

**Studies on Langmuir-Blodgett (LB) films of photosensitizer-bounded
cellulose derivatives for photocurrent generation system**

-Abstract version-

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Introduction

Cellulose is the most abundant organic polymer existing as a major constituent of the plant cell wall, and is considered an important renewable resource.¹ As a linear homopolymer consisting of regio- and stereo-specific β -1,4-glycosidic linked D-glucose units, cellulose is highly uniform polyacetal containing three reactive hydroxyl groups per anhydroglucose unit (AGU). The chemical modification of cellulose has been one of important way for commercial use of cellulose for more than 150 years.^{2,3} Recently, much attention has been still paid to synthesis advanced materials from cellulose because of its stiffness, hydrophilicity, biocomparatively, chirality and multifunctionality. For example, the cellulose derivatives have been reported for applications in shape memory-recovery,⁴ photoactive materials,⁵ single-molecule analysis,⁶ and drug delivery system.⁷ It is also accepted today that regioselectively substituted cellulose derivatives are potential materials for the well-defined, functional molecular assembly such as nonlinear-optical device,⁸ material for memory device,⁹ and organic light-emitting diode.¹⁰ Photosensitizer-bound cellulose derivatives, in which photosensitizers were introduced to hydroxyl groups at the *O*-6 position for photocurrent generation and acyl groups were attached to hydroxyl groups at *O*-2 and *O*-3 positions for Langmuir-Blodgett (LB) films formability, are one of useful materials with potential applications in biomaterials-based solar cells.¹¹⁻¹⁵ Indeed, LB films constructed from 6-*O*-porphyrinyl-2,3-di-*O*-stearoyl cellulose and 6-*O*-porphyrinyl-2,3-di-*O*-myristoyl cellulose, have been reported to exhibit higher photocurrent generation performances (photon-to-electron conversion performances) around 430 nm than those of LB films from low molecular weight porphyrin molecules.¹¹⁻¹⁴ The high performances were thought to be due to high packing of the porphyrin moieties along the cellulose backbone without any aggregation, because it is well-known that the self-aggregation of porphyrin causes the remarkable decline of photocurrent generation performance.^{16,17} In other words, the cellulose backbone of the cellulose derivatives plays an important role in inhibiting the self-aggregation of the porphyrin moieties as scaffolds in the LB films. The effective utilization of solar light by the LB films was, however, insufficient, because the main absorption band of porphyrin (Soret band) ranges from 400 to 450 nm.¹¹ The target wavelength range for an ideal solar cell is generally considered to span the range of 300–1200 nm.¹⁸ In particular, expanding the absorption profile from a visible light region to a near-infrared light region can be effective to improve photocurrent generation performance of solar cells.¹⁹

In the thesis, to expand the range of wavelength by the LB films of porphyrin-containing cellulose derivatives, the author describe the preparation of new photosensitizer-bound cellulose derivatives and fabrication and evaluation of photocurrent generation performances of their LB films.

Abstract

Chapter 1

LB film of (zinc (II) phthalocyanine)-containing cellulose derivative prepared by phthalocyanine-ring formation reaction

In this chapter the author describes the preparation of 2,3-di-*O*-myristyl-6-*O*-(zinc(II) phthalocyaninyl) cellulose (**1**) by using phthalocyanine-ring formation reaction, the preparation of LB monolayer films of compound **1** and preliminary evaluation of photocurrent generation performance of the LB films. 2,3-Di-*O*-myristyl-6-*O*-(zinc(II) phthalocyaninyl) cellulose with the $DS_{\text{phthalocyanine}}$ of 0.38 (**1**) was prepared from cellulose (**7**) using phthalocyanine-ring formation on the cellulose backbone by five reaction steps in 23.5 % overall yield. Compound **1** is the first regioselectively substituted phthalocyanine cellulose derivative. The LB monolayer film of compound **1** on mica, quartz and ITO substrates could be prepared by the vertical dipping method, although some aggregates were observed in AFM image of the monolayer. The LB monolayer film of compound **1** showed photocurrent performance in the range from 600nm to 700 nm, whereas the LB monolayer films of the porphyrin-containing celluloses generated photocurrent in the range of 400 nm to 600 nm,¹⁴ although its photocurrent generation performance of compound **1** is required to improve.

See: Saito, Y.; Toshiyuki, T.; Sakakibara, K.; Kamitakahara, H.; Fumiaki, N. Synthesis of (zinc(II) phthalocyanine)-containing cellulose derivative using phthalocyanine-ring formation reaction. *Cellulose*. **2012**, *19*, 2105-2114.

Chapter 2

Preparation of LB films of (zinc (II) phthalocyanine)-containing cellulose derivative prepared by esterification reaction

In chapter 1, the LB monolayer film of compound **1** with a degree of substitution of 0.38 for the phthalocyaninyl groups ($DS_{\text{phthalocyanine}}$) showed photocurrent generation performance at 680 nm, but

the performance was low. In this chapter, new (zinc (II) phthalocyanine)-containing cellulose derivatives **2** and **3** which were prepared by esterification reaction with *mono*-substituted phthalocyanine derivative were investigated. 2,3-Di-*O*-myristyl-6-*O*-[*p*-(9(10),16(17),23(24)-tri-*tert*-butyl-2-phthalocyaninyl)-benzoyl] cellulose (**2e**) with a $DS_{\text{phthalocyanine}}$ of 0.33 has been synthesized in a high yield via the esterification of ZnTBPC-COOH (**14**) with 2,3-di-*O*-myristyl cellulose (**8**), although the preparation ZnTBPC-COOH (**14**) was time consuming and laborious. A chloroform solution of compound **2e** was found to be more stable under illumination than that of ZnTBPC. The LB monolayer films of compound **2e** on a variety of different substrates were constructed using the vertical dipping method with an annealing time of 5 min. The results of the current study revealed that *J*-aggregated stacked structures of the phthalocyanine moieties of compound **2e** had formed along the cellulose backbone in the LB monolayer film. The LB monolayer film of **2e** on an ITO electrode showed photocurrent generation properties in the range of 600–700 nm, which corresponded to the Q bands of the phthalocyanine moieties as expected. The photocurrent generation performance of the LB monolayer film of compound **2e** was greater than that of compound **1**.

See: Saito, Y.; Kamitakahara, K.; Toshiyuki, T. Preparation of Langmuir-Blodgett monolayer films of (zinc(II) phthalocyanine)-containing cellulose derivative; The use of 2,3-di-*O*-myristyl cellulose as a scaffold. *Cellulose*. **2014**, *21*, 1885-1896.

Chapter 3

LB film of squaraine-appended cellulose derivative

The detail will be published later.

Chapter 4

LB film of 6-*O*-acetoacetyl (ruthenium (II) complex) cellulose derivative

The detail will be published later.

Chapter 5

LB films of (palladium (II) phthalocyanine)-containing cellulose derivative

The detail will be published later.

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