

Electro- and Photochemical Behavior of Porphyrin  
Monolayers for Optical Oxygen Sensor

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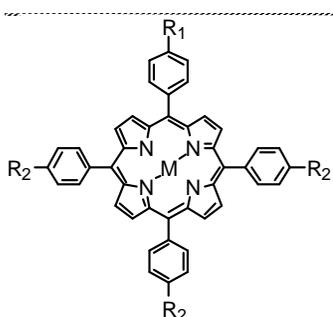
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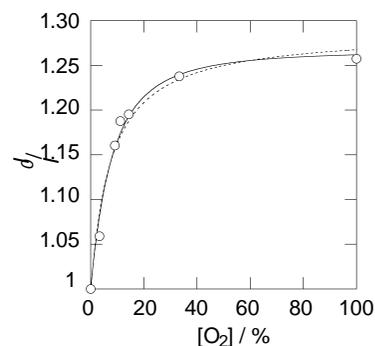
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Since a decade, the phosphorescence quenching phenomena of the organic dyes is widely applied for the device and sensors to measure oxygen concentration. On the same principle, pressure-sensitive paint (PSP) has been developed in order to measure pressure on the surface of aircraft and rockets in wind tunnel experiments. A typical optical oxygen sensor as PSP consists of an oxygen quenchable luminescent molecule, such as polycyclic aromatic hydrocarbons, transition metal complexes, and porphyrin derivatives embedded in an oxygen permeable polymer film. In experiments, a PSP coated model is illuminated by excitation light, and a CCD camera acquires the luminescent intensity with a band-pass filter, which is suitable for PSP emission. However, this technique has many difficulties and limitations associated with the choice of a dye and a polymer. The diffusion and solubility of oxygen in the polymer film cause variety phenomenon. From this point of view, it is indicated that most ideal coating for sensor is a monolayer consisted of pigment which bind on the surface directly. As a model for PSP coating without polymer matrix, we have developed an optical oxygen sensor consisting of porphyrin monolayers. Porphyrins having long alkyl chains, 5,10,15,20-tetrakis[4-(11-carboxylundecane-1-oxy)phenyl]porphyrin **1**, 5,10,15,20-tetrakis[4-(11-carboxylundecane-1-oxy)phenyl]porphyrinato platinum(II) **2**, 5-[4-(11-carboxylundecane-1-oxy)phenyl]porphyrinato platinum(II) **3**, and 5-[4-



**Figure 1.** Structures of tetraphenyl porphyrin derivatives. **1** ( $H_2TPP-(OC_{11}H_{22}COOH)_4$ ):  $M = H_2$ ,  $R_1 = R_2 = OC_{11}H_{22}COOH$ ; **2** ( $PtTPP-(OC_{11}H_{22}COOH)_4$ ):  $M = Pt$ ,  $R_1 = R_2 = OC_{11}H_{22}COOH$ ; **3** ( $H_2TPP-(OC_{11}H_{22}COOH)_1$ ):  $M = H_2$ ,  $R_1 = OC_{11}H_{22}COOH$ ,  $R_2 = H$ ; **4** ( $PtTPP-(OC_{11}H_{22}COOH)_1$ ):  $M = Pt$ ,  $R_1 =$

(11-carboxylundecane-1-oxy)phenyl]porphyrinato platinum(II) **4** (Figure 1) were synthesized and adsorbed on an ITO (indium-tin oxide) electrode by dipping method. The monolayers of porphyrin on the ITO electrode were characterized by cyclic voltammetry and UV-vis spectroscopy. In cyclic voltammograms, it is suggested that **1** and **2** are strongly adsorbed on the ITO electrode by four carboxyl groups compared with **3** and **4**. This observation indicates that the modification of the ITO surface depends on the number of carboxyl groups. Furthermore, the surface coverage of free base porphyrin, **1** and **3**, are larger than that of porphyrinato platinum(II), **2** and **4**. From this result, it suggests that the modification of the ITO surface is influenced by the presence of platinum(II). From UV-vis spectrum of **1** on an ITO electrode, the Soret band is broadened and red-shifted by 15 nm relative to that in THF solution. Similar broadening and red-shifted are also observed for **2** immobilized on an ITO electrode. Such behavior due to the aggregation structures of monolayer **1** and **2** indicate J-aggregate-like partially stacked structures. The monolayer of **1** immobilized on the ITO electrode was applied for an optical oxygen sensor using the luminescence quenching of porphyrin with oxygen gas. The oxygen sensing ability of the porphyrin **6** monolayer is  $I_0 / I_{100}$  as 1.25, where  $I_0$  and  $I_{100}$  are luminescence intensity in the absence and in the presence of oxygen. While the resulting plot shows considerable linearity in the lower oxygen concentration, nonlinearity was found in the higher oxygen concentration (Figure 2). The curve fitting using Stern-Volmer equation gave the parameters  $K_{SV1} = 0.170\%^{-1}$ ,  $K_{SV2} = 0\%^{-1}$  where  $K_{SV1}$  and  $K_{SV2}$  are Stern-Volmer constant (broken line, Figure 2). This curve reproduces the nonlinearity of the plot well. However, there is still significant deviation from the observation in the higher oxygen concentration region and the luminescence intensity from the monolayer of **1** is lower than that expected by curve fitting at higher oxygen concentration. In order to explain this phenomenon, we take into account the adsorbed oxygen molecules on the monolayer. The result of the curve fitting to the modified Stern-Volmer equation was shown in Figure 2 as a solid line. The parameter  $K_{SV2} = 0\%^{-1}$ , and  $0.073\%^{-1}$  and  $0.078\%^{-1}$  for  $K_{SV1}$  and  $K_{eq}$  are obtained, where  $K_{eq}$  is the equilibrium constant. Here, two parameters  $K_{SV1}$  and  $K_{eq}$  are identical mathematically, so it is impossible to assign each of them. The response times of the coating are 10 s on going from argon to oxygen gases and 23 s on going from oxygen to argon gases. This observation suggests that the faster response time was due to abridge the time for oxygen diffusion process into polymer matrix.



**Figure 2** Stern-Volmer plot for **1** immobilized on an ITO electrode. (Broken line means  $K_{SV1} = 0.170\%^{-1}$ ,  $K_{SV2} = 0\%^{-1}$ , and  $f_I = 0.224$ . Solid line means  $K_{SV1}$  and  $K_{SV1} = 0.073\%^{-1}$  and  $0.078\%^{-1}$ ,  $K_{SV2} = 0\%^{-1}$ , and  $f_I = 0.210$ ).