerable linearity. The K_{SV} values of [Eu(tta)$_3$phen], [Eu(tta)$_3$]·2H$_2$O, [Eu(pta)$_3$]·2H$_2$O and [Eu(fod)$_3$]·2H$_2$O in films were estimated to be 0.015, 0.005, 0.002 and 0.003 %$^{-1}$, respectively. The large K_{SV} value of the [Eu(tta)$_3$phen] film was obtained compared with the other europium(III) complexes. The response times of the europium(III) complex films are 6.7 s for [Eu(tta)$_3$phen], 6.7 s for [Eu(tta)$_3$]·2H$_2$O, 6.6 s for [Eu(pta)$_3$]·2H$_2$O and 7.6 s for [Eu(fod)$_3$]·2H$_2$O on going from argon to oxygen and 7.0 s for [Eu(tta)$_3$phen], 7.5 s for [Eu(tta)$_3$]·2H$_2$O, 8.1 s for [Eu(pta)$_3$]·2H$_2$O and 8.6 s for [Eu(fod)$_3$]·2H$_2$O on going from oxygen to argon, respectively. A highly sensitive oxygen sensor using [Eu(tta)$_3$phen] immobilized in poly-(styrene-*co*-TFEM) film has been developed.

Oxygen-sensing techniques are applied to various fields, such as chemical, clinical analysis and environmental monitoring.[1—3] The sensing system is classified into the following categories: titration,[4] amperometry,[5] chemiluminescence,[6] and thermoluminescence.[7] Among these systems, the most popular method is the amperometric method using an oxygen electrode[5] in which the rate of diffusion of oxygen 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 photo-luminescent quenching of organic dyes have been developed to measure the oxygen concentration on the solid surface. Many optical oxygen sensors are composed of organic dyes, such as polycyclic aromatic hydrocarbons (pyrene and its derivatives, quinoline and phenanthrene),[8—14] transition metal complexes (ruthenium,[15—20] osmium[21] or rhenium–polypyridine complexes[22]), and metalloporphyrins,[23—25] immobilized in an oxygen-permeable polymer (silicon polymer, polystyrene and so on). The essential demands for the organic dyes are strong luminescence with a high quantum yield and having a long lifetime, and are used as desirable probes for optical oxygen sensing materials. Recently, much atten-

tion has been given to the photochemical and photophysical properties of lanthanide complexes.[26—35] Europium(III) complexes display remarkably strong luminescence with a high quantum yield and have a long lifetime.[35] The luminescence processes of the europium(III) complexes are shown in Scheme 1. The intersystem crossing process form the photoexcited singlet state of the ligand to the photoexcited triplet state of the ligand occurs, and then energy transfer from the photoexcited triplet state of the ligand to the excited state of europium(III) ion (the energy level of $^5D_0$) takes place. The luminescence of the europium(III) complexes is attributed to the $4f$ orbital–$4f$ orbital transition (the energy level of excited state $^5D_0$ to the energy level of the ground state ^7F_n).[31—35] The europium(III) complexes are attractive candidates as novel optical oxygen sensing materials. In addition to the quantum yield and lifetime of the organic dyes, the 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. In general, fluoropolymer film has a high permeability to oxygen. Because the oxygen affinity is induced by the high electronegativity of fluorine, the oxygen perme-

Scheme 1.

Fig. 1. Chemical structures of the europium(III) complexes.
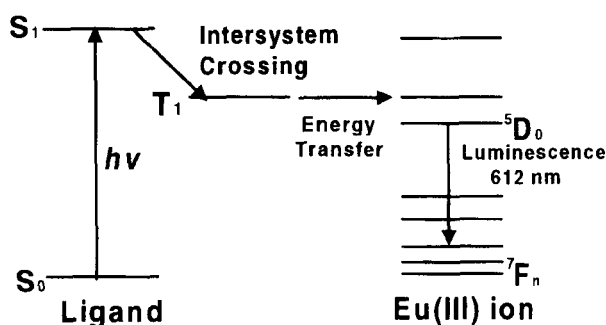
ability of the fluoropolymer is high. Also, the C–F bond length is short (13.17 nm); the bonding energy is large (485 kJ mol^{-1}) compared with C–H (416 kJ mol^{-1}), and the electron-withdrawing character of fluorine is large, and thus fluoropolymers are stable forward photo-oxidation.[36–38] Thus, fluoropolymers satisfy the above requirements. We have previously reported on the development of a highly oxygen sensitive optical sensor based on the phosphorescence intensity change of platinum octaethylporphyrin immobilized in poly-styrene-2,2,2-trifluoroethyl methacrylate copolymer (poly-(styrene-*co*-TFEM)) film[39] with a large diffusion constant (42.5×10^{-7} cm^2 s^{-1} at 30 °C). Platinum octaethylporphyrin immobilized in poly-(styrene-*co*-TFEM) film was photostable film induced by the trifluoromethyl group in the polymer matrix that exhibits minimal deterioration (ca. 2.0%) of the initial intensity after continuous irradiation for 24 h.[39] We have also reported the development of an optical oxygen sensor based on the luminescence intensity change of an europium(III) complex, (1,10-phenanthroline)tris(thenoyltrifluoroacetonato)europium(III) complex ([Eu(tta)$_3$phen]), immobilized in poly-(styrene-*co*-TFEM) film.[40]

