

Platinum tetrakis(pentafluorophenyl)porphyrin immobilized in polytrifluoroethylmethacrylate film as a photostable optical oxygen detection material

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Abstract

An optical oxygen detection material based on platinum tetrakis(pentafluorophenyl)porphyrin (PtTFPP) immobilized in fluoropolymer, polytrifluoroethylmethacrylate (poly-TFEM) film has been developed and characterized. The luminescence intensity of PtTFPP in poly-TFEM film decreased with increase of oxygen concentration. The ratio I_0/I_{100} is used as a sensitivity of the film, where I_0 and I_{100} represent the detected luminescence intensities from a film exposed to 100% argon and 100% oxygen, respectively. I_0/I_{100} value of PtTFPP in poly-TFEM film is estimated to be 15.4 and large Stern–Volmer constant is obtained compared with PtTFPP in polystyrene film. The response times of PtTFPP immobilized in poly-TFEM film are 5.6 s on going from argon to oxygen and 32 s from oxygen to argon, respectively. The fast response time is obtained using PtTFPP immobilized in poly-TFEM film. PtTFPP in poly-TFEM film exhibits minimal deterioration decrease of initial intensity after continuous irradiation for 24 h (ca. 0.5%). These results indicate that PtTFPP immobilized in poly-TFEM film is photostable and highly sensitive device for oxygen. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

Oxygen detection techniques are applied to various fields, such as chemical, clinical analysis and environmental monitoring [1–3]. The most popular method is the amperometric method using oxygen electrode in which the rate of diffusion of oxygen to the cathode is measured [4]. 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 are developed to measure oxygen concentration on the solid surface. Many optical oxygen sensors are composed of organic dyes, such as polycyclic aromatic hydrocarbons [5–11], transition metal complexes [12–19], and metalloporphyrins [20–24], immobilized in oxygen permeable polymer as a matrix. Among these dyes, platinum, palladium and ruthenium porphyrins show strong room temperature phosphorescence with high quantum yield ($\Phi_P < 0.5$) and long lifetime more

than 100 μ s [25]. Among these porphyrins, platinum octaethylporphyrin (PtOEP) is widely used as probe for optical oxygen sensor and some optical oxygen sensors based on luminescence quenching of PtOEP immobilized in polymer film by oxygen are developed [24,26,27]. However, this type of the sensor somewhat lacks in photostability under continuous operating conditions. PtOEP showed decrease of intensity during the initial illumination period, although stable phosphorescence intensity was observed with only minor changes in intensity after hours of illumination. This is attributed to the photobleaching nature of indicator, leaching of indicator from matrix and deterioration of matrix itself. However, so far a few attempts have been tried to increase photostability of organic dye and resulting optical detection performance. Among them, there are endeavors to enhance the photostability of optical sensors by modifications of existing dyes [22], and the matrices [28,29]. Among these factors, the choice of indicator in detection material is often the controlling factor in determining detection characteristics, especially sensor lifetime. Photostable optical sensors developed by using platinum or palladium octaethylporphyrin to corresponding photostable

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ketones [22]. Their platinum octaethylporphyrin ketone immobilized in polystyrene sensor showed 12% intensity diminishing under continuous illumination for 18 h, detected by absorbance measurement [22]. Platinum fluorinated porphyrin, platinum tetrakis(pentafluorophenyl)porphyrin (PtTFPP), also has paid much attention as a photostable optical oxygen sensing material. As the electron-withdrawing character of the perfluorophenyl substituents of PtTFPP strongly raises the redox potentials and reduces the electron density of porphyrin ring, PtTFPP is stable against photo-oxidation/reduction [30]. On the other hand, the oxygen permeable polymers with lower diffusion barrier for oxygen and with stability against photo-oxidation/reduction are desired as a matrix for optical oxygen detection system. In general, fluoropolymer film possesses large permeability of oxygen and stability against the irradiation [31]. As C–F bond length is short (1.31 Å) compared with C–H bond (1.09 Å), the bonding energy is large (485 kJ mol⁻¹) compared with C–H (416 kJ mol⁻¹). The electron-withdrawing character of the fluorine strongly raises the redox potential of the fluoropolymer. Thus, fluoropolymers are stable against photo-oxidation/reduction. As an oxygen affinity is induced by large electronegativity of fluorine, on the other hand, an oxygen permeability of the fluoropolymer is large [32–36]. Thus, fluoropolymers are suitable for the above requirements. Moreover, PtTFPP immobilized in fluoropolymer film is attractive to develop a photostable optical oxygen detection material.

