

Development of Pressure-Sensitive Paints: Electro- and Photochemical Behavior of a Porphyrin Monolayer

Naoko Araki¹, Akio Ichimura², Kazunori Mitsuo^{3,†}, Keisuke Asai^{3,‡}, Makoto Obata¹, Shigenobu Yano^{1,*}

¹Division of Natural Science and Ecological Awareness, Graduate School of Humanities and Sciences, Nara Women's University, Kita-uoya-nishi-machi, Nara-shi 630-8506, Japan, FAX: 81-742-20-3392, yano@cc.nara-wu.ac.jp

²Department of Chemistry, Graduate School of Science, Osaka City University, 3-3-138 Sugimoto, Sumiyoshi-ku, Osaka 558-8585, Japan

³Fluid Science Research Center, National Aerospace Laboratory, 7-4-11 Jindaiji-higashi, Chofu-shi, Tokyo 182-8522, Japan

As an ideal model for PSP coating, we have developed an optical oxygen sensor consisting of porphyrin monolayer. A porphyrin having long alkyl chains, 5,10,15,20-tetrakis[4-(11-carboxylundecane-1-oxy)phenyl]porphyrin **6** was synthesized by Lindsey's method and adsorbed on an ITO (indium-tin oxide) electrode by dipping in 1 mM KOH-EtOH solution of **6** for 2 days. In the cyclic voltammograms of the ITO electrode modified with **6**, the peak current of the first oxidation wave was in proportion to the sweep rate, indicating the formation of porphyrin **6** monolayer on the ITO electrode. The surface coverage of **6** on the ITO electrode was estimated as $2.3\text{--}2.5 \times 10^{-10}$ mol·cm⁻² on the basis of cyclic voltammograms and UV-vis spectra. The UV-vis spectrum of the monolayer showed that the Soret band shifted to longer wavelength and was getting broad. These features suggest the porphyrin moieties of **6** is packed to form *J*-type structure. The fluorescence intensity of the monolayer decreased with an increase of the oxygen pressure according to Stern-Volmer equation.

Key words: pressure-sensitive paint, porphyrin monolayer, cyclic voltammetry, oxygen sensor, Stern-Volmer equation

1. INTRODUCTION

Since a decade, the phosphorescence quenching phenomena of the organic dyes is widely applied for the device and sensors to measure a O₂ gas concentration.^{1,3} By using the same principle, pressure-sensitive paints (PSP) is specially designated sensors for surface pressure measurement of on the aircraft and rockets model in wind tunnel experiments.^{4,5} For the surface pressure measurement using PSP, a fluorescence or phosphorescence dye dissolved or dispersed in the polymer matrix was coated on an object (Fig. 1).

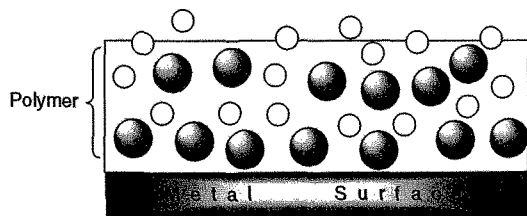


Fig. 1 PSP painting style. White circles and gray circles indicate oxygen molecules and PSP dyes, respectively.