In this work, a series of europium(III) complexes, ((1,10-phenanthroline)tris(thenoyltrifluoroacetonato)europium(III) complex ([Eu(tta)$_3$phen]), tris(thenoyltrifluoroacetonato)europium(III) dihydrate complex ([Eu(tta)$_3$]·2H$_2$O), tris(1,1,1-trifluoro-5,5-dimethyl-2,4-hexanedionato)europium(III) dihydrate complex ([Eu(pta)$_3$]·2H$_2$O and tris(1,1,1,2,2,3,3-heptafluoro-7,7-dimethyl-4,6-octanedionato)europium(III) dihydrate complex ([Eu(fod)$_3$]·2H$_2$O)) (the chemical structures are shown in Fig. 1)), were applied to an optical oxygen sensing probe, and the oxygen-sensing properties of the europium(III) complex films were studied.

Experimental

[Eu(tta)$_3$]·2H$_2$O was obtained from Acros Organics. [Eu(pta)$_3$]·2H$_2$O and [Eu(fod)$_3$]·2H$_2$O were obtained from Dojin Laboratory. Styrene and 2,2,2-trifluoroethyl methacrylate (TFEM) were purchased from Wako Chemical Co. Ltd. Azobis(isobutyronitrile) (AIBN) were purchased from Tokyo Chemical Industry Co. Ltd. Styrene and TFEM were distilled under reduced pressure to use in order to remove the inhibitor. AIBN was recrystallized from ethanol.

[Eu(tta)$_3$(phen)] was prepared by adding 40 ml of a warm ethanolic solution of 1,10-phenanthroline (1 mmol) to an ethanolic solution containing 1 mmol of [Eu(tta)$_3$]·2H$_2$O at 70 °C for 5 h. [Eu(tta)$_3$(phen)] was characterized by the UV-vis absorption
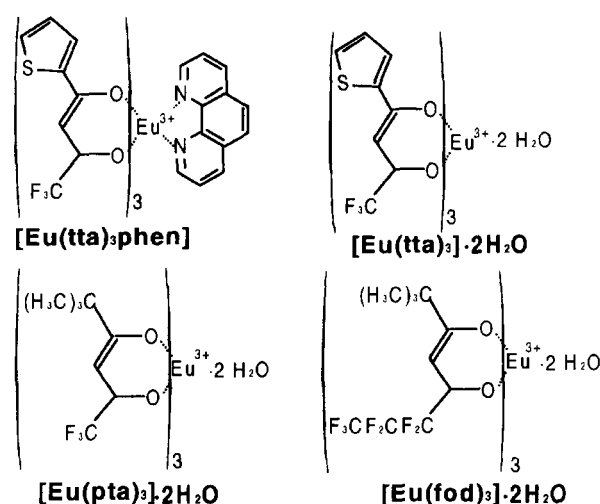
spectrum. During the synthesis of [Eu(tta)$_3$(phen)], the intensity of the absorption band at 268.1 nm, attributed to the coordination of 1, 10-phenanthroline, increased. The precipitate was filtered, washed with ethanol and dried in a vacuum. Purification was performed by recrystallization from an ethanol–water (1 : 2) mixture.

Poly-(styrene-*co*-TFEM) was synthesized according to the previous literature.[39] Styrene (0.16 mol), TFEM (0.15 mol) and AIBN (25 mmol) were dissolved in 80 ml of toluene. The reaction mixture was heated at 80 °C for 5 h under a 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 any unreacted monomer, and finally dried in a vacuum. The composition ratio of styrene and the TFEM unit was determined using the molar-absorption coefficient styrene and TFEM at 270 nm. The molecular weight was determined using gel-permeation chromatography (TSK HLC-802A TOYO SODA). Styrene/TFEM = 1.0; GPC: M_n = 93280, M_w = 148800, and M_w/M_n = 1.59.