In this work, in an attempt to obtain a photostable optical detection material for gaseous oxygen, PtTFPP and polytrifluoroethylmethacrylate (poly-TFEM) (chemical structures are shown in Fig. 1) were used as a visible light-absorbable O₂-sensitive organic dye and its support matrix, respectively. Ultimately, photostability of oxygen detection material determines the long-term operational stability, lifetime and other performances of optical oxygen detection material and to enhance photostability is the main aim in the present work.

2. Experimental

2.1. Materials

PtTFPP was obtained from porphyrin products (Logan, UT, USA). Polystyrene (PS, average MW 280 000, GPC grade) was purchased from Aldrich (Milwaukee, WI, USA). Trifluoroethylmethacrylate (TFEM) was purchased from Wako Chemical Co. Ltd. (Osaka, Japan). Azo-bis(isobutyronitrile) (AIBN) was purchased from Tokyo Chemical Industry Co. Ltd. (Tokyo, Japan). TFEM was distilled under reduced pressure in order to remove the inhibitor. AIBN was recrystallized from ethanol.

2.2. Synthesis of poly-TFEM

Poly-TFEM is synthesized as the following method. TFEM and AIBN are dissolved in toluene. The reaction mixture was heated at 80°C for 8 h under argon atmosphere. After the mixture was cooled to room temperature, the polymer was precipitated in ethanol. The solid was collected by filtration, washed with ethanol to remove unreacted monomer, and finally dried in vacuum. The molecular weight was determined using gel permeation chromatography (column: Plegel 5 µm MIXED-D, Polymer Laboratories; detector: Shimadzu, RID-10A; eluent, THF). The system was calibrated using polystyrene standards. $M_n = 3178$, $M_w = 4360$, and $M_w/M_n = 1.37$.

2.3. Preparation of PtTFPP immobilized in poly-TFEM film

PtTFPP immobilized in poly-TFEM film was formed by casting the mixture of 10 wt.% poly-TFEM film and PtTFPP in toluene on to 1.4 cm × 5.0 cm non-luminescent glass slides. PtTFPP concentration in the film was approximately to be 2.9×10^{-5} mol dm⁻³. As a reference, PtTFPP immobilized in polystyrene film was prepared. The films were

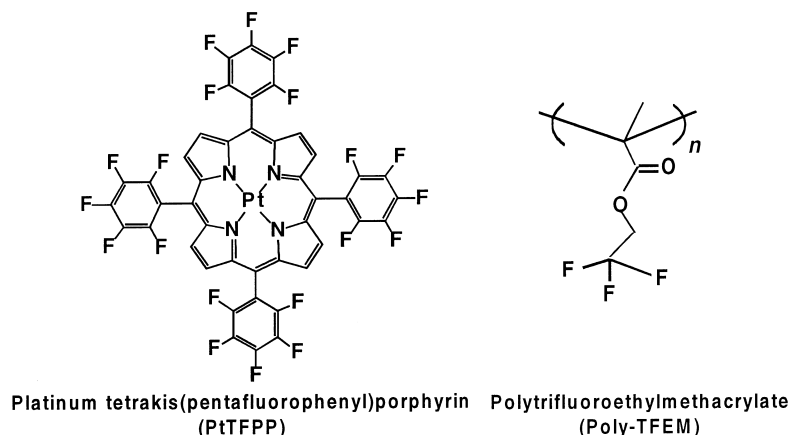


Fig. 1. Chemical structures of PtTFPP and poly-TFEM.

dried at room temperature and stored in dark prior to use. Thickness of the films was determined by use of a micron-sensitive caliper. The thickness of the film prepared was between 10 and 20 μm .

