



Preparation of a squaraine-bounded cellulose derivative for photocurrent generation system



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ABSTRACT

A regio-selectively squaraine (SQ)-bounded cellulose derivative (**4**) with a degree of substitution of SQ (DS_{SQ}) of 0.55 was prepared from 6-*O*-(4-methoxytrityl) cellulose (**1**) by three reaction steps in 77% total yield. Lauryl SQ carboxylate (**8**) was also prepared as a reference sample. The photostability of SQ moieties of compound **4** in $CHCl_3$ was not improved when compared with SQ-COOH (**7**), but that of SQ moiety of compound **8** was improved unexpectedly. The Langmuir–Blodgett monolayer films **4B** and **8B** on an indium tin oxide (ITO) electrode were successfully prepared from compounds **4** and **8** by a vertical dipping method, respectively. The films **4B** and **8B** showed photocurrent generation performances in the region of 550–680 nm. The quantum yield at 650 nm of film **4B** was higher than that of film **8B**. These results showed that the cellulose backbone of compound **4** acts as an effective scaffold for the good photocurrent generation performances and that compound **4** was a promising complementary material of the porphyrin-bounded cellulose derivatives (for photocurrent generation at 400–420 nm) for effective utilization of solar light, as well as the phthalocyanine-bounded cellulose derivatives (for photocurrent generation at 650–720 nm).

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1. Introduction

Cellulose is a linear homopolymer consisting of regio- and stereo-specific β -1,4-glycosidic bonded D-glucopyranose. The use of the well-defined regular structure as a scaffold for good arrangement of functional groups is one of the points for the development of functional cellulose derivatives. From the point of view, our group has reported that Langmuir–Blodgett (LB) films constructed from regio-selectively porphyrin-bounded cellulose derivatives exhibited high photocurrent generation performances, suggesting that the cellulose derivatives are promising materials with potential applications in biomaterials-based solar cell.^{1,2} However, the effective utilization of solar light by the LB films was insufficient, because the photocurrent was generated only at the range of the porphyrin absorption band from 400 and 420 nm as shown in Fig. 1, although the target wavelength range for a solar cell should be considered from 300 to 1200 nm.³ Therefore, other regio-selectively photosensitizer-bounded cellulose derivatives which generate photocurrent at the unused region of solar light were strongly desired for the combination of the porphyrin-bounded cellulose derivatives. In the previous papers, regio-selectively phthalocyanine-

bounded cellulose derivatives which covered photocurrent generation at the range from 650 and 720 nm have been reported as a first complementary material of the porphyrin-bounded cellulose derivatives (Fig. 1), although their photocurrent generation performances were not high.^{4,5}

Squaraine (SQ) dyes are synthesized *via* condensation of electron-rich molecules and squaric acid. These dyes exhibit intense absorption in the red to near-infrared region^{6–8} and show promise as bio-imaging probes, photodynamic therapy agents, chemical sensors and photosensitizers for dye-sensitized solar cells,^{9,10} and bulk heterojunction solar cells.¹¹ As for the application for solar cells, LB films of *bis*[(4-alkylamino)phenyl] SQ dyes have been reported to exhibit good photon–electron conversion performances in the red to near-infrared region.^{12,13} Then, a regio-selectively SQ-bounded cellulose derivative which covers photocurrent generation at the range from 600 and 680 nm is attractive as a second complementary material of the porphyrin-bounded cellulose derivatives (Fig. 1). An SQ-bounded carbohydrate (D-glucopyranose) has been investigated for cellular recognition in photodynamic therapy applications.¹⁴ However, to the best of our knowledge, there are no reports of SQ-bounded cellulose derivatives.