An europium(III) complex immobilized in poly-(styrene-*co*-TFEM) films was formed by casting a mixture of 10 wt% poly-(styrene-*co*-TFEM) and europium(III) complex in tetrahydrofuran (THF) onto 1.4×5.0 cm non-luminescent glass slides. The europium(III) complex 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.

The UV-vis absorption spectra of the europium(III) complex films were recorded using a Shimadzu UV-2400PC spectrometer. Steady state luminescence spectra and the excitation spectra of the europium(III) complex films were measured using a Shimadzu RF-5300PC Spectrofluorophotometer with a 150 W xenon lamp as a visible excitation light source. Excitation and emission bandpasses were 5.0 nm.

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).[39] All of the experiments

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were carried out at room temperature. The oxygen-sensing properties of europium(III) complex 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 $[O_2]$.

Results and Discussion

The UV-vis absorption spectra of europium(III) complexes in poly-(styrene-co-TFEM) film are shown in Fig. 2. The shape of the spectra of europium(III) complexes in film were almost the same as in the THF solution (absorption peak position = 268.3 and 341.9 nm for [Eu(tta)$_3$(phen)], 270.0, 342.4 nm for [Eu(tta)$_3$]·2H$_2$O, 294.5 nm for [Eu(pta)$_3$]·2H$_2$O and 293.0 nm for [Eu(fod)$_3$]·2H$_2$O in film; 268.1 and 341.5 nm for [Eu(tta)$_3$(phen)], 270.0, 342.2 nm for [Eu(tta)$_3$]·2H$_2$O, 294.3 nm for [Eu(pta)$_3$]·2H$_2$O and 293.0 nm for [Eu(fod)$_3$]·2H$_2$O in THF solution) and no peak shift was observed. Thus, europium(III) complexes are homogeneously dispersed in poly-(styrene-co-TFEM) film. These results indicate no electronic interaction between europium(III) complexes and poly-(styrene-co-TFEM) at the ground state. The luminescence spectra of the europium(III) complex films are shown in Fig. 3. For all europium(III) complexes, the luminescence peak positions were observed at 580, 592, 612 and 651 nm. The excitation wavelengths for [Eu(tta)$_3$(phen)], [Eu(tta)$_3$]·2H$_2$O, [Eu(pta)$_3$]·2H$_2$O and [Eu(fod)$_3$]·2H$_2$O were 341.9, 342.4, 294.5 and 293.0 nm, respectively. The intensities of the luminescence peak positions of the europium(III) complex films depended on the oxygen concentration. The intensity of europium(III) complex film at 612 nm decreased with increasing the oxygen concentration, as shown in Fig. 4. The ratio I_0/I_{100} is used as a
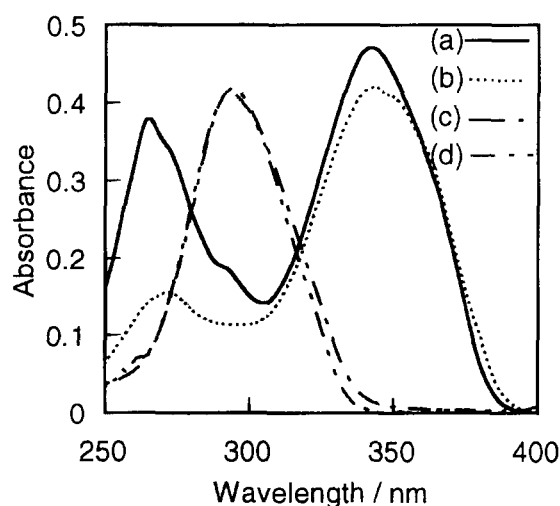
Fig. 2. The UV-vis absorption spectra of the europium(III) complex immobilized in poly(styrene-co-TFEM) films. (a) [Eu(tta)$_3$phen]; (b) [Eu(tta)$_3$]·2H$_2$O; (c) [Eu(pta)$_3$]·2H$_2$O and (d) [Eu(fod)$_3$]·2H$_2$O.
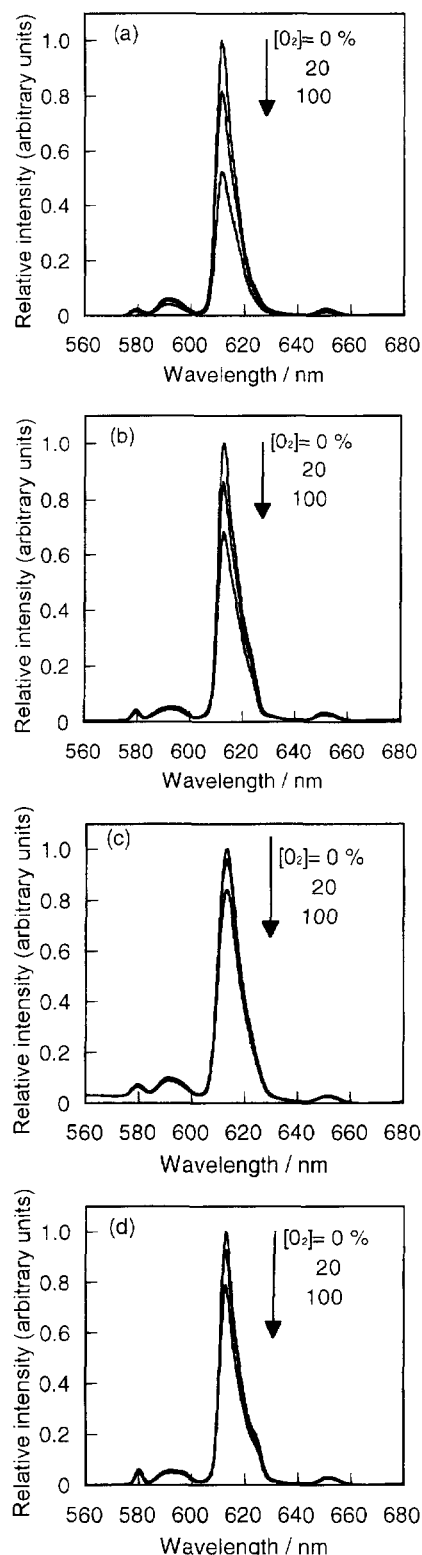
Fig. 3. The luminescence spectra of the europium(III) complex immobilized in poly(styrene-co-TFEM) films. (a) [Eu(tta)$_3$phen]; (b) [Eu(tta)$_3$]·2H$_2$O; (c) [Eu(pta)$_3$]·2H$_2$O and (d) [Eu(fod)$_3$]·2H$_2$O. Excitation wavelengths for [Eu(tta)$_3$phen], [Eu(tta)$_3$]·2H$_2$O, [Eu(pta)$_3$]·2H$_2$O and [Eu(fod)$_3$]·2H$_2$O were 341.9, 342.4, 294.5 and 293.0 nm, respectively.