2.4. Spectroscopic measurements

The UV–VIS absorption spectrum of PtTFPP immobilized in poly-TFEM film between 350 and 650 nm was recorded using a Shimadzu (Tokyo, Japan) UV-2400PC spectrometer with a tungsten lamp as a monitor light source. Steady state luminescence spectra and excitation spectra of the PtTFPP in films were measured using a Shimadzu (Tokyo, Japan) RF-5300PC spectrofluorophotometer with a 150 W xenon lamp as a visible excitation light source. Excitation and emission bandpasses were 5.0 nm.

2.5. Oxygen detection properties of PtTFPP immobilized in poly-TFEM film

Oxygen detection was carried out using a spectrofluorophotometer with a 150 W xenon lamp as a visible excitation light source. The sample films were mounted at an angle of 45° to the excitation light source 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 a mixing chamber. The total pressure was maintained at 760 Torr (1 Torr = 133.322 Pa) [26,27]. All the experiments were carried out at room temperature. Oxygen detection properties of PtTFPP immobilized in poly-TFEM film was characterized by Stern–Volmer quenching constant K_{SV} , obtained from following equation.

$$\left(\frac{I_0}{I}\right) - 1 = K_{SV}[\text{O}_2] \quad (1)$$

where I_0 , I and $[\text{O}_2]$ are luminescence intensities in the absence and in the presence of oxygen and oxygen concentration, respectively. K_{SV} was obtained from a linear plot of $(I_0/I) - 1$ versus $[\text{O}_2]$.

3. Results and discussion

3.1. Spectroscopic properties of PtTFPP immobilized in poly-TFEM film

The absorption spectrum of PtTFPP in poly-TFEM film was almost the same as in the toluene solution (absorption peak positions = 544 and 510 nm attributed to Q-band and 396 nm attributed to Soret-band for PtTFPP in poly-TFEM film; 541 and 508 nm attributed to Q-band and 395 nm attributed to Soret-band for PtTFPP in toluene solution) and no peak shift was observed. These results indicate no

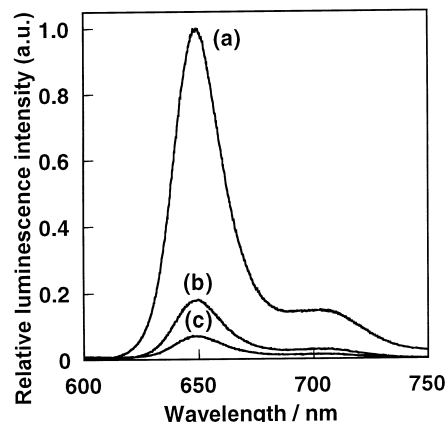


Fig. 2. Luminescence spectra of PtTFPP immobilized in poly-TFEM film: (a) 100% argon; (b) 33.3% oxygen and (c) 100% oxygen. Excitation wavelength was 544.0 nm.

electrical interaction between PtTFPP and poly-TFEM at the ground state.