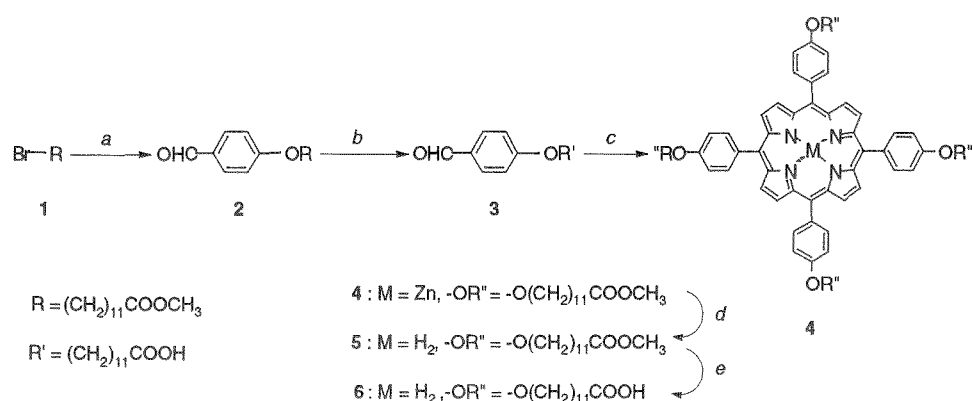
When the polymer film on a substrate is exposed to air, the solubility of O₂ in the film will be proportional to the partial pressure of O₂ (P_{O_2}). If the film is thin enough and the air pressure is different at different points on the surface, the local concentration of O₂ gas depends on the local air pressure at that point on the surface. The quenching of luminescence by oxygen is well known and could be described by Stern-Volmer equation.⁶ Thus, a dye dissolved in the film will sense that local concentration of O₂ gas when excited by light. A digital video image of the illuminated object subjected to a wind flow will have brighter luminescence in regions of lower surface air pressure.

However, this technique has many difficulties and limitations associated with the choice of a dye and the choice of a polymer. The essential demands for the organic dyes are long lifetimes; convenient excitation and emission wavelengths; large Stokes shift; reasonable luminescence quantum yields; and relatively good thermal, chemical, and photochemical stabilities.⁷ On the other hand, the key parameters of the system in the presence of O₂ gas are the diffusion coefficient and solubility of O₂ in the polymer matrix.⁸

In order to get rid of the influence of an oxygen diffusion process in a polymer matrix, we have developed an optical oxygen sensor consisting of monolayer of porphyrin having long alkyl chains. In this paper, we report the synthesis of porphyrin derivative, preparation and characterization of porphyrin monolayer on the ITO electrode, and O₂ sensing ability

[†] Present address: Aerodynamics Research Group, Institute of Space Technology and Aeronautics, Japan Aerospace Exploration Agency, 7-44-1, Jindaiji Higashi Chofu City, Tokyo 182-8522, Japan.

[‡] Present address: Department of Aeronautics and Space Engineering, Tohoku University, 01 Aoba, Aoba-ku, Sendai 980-8579, Japan.



Scheme 1 Condition: *a* *p*-hydroxybenzaldehyde, 5 % NaOH(aq), tetra-*n*-butylammonium bromide, CH_2Cl_2 ; *b* HCl(g), CH_3OH , benzene; *c* (i) $\text{BF}_3\cdot\text{OEt}_2$, $\text{Zn}(\text{OAc})_2\cdot 2\text{H}_2\text{O}$, CHCl_3 (ii) *p*-chloranil; *d* 6N HCl; *e* (i) KOH / CH_3OH -THF (ii) 1N HCl, H_2O .

of this porphyrin monolayer.

2. EXPERIMENTAL SECTION

2.1 Synthesis.

Free base porphyrin **6** was prepared according to Scheme 1. Aldehyde **3** was obtained in 19.1% yield from **1**. Condensation of **3** with pyrrole by Lindsey's method afforded zinc porphyrin **4**. To remove Zn(II) from porphyrin center, zinc porphyrin **4** was washed with 6M HCl(aq). And then, treatment of porphyrin **5** with KOH/MeOH-THF solution was obtained porphyrin **6**. All compounds were characterized with NMR, UV-vis, mass, and elemental analysis. The experimental details and spectroscopic data of compounds will be published elsewhere.

2.2 Preparation of Porphyrin Monolayer.

An ITO (indium-tin oxide) electrode was purchased from Sanyoshinku Co., Ltd. ITO electrodes were cut into slides (ca. 0.5 cm x 3.0 cm), rinsed with acetone and dried just before being soaked in a porphyrin solution. Porphyrin solution was prepared as follows: first, **6** was mixed in EtOH (porphyrin concentration was 1 mM), and then 1 wt% KOH/EtOH solution was added until **6** was dissolved. An ITO electrode was immersed in 1 mM of **6** in KOH/EtOH solution for 2 days to form a monolayer at 25 °C. The ITO plate was washed with EtOH and dried under the air. The monolayer of **6** on the ITO surface was characterized by cyclic voltammetry and UV-vis spectroscopy.