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} values of [Eu(tta)₃(phen)], [Eu(tta)₃]·2H₂O, [Eu(pta)₃]·2H₂O and [Eu(fod)₃]·2H₂O in film are estimated to be 2.40, 1.50, 1.19 and 1.27, respectively. This result indicates that the luminescence of europium(III) complexes in poly-(styrene-co-TFEM) film is quenched by oxygen, and that this film can thus be used as an optical oxygen sensing device by employing its oxygen-induced luminescence quenching ability as an indicator of oxygen concentration. Especially, a large I_0/I_{100} value of the [Eu(tta)₃(phen)] film was obtained compared with the other europium(III) complexes.

Figure 5 shows the Stern–Volmer plots for the europium-(III) complex films. For all of the europium(III) complexes, the plots of exhibit considerable linearity supported by the correlation factor, r^2, estimated by the least-squares method at the oxygen concentration range between 0 and 100%. The K_{SV} and r^2 values of [Eu(tta)₃(phen)], [Eu(tta)₃]·2H₂O, [Eu(pta)₃]·2H₂O and [Eu(fod)₃]·2H₂O in film are estimated to be 0.015, 0.005, 0.002 and 0.003 %⁻¹ and 0.996, 0.992, 0.998 and 0.992, respectively. The large K_{SV} value of the [Eu(tta)₃(phen)] film was obtained compared with the other europium(III) complexes. These results indicate that the [Eu(tta)₃(phen)] film possesses a high sensitivity for oxygen compared with the other europium(III) complexes.