3.2. Luminescence spectrum change of PtTFPP immobilized in poly-TFEM film by oxygen

PtTFPP immobilized in poly-TFEM film showed luminescence at 648.4 nm attributed to the transition from the photoexcited triplet state to the ground state $T(0,0)$, when excited at wavelength attributed to the low energy band in the electronic origin $Q(0,0)$ of the lowest-energy excited singlet state (544.0 nm), as shown in Fig. 2. Luminescence intensity of the film depended on the oxygen concentration. The luminescence intensity decreased with increase of oxygen concentration as shown in the Fig. 3. These results indicate that the luminescence of PtTFPP in poly-TFEM film was quenched by oxygen. These results show that PtTFPP immobilized in poly-TFEM film can be used as an optical oxygen detection device based on luminescence quenching by oxygen. The I_0/I_{100} value is used as a measure

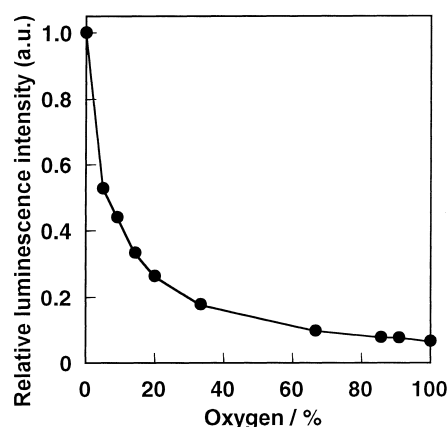


Fig. 3. Relative luminescence intensity change of PtTFPP immobilized in poly-TFEM film under various oxygen concentrations. Excitation and emission wavelengths were 544.0 and 648.4 nm, respectively.

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. In general, the sensor having the I_0/I_{100} value more than 3.0 is a suitable oxygen detection device [37]. The I_0/I_{100} values of PtTFPP immobilized in polystyrene film, as reference and in poly-TFEM film were estimated to be 3.0 and 15.4, respectively. This result indicates that PtTFPP immobilized in poly-TFEM film is highly sensitive device for oxygen.

3.3. Oxygen detection properties of PtTFPP immobilized in poly-TFEM film

Fig. 4 shows the Stern–Volmer plots of PtTFPP immobilized in poly-TFEM film (●) and in polystyrene film (■). For PtTFPP immobilized in poly-TFEM film, the plot exhibits considerable linearity at the oxygen concentration range between 0 and 100%. K_{SV} value of PtTFPP immobilized in poly-TFEM film was 0.14 per percentage. On the other hand, the plot for PtTFPP immobilized in polystyrene exhibits considerable linearity at the lower oxygen concentration, although the curvature decreases at higher oxygen concentrations. At lower oxygen concentration, the intensities from the PtTFPP film are quenched by oxygen according to Stern–Volmer equation as well as in homogeneous system. At higher concentrations, on the other hand, Stern–Volmer plot of sensor based on luminescence quenching is nonlinear, because of the simultaneous presence of some different oxygen-accessible site. We reported that PtOEP immobilized in polystyrene film has some different oxygen-accessible site [27]. There are two oxygen accessible sites in the detection film; one is an oxygen easily accessible site attributed to PtTFPP on the surface of polymer film and the other is an oxygen difficult accessible site attributed to PtTFPP in the bulk of polymer film. The luminescence of PtTFPP on the surface of polymer film is quenched effectively compared with that of PtTFPP in the bulk of polymer film. Demas et al. also reported that multi-site model;

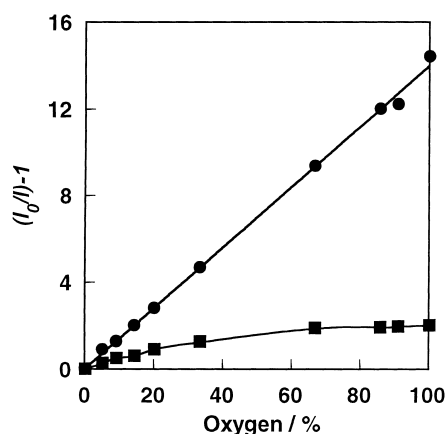


Fig. 4. Stern–Volmer plots for PtTFPP immobilized in poly-TFEM film (●) and in polystyrene (■). Excitation and Emission wavelengths were 544.0 and 648.4 nm, respectively.