2.3 Spectroscopic Measurements.

Electrochemical Measurement: Electrochemical properties of **6** in solution and of monolayer deposited on an ITO electrode were investigated with a cyclic voltammetry (BAS 100B/W (CV50W) Version 2.0). Electrochemical measurement was performed under nitrogen atmosphere using a conventional three-electrode cell equipped with an ITO electrode (working electrode), Pt wire (counter electrode), and Ag/AgPF₆ (reference electrode).

Absorption, Excitation, and Emission Spectroscopy: Absorption spectra of **6** dissolved in THF (porphyrin

concentration was 2.4×10^{-7} mol·dm⁻³) and monolayer on an ITO electrode were recorded using a JASCO V-570 UV/VIS/NIR Spectrophotometer. Steady state phosphorescence spectra and excitation spectra of the monolayer were measured using a Shimadzu RF-5300PC spectrofluorophotometer with a 150 W Xenon lamp as a visible excitation light source. Excitation and emission band passes were 3 nm.

2.4 Oxygen Sensing System.

An ITO plate modified with **6** (250 mm x 242 mm) was set in a chamber. The coating was excited by a Xenon light (300 W) with a band pass filter (380–530 nm) and different air pressure gases (in the range of 5–100 kPa) produced by controlling of a vacuum pump were entered in the chamber. The emission from the coating was detected by a digital camera with a cooled CCD on which an infrared rejection filter (300–800 nm) and a red long pass filter (650±20 nm) were placed. All experiments were carried out at room temperature. Oxygen sensing properties of a porphyrin **6** monolayer on the ITO electrode was characterized by the Stern-Volmer quenching constant, K_{SV} , obtained from modified form of Stern-Volmer equation:

$$\frac{I_{ref}}{I} = \frac{1}{1 + KP_{ref}} + KP_{ref} \cdot \frac{1}{1 + KP_{ref}} \cdot \frac{P}{P_{ref}} \quad (1)$$

$$K = 0.21 \cdot K_{SV} \quad (2)$$

where I_{ref} , I , P , and K_{SV} are luminescence intensities in the pressure of P_{ref} in the pressure of P , pressure in a chamber, and Stern-Volmer constant, respectively. In this measurement, P_{ref} was 100 kPa.

3. RESULT AND DISCUSSION

3.1 Electrochemistry.

The redox properties of **6** deposited onto an ITO electrode were measured by cyclic voltammetry. Fig. 2 shows the cyclic voltammograms of **6** on the ITO electrode at various potential scan rates. In a main oxidation wave at $E_p = 728$ mV vs Ag/AgPF₆, the peak current increase linearly with the potential scan rates, as

expected from the equation that is derived for adsorbed redox species on a thin-layer cell, $i_c = n^2 C_r F^2 v / (4RT)$, where i_c , n , C_r , F , and v are the peak current, the number of electrons, the surface concentration, the Faraday constant, and the potential scan rate, respectively (Fig. 3).⁷ Integration of the area under the anodic surface waves due to the first oxidation of the porphyrin provides an estimate of the surface coverage (Γ) as $2.3 \times 10^{-10} \text{ mol}\cdot\text{cm}^{-2}$ when the redox number of electrons (n) is one. Furthermore, the surface coverages of 3 samples were ranged from $2.3\text{--}2.5 \times 10^{-10} \text{ mol}\cdot\text{cm}^{-2}$, this means that the modification of the ITO electrode was successfully performed with fairly good reproducibility.