Figure 6 shows an operational stability test conducted by reading the luminescence intensity signal while oxygenated and deoxygenated gases were switched for 200 s. The response times are defined by the 95% response and recovery times, exhibited by the sensors when they are exposed to an alternating atmosphere of oxygen and argon, respectively. The response times of the europium(III) complex films are 6.7 s for [Eu(tta)₃(phen)], 6.7 s for [Eu(tta)₃]·2H₂O, 6.6 s

for [Eu(pta)₃]·2H₂O and 7.6 s for [Eu(fod)₃]·2H₂O on going from argon to oxygen and 7.0 s for [Eu(tta)₃(phen)], 7.5 s for [Eu(tta)₃]·2H₂O, 8.1 s for [Eu(pta)₃]·2H₂O and 8.6 s for [Eu(fod)₃]·2H₂O on going from oxygen to argon, respectively. 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 all of the europium(III) complex films, however, K_{SV} was little affected by the differences of 50 and 80 μm in the film thickness. An important factor for applying europium-(III) complex films as an optical oxygen sensing material is their photostability. To characterize the photostability of the europium(III) complex films, the UV-vis 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 europium(III) complex films are stable against irradiation.

The oxygen-sensing properties, the I_0/I_{100}, K_{SV}, r^2 and response times, of the europium(III) complex films were summarized in Table 1. From Table 1, [Eu-(tta)₃phen] film possessed a highly sensitivity for oxygen compared with the other europium(III) complexes. For [Eu(tta)₃]·2H₂O, [Eu(pta)₃]·2H₂O and [Eu(fod)₃]·2H₂O, hydrated water molecules may be coordinated to the europium-(III) ion. As the vibrational excitation of the excited state of europium(III) ion was induced by the coordinated water molecules, the luminescence intensity, quantum yield of the luminescence and the luminescence lifetime of europium-(III) complexes decreased.[41] Thus, the oxygen quenching efficiency of these europium(III) complexes decreased compared with that of [Eu(tta)₃phen]. Hence, the effective

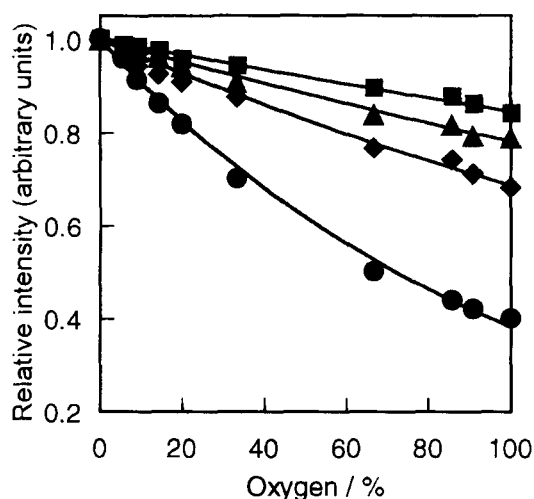Fig. 4. The relative luminescence intensity changes of the europium(III) complex immobilized in poly(styrene-co-TFEM) films under various oxygen concentrations. Emission wavelength was 612.0 nm. (●) [Eu(tta)₃phen]; (◆) [Eu(tta)₃]·2H₂O; (■) [Eu(pta)₃]·2H₂O; (▲) [Eu(fod)₃]·2H₂O.
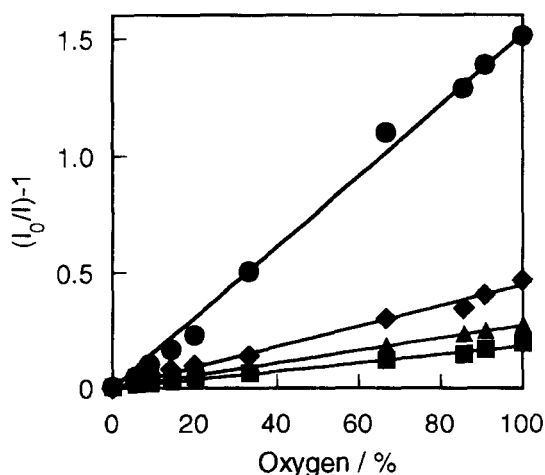

Fig. 5. Stern–Volmer plot for the europium(III) complex immobilized in poly(styrene-co-TFEM) films. (●) [Eu(tta)₃phen]; (◆) [Eu(tta)₃]·2H₂O; (■) [Eu(pta)₃]·2H₂O; (▲) [Eu(fod)₃]·2H₂O. Excitation wavelengths for [Eu(tta)₃phen], [Eu(tta)₃]·2H₂O, [Eu(pta)₃]·2H₂O and [Eu(fod)₃]·2H₂O were 341.9, 342.4, 294.5 and 293.0 nm, respectively. Emission wavelength was 612.0 nm.