oxygen-accessible site and oxygen-difficult accessible site, respectively [38]. In this model, the sensor molecule can exist in two or more sites each with its own characteristic quenching constant. Stern–Volmer plot becomes as follows.

$$\frac{I_0}{I} = \left[\sum \left(\frac{f_n}{(1 + K_{SVn}[O_2])} \right) \right]^{-1} \quad (2)$$

where f_n is the fractional contributions to the oxygen accessible site or oxygen-difficult accessible site, K_{SVn} the quenching constant for each accessible site. In Fig. 4, for polystyrene film, the solid line is the best fit using the above equation ($n = 2$). Thus, there are two oxygen accessible sites for detection film; one is an oxygen accessible site attributed to PtTFPP on the surface of polystyrene film ($K_{SV1} = 0.070$ per percentage, $f_1 = 0.980$) and the other is an oxygen difficult accessible site attributed to PtTFPP in the bulk of polystyrene film ($K_{SV2} = 0.051$ per percentage, $f_2 = 0.020$). The K_{SV2} is a very low value and little contribution compared with K_{SV1} . The K_{SV} value of PtTFPP immobilized in poly-TFEM film is larger than the K_{SV1} value of polystyrene film. These results indicate that PtTFPP immobilized in poly-TFEM film is useful optical oxygen sensor at the oxygen concentration range between 0 and 100%. These results suggest that the oxygen permeability of poly-TFEM film is larger than that of the polystyrene. An oxygen affinity is induced by larger electronegativity of fluorine atom and the interfacial intermolecular force between gaseous phase and surface on poly-TFEM film is lower than that of polystyrene film by lower surface free Gibbs energy of fluorine atom. Diffusion coefficient for oxygen (D_{oxygen}) at room temperature of poly-TFEM film and polystyrene film were 6.34×10^{-7} and $1.00 \times 10^{-7} \text{ m}^2 \text{ s}^{-1}$, respectively. The D_{oxygen} of poly-TFEM film is six times larger than that of polystyrene film. As an oxygen permeability of poly-TFEM film is large, the luminescence of PtTFPP on the surface and in the bulk of poly-TFEM film is quenched by oxygen effectively. Thus, higher sensitive optical sensor is developed using poly-TFEM as a polymer matrix.

3.4. Operational stability, and response time of PtTFPP immobilized in poly-TFEM film

Fig. 5 shows an operational stability test conducted by reading intensity signal from PtTFPP immobilized in poly-TFEM film when oxygenated and deoxygenated gases were switched for 200 s. In general, the response times for optical oxygen sensor are defined 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 film are 5.6 s on going from argon to oxygen and 32.0 s on going from oxygen to argon, respectively (18.0 s on going from argon to oxygen and 60 s on going from oxygen to argon for PtTFPP immobilized in polystyrene). By using poly-TFEM as polymer matrix, the

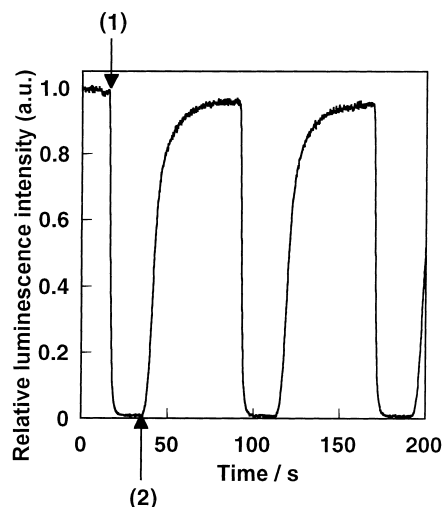


Fig. 5. Response time and relative intensity change for PtTFPP immobilized in poly-TFEM film on switching between 100% argon (1) and 100% oxygen (2) for 200 s. Excitation and emission wavelengths were 544.0 and 648.4 nm, respectively.

fast response time was obtained compared with polystyrene film. As the D_{oxygen} value of poly-TFEM film is six times larger than that of polystyrene film, the fast response time was obtained using PtTFPP immobilized in poly-TFEM film.