3.2 Spectroscopic Studies.

Absorption Spectra: Fig. 4 shows the absorption spectra of **6** dissolved in THF and **6** on an ITO electrode in air using transmission mode. The Soret band on the ITO electrode is broadened and red-shifted by 15 nm relative to the corresponding spectra in THF. Similar red shift and broadening of the Soret band were reported on porphyrin SAMs on gold electrodes, LB monolayers of porphyrins on glass or semiconductors, and porphyrin aggregates in solutions.¹⁰⁻¹² It is well known that a stacked face-to-face porphyrin π -aggregation (sandwich-type, *H*-aggregate) leads to a blue shift, while side-by-side porphyrin π -aggregation (*J*-aggregate) leads to a red shift. Thus, the spectral change is probably due to the

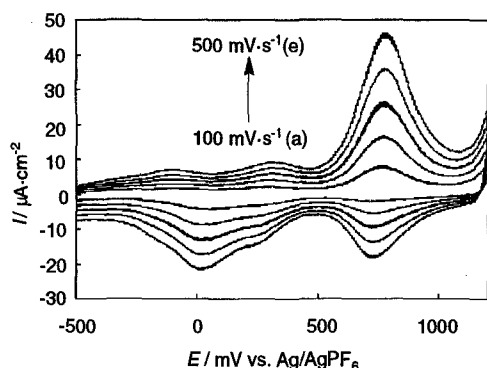


Fig. 2 Cyclic voltammograms of an ITO electrode modified with compound **6** in CH_3CN containing $0.1 \text{ M } [\text{CH}_3(\text{CH}_2)_3]_4\text{N}^+\text{PF}_6^-$ as an electrolyte at various scan rates of $100 \text{ mV}\cdot\text{s}^{-1}$ (a), $200 \text{ mV}\cdot\text{s}^{-1}$ (b), $300 \text{ mV}\cdot\text{s}^{-1}$ (c), $400 \text{ mV}\cdot\text{s}^{-1}$ (d), and $500 \text{ mV}\cdot\text{s}^{-1}$ (e).

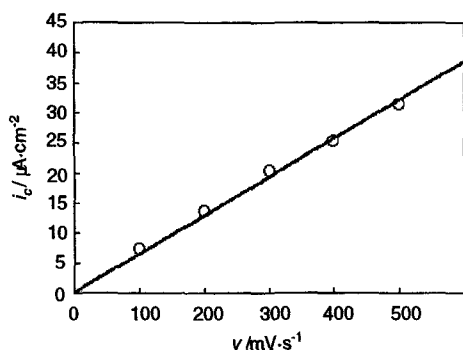


Fig. 3 Dependence of peak current (i_c) on the potential scan rate (v) for monolayer on an ITO electrode. Peak current was calculated from cyclic voltammograms.

J-aggregate-like partially stacked structures of the porphyrins in the monolayer microenvironment. The surface coverage of a monolayer was also evaluated from absorption spectrum. On the basis of the Lambert-Beer's law modified for two-dimensional concentration ($\Gamma = 10^{-3} \cdot D/\epsilon$; Γ , surface coverage; ϵ , molar absorption coefficient ($\text{L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$)), the surface coverage (Γ) of **6** deposited on the ITO electrode is calculated as $2.19 \times 10^{-10} \text{ mol}\cdot\text{cm}^{-2}$.⁹ This value is almost same that calculated from cyclic voltammetry.

Excitation, and Emission Spectra: Compound **6** dissolved in THF (porphyrin concentration was $2.1 \times 10^{-6} \text{ mol}\cdot\text{dm}^{-3}$) emitted at 658 and 722 nm when excited at the wavelength attributed to the Soret band (422 nm), as shown in Fig. 5.

3.3 Structure of Porphyrin monolayer.

Fig. 6 shows possible models of **6** immobilized on an ITO electrode. In model A, macrocyclic plane of **6** is almost perpendicular to the ITO surface, and the projection area of the molecule **6** is calculated as 58 \AA^2 . On the other hand, the plane of **6** should be parallel to cover the area of 174 \AA^2 per a molecule. These occupied areas of molecules lead to the maximum surface coverage of **6** as $2.9 \times 10^{-10} \text{ mol}\cdot\text{cm}^{-2}$ for model A and of $9.5 \times 10^{-11} \text{ mol}\cdot\text{cm}^{-2}$ for model B. Surface coverage of the perpendicular model as $2.9 \times 10^{-10} \text{ mol}\cdot\text{cm}^{-2}$ is almost same with the surface coverage as $2.3\text{--}2.5 \times 10^{-10} \text{ mol}\cdot\text{cm}^{-2}$ calculated from cyclic voltammetry. Hence, major binding structure of **6**