In this work, compound **4** was selected as a target regio-selectively SQ-bounded cellulose derivative (Fig. 2), because a monocarboxyl SQ derivative with an indolium moiety (**7**, SQ-COOH) has been reported as a dye with the absorption band from 500 and 680 nm¹⁵ and the presence of myristoyl groups at *O*-2 and *O*-3 positions of the cellulose derivatives is favorable for the fabrication

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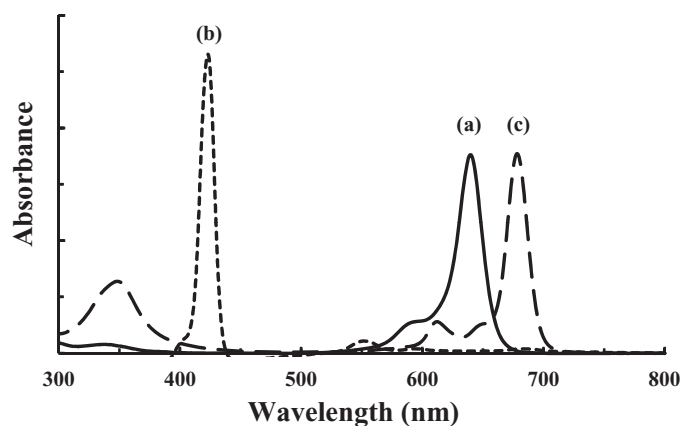


Fig. 1. Target absorption spectrum of a SQ-bounded cellulose derivative in this study: (a) and the spectra of the cellulose derivatives in the previous studies: (b) porphyrin-bounded cellulose derivative, (c) phthalocyanine-bounded cellulose derivative.

of LB monolayer films.¹⁶ And lauryl SQ carboxylate (**8**) was also selected as a model compound with low molecular weight to investigate the usefulness of the cellulose backbone of compound **4** to the photocurrent generation performances. Then, the preparation and evaluation for the photocurrent generation performances of LB films of compounds **4** and **8** were carried out.

2. Experimental

2.1. Generals

6-*O*-(4-Methoxytrityl) cellulose (**1**) with the degree of substitution of 4-methoxytrityl group (DS_{4MTT}) of 1.00 (determined by elementary analysis) and the degree of polymerization (DP_n) of 138 ($M_w/M_n = 3.29$) was prepared according to the conventional method.¹⁷ SQ-COOH (**7**) was prepared according to the method of Inoue et al.¹⁵ Silica Gel 60N (Kanto Chemical Co., Tokyo, Japan) was used for silica gel column chromatography, and TLC plate made by silica gel 60 F₂₅₄ (Merck, Darmstadt, Germany) with a thickness of 2 mm was used for preparative thin-layer chromatography. Ultrapure water was made by a Merck Millipore Simplilab-UV ultrapure water purifica-

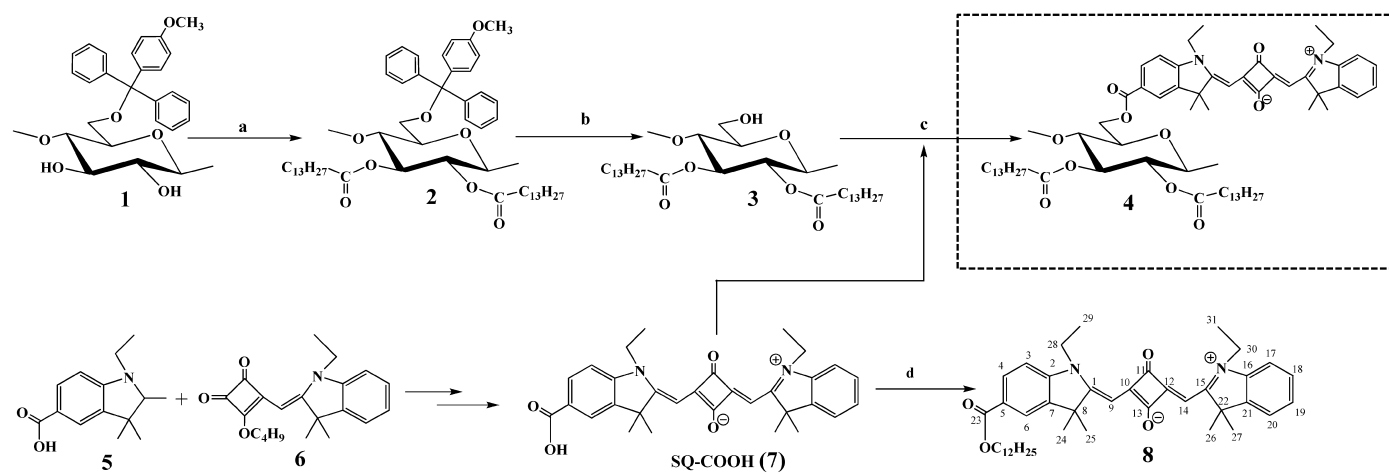
tion system (Merck Millipore, Billerica, MA, USA). All chemicals were purchased from commercial sources and used without further purification unless otherwise specified. Tetrahydrofuran (THF) was distilled from potassium before use.