PtTFPP immobilized in poly-TFEM film are the photostable film induced by fluoro-group of PtTFPP and poly-TFEM that exhibits minimal deterioration (ca. 0.5%) decrease of initial intensity after continuous irradiation for 24 h. The electron-withdrawing character of the perfluorophenyl substituents of PtTFPP and trifluoroethyl substituent of poly-TFEM strongly raise the redox potentials and reduce the electron density of PtTFPP and poly-TFEM [39]. Hence, the PtTFPP and poly-TFEM are stable against photo-oxidation/reduction and increase photostability.

Next, let us focus on the comparison of the typical optical oxygen sensor. The I_0/I_{100} and K_{SV} values of optical oxygen sensors using pyrene butyric acid [7], tris(4,7-diphenyl-1,10-phenanthroline)ruthenium (II) [17] and tris(4,7-diphenyl-1,10-phenanthroline)osmium (II) [20] immobilized in poly(dimethylsiloxane) film were reported to be 12, 5.0 and 0.5, and 0.13, 0.05 and 0.005 per percentage, respectively. The Stern–Volmer plots for these materials exhibit considerable linearity at the lower oxygen concentration between 0 and 20%, although the curvature decreases at higher oxygen concentrations. These materials exhibit the deterioration (ca. 1.0–20%) decrease of initial intensity after continuous irradiation for 24 h. On the other hand, the I_0/I_{100} and K_{SV} values of PtTFPP in poly-TFEM film are estimated to be 15.4 and 0.14 per percentage, respectively. The Stern–Volmer plot for PtTFPP in poly-TFEM film exhibits considerable linearity at the oxygen concentration range between 0 and 100%. Thus, the PtTFPP immobilized in poly-TFEM film is a novel optical oxygen sensing material.

4. Conclusions

An optical oxygen detection material based on PtTFPP immobilized in fluoropolymer, poly-TFEM film has been developed and characterized. The luminescence intensity of PtTFPP in poly-TFEM film decreased with increase of oxygen concentration. The I_0/I_{100} value of PtTFPP in poly-TFEM film is estimated to be 15.4 and large Stern–Volmer constant ($K_{SV} = 0.14$ per percentage) is obtained compared with PtTFPP in polystyrene film ($K_{SV} = 0.070$ per percentage). The response times of PtTFPP immobilized in poly-TFEM film are 5.6 s on going from argon to oxygen and 32 s from oxygen to argon, respectively. PtTFPP immobilized in poly-TFEM film exhibits minimal deterioration (ca. 0.5%) decrease of initial intensity after continuous irradiation for 24 h. These results indicate that PtTFPP immobilized in poly-TFEM film is photostable and highly oxygen sensitive device.