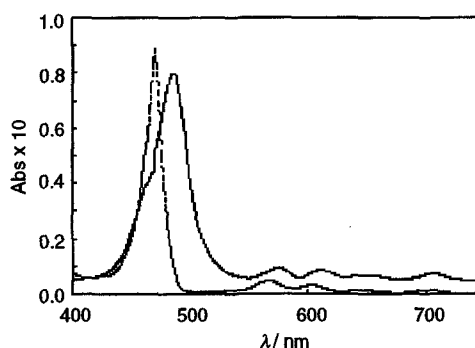


Fig. 4 Absorption spectra of **6** in THF (broken line) and an ITO electrode modified with **6** (solid line).

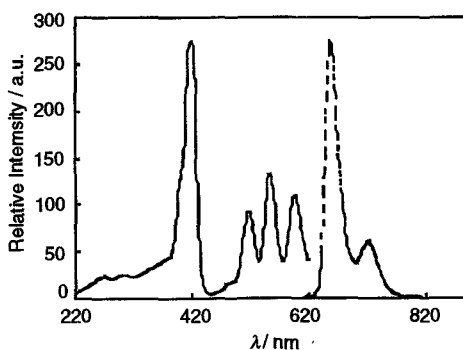


Fig. 5 Excitation (solid line) and emission spectra (broken line) of **6** in THF. $\lambda_{\text{em}} = 658 \text{ nm}$ and $\lambda_{\text{exc}} = 422 \text{ nm}$ were used for excitation and emission spectra, respectively.

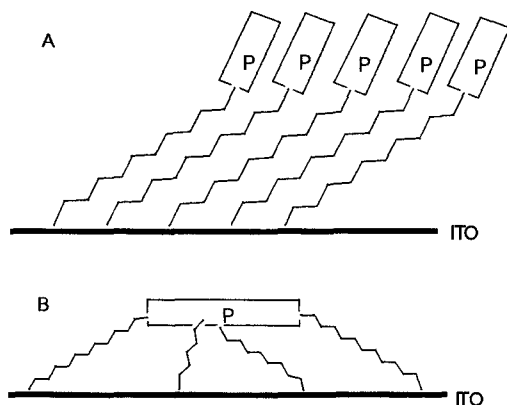


Fig. 6 Possible structures of monolayer of **6** immobilized on an ITO electrode in which one or two carboxylic groups bind on the surface (model A, loose binding model) or four carboxylic groups bind on the surface (model B, tight binding model) (P; porphyrin core).

should be shown in model A.

3.4 Stern-Volmer relationship for $H_2TPP-(OC_{11}H_{22}COOH)_4$ on ITO electrode.

Fig. 7 is the best-fit curve for the porphyrin monolayer of **6** immobilized on an ITO electrode by the least squares method. The correlation factor of the plot, r^2 , estimated to be 0.992 indicates that the monolayer is calibrated by the modified Stern-Volmer equation [eqn. (1)]. Two K_{sv} values were calculated from the plot, I_{ref}/I versus P/P_{ref} ; one is obtained from the slope as $4.96 \times 10^{-4} \text{ Torr}^{-1}$ and the other is obtained from the intercept as $4.76 \times 10^{-4} \text{ Torr}^{-1}$, due to two oxygen accessible sites (an oxygen accessible and an oxygen difficult accessible site) in the monolayer. These results indicate that a porphyrin monolayer immobilized on the ITO electrode is useful for optical oxygen sensor at various air pressures in the range of 5–100 kPa.

