

Redox and photochemical behaviour of a porphyrin monolayer on an indium-tin oxide electrode

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Abstract

In order to investigate photoluminescence behaviour of an ordered molecular porphyrin monolayer and its quenching properties by oxygen gas, a porphyrin with long alkyl chains, 5,10,15,20-tetrakis[4-(11-carboxylundecane-1-oxy)phenyl]porphyrin (**4**), was synthesized and adsorbed onto an indium-tin oxide (ITO) substrate by a chemical dipping method. Cyclic voltammetry was used to analyze the ITO electrode coated with **4**. The peak current of the first oxidation was proportional to the sweep rate, and the surface coverage was estimated to be $2.3\text{--}2.5 \times 10^{-10} \text{ mol cm}^{-2}$. The UV–vis spectrum of the monolayer showed a broadened Soret band, which shifted to longer wavelength. These features suggest that the porphyrin moieties of **4** are packed to form a *J*-type structure. The oxygen quenching ratio of the porphyrin **4** monolayer on the ITO electrode, I_0/I_{100} , was estimated to be 1.25, where I_0 and I_{100} are, respectively, luminescence intensity values in 100% argon and 100% oxygen. On repeated step cycling between 100% argon and 100% oxygen atmospheres, the response times of luminescence quenching were 10 s (argon to oxygen) and 23 s (oxygen to argon). These findings suggest that a monolayer of sensing dye is applicable for oxygen sensing system without deterioration of size-accuracy of models.

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1. Introduction

Self-assembled monolayers (SAMs) have emerged as an alternative and useful strategy for assembling molecular components on surface. SAMs have been used to develop novel surface-patterning methodologies, to fabricate new types of chemically sensitive devices, to study interfacial electron transfer processes and to prepare a variety of unusual and potentially useful electronic, photonic and redox-active mate-

rials [1,2]. Porphyrins on gold surfaces using S–Au linkages have been widely studied for application to molecular devices. One reason for this interest is the porphyrin's large molar absorption coefficient in the visible light region. Another reason is efficient electron transfer from the excited state of porphyrin to ground state of various acceptors and donors such as ferrocene and fullerene derivatives [3–7]. Furthermore, the oxygen-induced luminescence quenching properties have been examined for thin films consisting of porphyrins, such as polymer films, Langmuir–Blodgett (LB) films and chemisorption films [8–12]. However, the photoluminescence behaviour and its quenching properties by oxygen gas remain to be fully understood for ordered molecular

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porphyrin SAMs. In this study, we focused on the photoluminescence behaviour of a porphyrin SAMs. While the most established SAM system is alkanethiols on gold surfaces [13,14], a strong quenching of the porphyrin excited singlet state by the gold surface enhances non-radiative losses. Indium-tin oxide (ITO) is a promising candidate as a substrate for photoluminescence study because the ITO electrode has high optical transmission and suppresses the quenching of the porphyrin excited states [13]. Therefore, we investigated photoluminescence behaviour of porphyrin SAM on an ITO electrode and its quenching properties by oxygen gas.

Spontaneous adsorption of long-chain *n*-alkanoic acid ($C_nH_{2n+1}COOH$) on AgO, Al₂O₃ and gold surfaces, has been studied in the past few years [15–18]. However, we are not aware of any studies on stable porphyrin SAMs formed from *n*-alkanoic acids on an ITO surface. We report, herein the synthesis of a functionalized porphyrin derivative, namely 5,10,15,20-tetrakis[4-(11-carboxylundecane-1-oxy)phenyl]porphyrin, and the preparation of a self-assembled monolayer of the porphyrin on an ITO electrode. The monolayer on the electrode was characterized by cyclic voltammetry and UV–vis absorption spectroscopy. The photoluminescence behaviour of the porphyrin monolayer and its quenching property by oxygen gas are discussed on the basis of luminescence measurements in the presence of argon and oxygen gases.

2. Experimental

2.1. Materials

All solvents and chemicals were of reagent grade quality obtained from Wako Pure Chemical Industries Ltd., Osaka, Japan, and were used without further purification unless otherwise noted. The solvents for cyclic voltammetry were passed through a short alumina column just before use. Tetrabutylammonium hexafluorophosphate (Bu₄NPF₆) was obtained from Tokyo Kasei Kogyo Co. Ltd., Tokyo, Japan, and recrystallized from EtOH just before use.