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References

- [1] C. Prininger, I. Klimant, O.S. Wolfbeis, *Anal. Chem.* 66 (1994) 1841.
- [2] R.C. Martin, S.F. Malin, D.J. Bartnil, A.M. Schilling, S.C. Furlong, *Proc. SPIE* 2131 (1994) 426.
- [3] D.A. Skoog, D.M. West, F.J. Holler, *Fundamentals of Analytical Chemistry*, Saunders, Philadelphia, 1988, p. 344.
- [4] L.C. Clark, *Trans. Am. Artif. Int. Organs.* 2 (1956) 41.
- [5] T.M. Freeman, W.R. Seitz, *Anal. Chem.* 53 (1981) 98.
- [6] H.D. Hendricks, US Patent 3,709,663 (1973).
- [7] T. Ishiji, M. Kaneko, *Analyst* 120 (1995) 1633.
- [8] A. Sharma, O.S. Wolfbeis, *Appl. Spectrosc.* 42 (1988) 1009.
- [9] E.D. Lee, T.C. Werner, R. Seitz, *Anal. Chem.* 59 (1987) 279.
- [10] S.M. Ramasamy, R.J. Hurubise, *Anal. Chim. Acta* 152 (1983) 83.
- [11] H.W. Kroneis, H.J. Marsoner, *Sens. Actuators* 4 (1983) 587.
- [12] W. Xu, R. Schmidt, M. Whaley, J.N. Demas, B.A. DeGraff, E.K. Karikari, B.L. Farmer, *Anal. Chem.* 67 (1995) 3172.
- [13] J. Olmsted, *Chem. Phys. Lett.* 26 (1974) 33.
- [14] P. Hartmann, M.J.P. Leiner, M.E. Lippitsch, *Anal. Chem.* 67 (1995) 88.
- [15] M.G. Sasso, F.H. Quina, E.J.H. Bechera, *Anal. Biochem.* 156 (1986) 239.
- [16] E. Singer, G.L. Duvencek, M. Ehrat, M. Widmer, *Sens. Actuators A* 41/42 (1994) 542.
- [17] E.R. Carraway, J.N. Demas, B.A. DeGraff, J.R. Bacon, *Anal. Chem.* 63 (1991) 332.
- [18] J.R. Bacon, J.N. Demas, *Anal. Chem.* 59 (1987) 2780.
- [19] X.M. Li, H.Y. Wong, *Anal. Chim. Acta* 262 (1992) 27.
- [20] W.Y. Xu, K.A. Kneas, J.N. Demas, B.A. DeGraff, *Anal. Chem.* 68 (1996) 2605.
- [21] L. Sacksteder, J.N. Demas, B.A. DeGraff, *Anal. Chem.* 65 (1993) 3480.

- [22] D.B. Papkovsky, G.V. Ponomarev, W. Trettnak, P. O'Leary, *Anal. Chem.* 67 (1995) 4112.
- [23] J. Vanderkooi, G. Maniara, J. Green, D.F. Wilson, *J. Biol. Chem.* 262 (1987) 5476.
- [24] A. Mills, A. Lepre, *Anal. Chem.* 69 (1997) 4653.
- [25] K. Kalyanasundaram, *Photochemistry of Polypyridine and Porphyrin Complexes*, Academic Press, New York, 1992, p. 500.
- [26] S-K. Lee, I. Okura, *Anal. Sci.* 13 (1997) 535.
- [27] S-K. Lee, I. Okura, *Spectrochim. Acta A* 54 (1998) 91.
- [28] S-K. Lee, I. Okura, *Anal. Chim. Acta* 342 (1997) 181.
- [29] S-K. Lee, I. Okura, *Analyst* 122 (1997) 81.
- [30] S-K. Lee, I. Okura, *Anal. Commun.* 34 (1997) 185.
- [31] N. Yi-Yan, R.M. Felder, W.J. Koros, *J. Appl. Polym. Sci.* 25 (1980) 1755.
- [32] W.A. Zisma, *Adv. Chem. Ser.* 43 (1964) 1.
- [33] A.G. Pittman, *Fuluropolymers*, Wiley/Interscience, New York, 1972, p. 446.
- [34] E. Wicke, E.U. Frank, *Angew. Chem.* 66 (1954) 701.
- [35] K.G. Denbigh, *Trans. Faraday Soc.* 36 (1940) 936.
- [36] A.Y. Kupryazhkin, E.V. Popof, *Vysokomol. Soedin. Ser. B* 21 (1976) 287.
- [37] B.D. MacCraith, C.M. McDonagh, G. O'Keefe, E.T. Keyes, J.G. Vos, B. O'Kelly, J.F. McGilp, *Analyst* 118 (1993) 385.
- [38] J.N. Demas, B.A. DeGraff, W. Xu, *Anal. Chem.* 67 (1995) 1377.
- [39] F.J. Kampas, M. Gouterman, *J. Phys. Chem.* 81 (1977) 690.