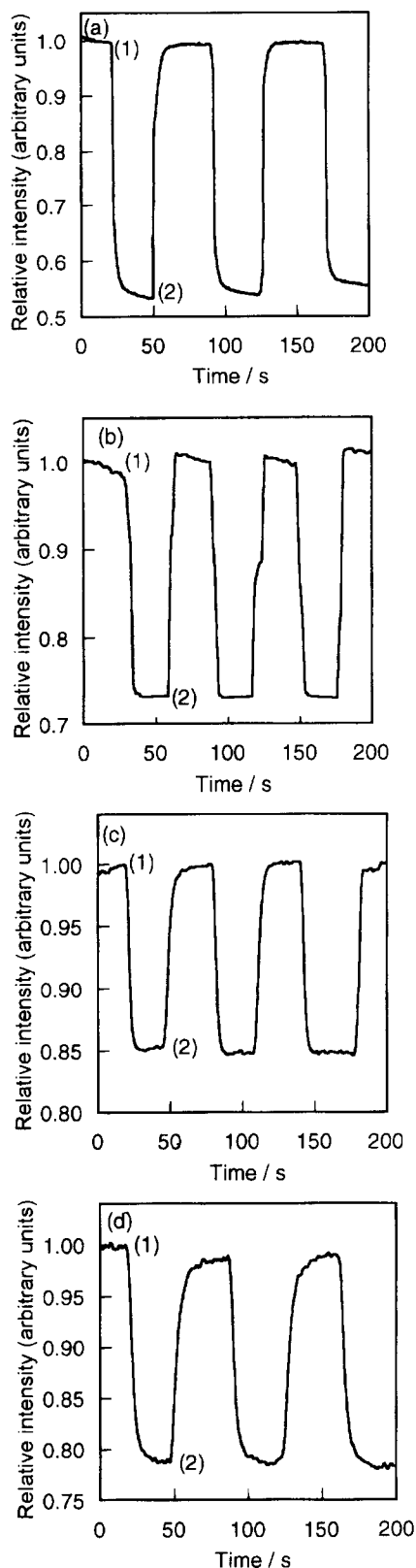Y. Amao et al.

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Fig. 6. Response time and relative intensity change for the europium(III) complex immobilized in poly(styrene-co-TFEM) films on switching between 100% argon (1) and 100% oxygen (2) for 200 s. Excitation wavelengths for [Eu(tta)₃phen], [Eu(tta)₃]·2H₂O, [Eu(pta)₃]·2H₂O and [Eu(fod)₃]·2H₂O were 341.9, 342.4, 294.5 and 293.0 nm, respectively. Emission wavelength was 612.0 nm.

Table 1. Optical Oxygen Sensing Properties of the Europium(III) Complex Immobilized in Poly(styrene-co-TFEM) Films

	I_0/I_{100}	$K_{SV}/\%^{-1}$	r^2	Response time/s $t(\text{Ar to O}_2) : t(\text{O}_2 \text{ to Ar})$
[Eu(tta)₃phen]	2.40	0.015	0.996	6.7 : 7.0
[Eu(tta)₃]·2H₂O	1.50	0.005	0.992	6.7 : 7.5
[Eu(pta)₃]·2H₂O	1.19	0.0019	0.998	6.6 : 8.1
[Eu(fod)₃]·2H₂O	1.27	0.0027	0.992	7.6 : 8.6

quenching luminescence of [Eu(tta)₃phen] by oxygen occurred compared with the other complexes with coordinated water molecules ([Eu(tta)₃]·2H₂O, [Eu(pta)₃]·2H₂O and [Eu(fod)₃]·2H₂O) and a highly sensitive oxygen sensor is developed using [Eu(tta)₃phen].

Conclusion

New optical oxygen sensors based on the luminescence intensities of four different europium(III) complexes, ([Eu(tta)₃ phen], [Eu(tta)₃]·2H₂O, [Eu(pta)₃]·2H₂O and [Eu(fod)₃]·2H₂O) immobilized in poly-(styrene-co-TFEM) films were developed. Stern–Volmer plots of the europium(III) complex films exhibited considerable linearity, and large I_0/I_{100} and K_{SV} values were obtained using [Eu(tta)₃phen] ($I_0/I_{100} = 2.40$ and $K_{SV} = 0.015\ \%^{-1}$) compared with the other europium(III) complexes. A highly sensitive oxygen sensor using [Eu(tta)₃phen] immobilized in poly-(styrene-co-TFEM) film was developed.

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