CONCLUSION

A porphyrin having long alkyl chains **6** was synthesized and immobilized on an ITO electrode with dipping method. From cyclic voltammetry, it means that the modification of the ITO electrode was successfully performed with fairly good reproducibility. Furthermore, an UV-vis spectrum of the monolayer of **6** on the ITO electrode was indicated that the aggregation structure was performed *J*-aggregate-like partially stacked structures. The major binding structure of **6** on the ITO electrode was perpendicular model in which one or two carboxylic groups bind on the surface from occupied areas of molecules. The monolayer of **6** immobilized on an ITO electrode was subjected to the O_2 sensing ability test. The plot of I_{ref}/I versus P/P_{ref} exhibits considerable linearity at various air pressures in the range of 5–100 kPa. This is a first application of monolayer for PSP technique, and it can afford simple model of PSP to get rid of the influence of an O_2 diffusion process in a polymer matrix. Amao et al. reported that a faster response time was obtained

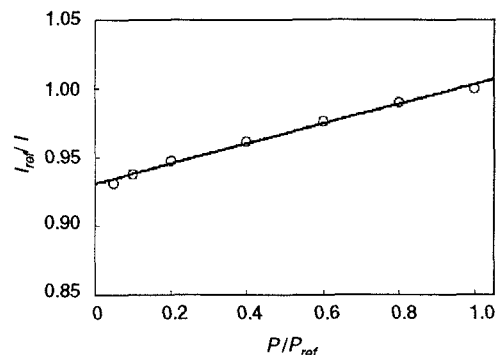


Fig. 7 Stern-Volmer plot for **6** immobilized on an ITO electrode ($P_{ref} = 100 \text{ kPa}$).

compared with PtOEP immobilized in polystyrene films for tetrakis(4-carboxyphenyl)porphyrin physically adsorbed on alumina plates (chemisorption film onto alumina plates).¹³ Therefore, it is expected that porphyrin monolayer on the ITO electrode has fairly good sensing ability for oxygen as chemisorption film onto alumina plates. Work is underway to obtain response and recovery times of the porphyrin monolayer on the ITO electrode.

ACKNOWLEDGEMENT

This work was partially supported by 'Molecular Sensors for Aero-Thermodynamic Research (MOSAIC)'.

REFERENCES

- [1] C. N. Jayarajah, A. Yekta, I. Manners, and M. A. Winnik, *Macromolecules*, **33**, 5693-5701 (2000).
- [2] E. D. Lee, T. C. Werner, and W. R. Seitz, *Anal. Chem.*, **59**, 279-283 (1987).
- [3] A. K. McEvoy, C. M. McDonagh, and B. D. MacCraith, *Analyst*, **121**, 785-788 (1996).
- [4] Y. Amao, K. Miyakawa, and I. Okura, *J. Mater. Chem.*, **10**, 305-308 (2000).
- [5] Y. Amao and I. Okura, *Analyst*, **125**, 871-875 (2000).
- [6] M. Gouterman, *J. Chem. Educ.*, **74**, 697-702 (1997).
- [7] X. Lu and M. A. Winnik, *Chem. Mater.*, **13**, 3449-3463 (2001).
- [8] X. Lu, I. Manners, and M. A. Winnik, *Macromolecules*, **34**, 1917-1927 (2001).
- [9] T. Taniguchi, Y. Fukasawa, and T. Miyashita, *J. Phys. Chem. B*, **104**, 1920-1924 (1999).
- [10] H. Imahori, H. Norieda, Y. Nishimura, I. Yamazaki, K. Higuchi, N. Kato, T. Motohiro, H. Yamada, K. Tamaki, M. Arimura, and Y. Sakata, *J. Phys. Chem. B*, **104**, 1253-1260 (2000).
- [11] H. Imahori, H. Yamada, Y. Nishimura, I. Yamazaki, and Y. Sakata, *J. Phys. Chem. B*, **104**, 2099-2108 (2000).
- [12] R. F. Khairutdinov and N. Serpone, *J. Phys. Chem. B*, **103**, 761-769 (1999).
- [13] Y. Amao and I. Okura, *Analyst*, **125**, 1601-1604 (2000).