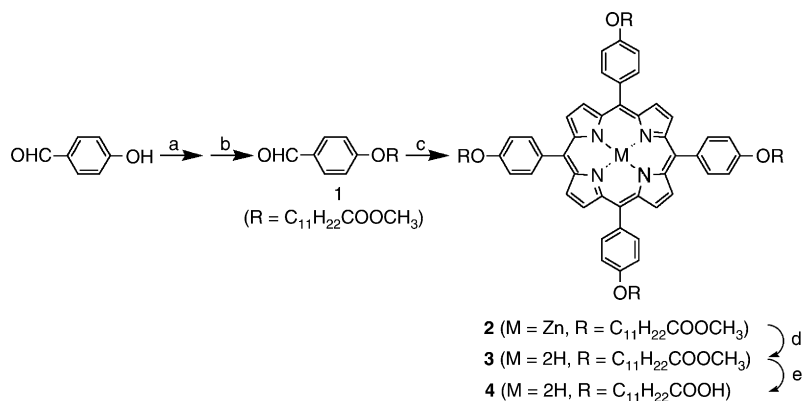
2.2. Synthesis

2.2.1. General

Porphyrin derivative **4** was prepared according to Scheme 1. ¹H NMR spectra were recorded on a Varian Gemini 2000 (300 MHz) instrument. Fast atom bombardment mass spectra (FAB-MS) were measured on a JMS-700T spectrometer (Osaka City University) using 3-nitrobenzyl alcohol as a matrix. Elemental analysis was carried out using a Perkin-Elmer 240C Elemental Analyzer (Osaka City University).

2.2.2. Methyl 12-(4-formylphenoxy)dodecanate (**1**)

A solution of *p*-hydroxybenzaldehyde (6.07 g, 49.7 mmol) in 5% NaOH (aq) (70 mL) was vigorously stirred at room temperature with CH₂Cl₂ (50 mL) and tetrabutylammonium bromide (3.07 g, 9.52 mmol). To the mixture was added a solution of 12-bromododecanoic acid (2.34 g, 8.38 mmol) in CH₂Cl₂ (20 mL) and the whole was stirred at room temperature for 60 h. The organic layer was washed with 5% NaOH (aq) and water, and then dried over Na₂SO₄, and the solvent was removed under reduced pressure. The residue was reprecipitated from hot MeOH to afford crude 12-(4-formylphenoxy)dodecanoic acid as a white powder (1.80 g). The crude product (5.82 g) was taken up in a mixture of MeOH (500 mL) and benzene (100 mL). Hydrogen chloride gas was introduced into the mixture for 2 h, and then the mixture was refluxed at 90–95 °C for 3 days with azeotropic distillation of water. After cooling, the mixture was poured into water and extracted with CHCl₃. The organic layer was washed with saturated NaHCO₃ (aq) and water, dried over Na₂SO₄, and evaporated. The residue was purified by silica gel column chromatography with ethyl acetate/hexane (5/12, v/v) as an eluent (*R*_f = 0.58), followed by precipitation from hot hexane to afford methyl 12-(4-formylphenoxy)dodecanate (**1**) as a white solid (1.39 g, 4.37 mmol, 19.1%). ¹H NMR (300 MHz, CDCl₃): δ 9.88 (s, 1H, –CHO), 7.81 (d, ³*J* = 8.85 Hz, 2H, ArH), 6.98 (d, ³*J* = 8.54 Hz, 2H, ArH), 4.03 (t, ³*J* = 6.68 Hz, 2H, –OCH₂–),



Scheme 1. Reagents and conditions: (a) 12-bromododecanoic acid, Bu₄NBr, 5 wt% NaOH (aq), CH₂Cl₂, r.t., (b) MeOH, HCl (gas), benzene, reflux, (c) pyrrole, Zn(OAc)₂·2H₂O, BF₃·OEt₂, CHCl₃, *p*-chloranil, (d) 6 M HCl and (e) KOH, MeOH, THF.

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