Fourier transform infrared (FT-IR) spectra were recorded using KBr pellets with a Shimadzu IR Prestige-21 spectrophotometer (Shimadzu Co., Kyoto, Japan). ¹H and ¹³C nuclear magnetic resonance (NMR) spectra were recorded with a Varian FT-NMR (500 MHz) spectrometer (Agilent Technologies, Santa Clara, CA, USA) in CDCl₃ or DMSO-*d*₆. Chemical shifts (δ) were given in parts per million (ppm). Ultraviolet (UV)-visible spectra were recorded on a Jasco V-560 UV-visible spectrophotometer (Jasco, Tokyo, Japan). Gel permeation chromatography was performed on a Shimadzu LC-10 system equipped with a Shimadzu UV-visible detector (SPD-10Avp) and a Shimadzu RI detector (RID-10A) under the following conditions: columns: Shodex columns K-802, K-802.5 and K-805 connected in series (Showa Denko K. K., Tokyo, Japan); column temperature: 40 °C; eluent: CHCl₃; flow rate: 1.0 mL/min; standards: polystyrene standards (Shodex, Showa Denko K. K.). Matrix-assisted laser desorption/ionization time-of-flight mass spectra (MALDI-TOF MS) were recorded on a Bruker MALDI-TOF MS autoflex III (Bruker Daltonics, Bremen, Germany) using 2,5-dihydroxybenzoic acid as a matrix.

2.2. 2,3-Di-*O*-myristoyl cellulose (**3**)

To a suspension of compound **1** (0.500 g, 1.15 mmol) in toluene (7.0 mL), 4-(dimethylamino)pyridine (DMAP) (0.141 g, 11.5 mmol) and pyridine (0.94 mL, 11.6 mmol) were added at ambient temperature. Myristoyl chloride (3.2 mL, 11.8 mmol) in toluene (3.0 mL) was added dropwise to the suspension at 0 °C. After stirring at 70 °C for 24 h, the reaction mixture was poured into EtOH (200 mL). The resulting precipitate was collected by centrifugation (14,000 × *g*, 10 min), and dissolved in CHCl₃ (15 mL). The solution was added dropwise in EtOH (200 mL). The resulting precipitate was collected by centrifugation (14,000 × *g*, 10 min), washed with EtOH, and dried in vacuo at ambient temperature overnight to afford 6-*O*-(4-methoxytrityl)-2,3-di-*O*-myristoyl cellulose (**2**) (0.909 g, 92.4% yield).

To the solution of compound **2** (0.899 g, 1.05 mmol) in CHCl₃ (10 mL), *p*-toluenesulfonic acid monohydrate (*p*-TsOH) (0.401 g, 2.11 mmol) was added. The reaction solution was stirred at ambient



- a) C₁₃H₂₇COCl/ pyridine/ DMAP/ toluene, 70°C, 24h, b) *p*-TsOH/ CHCl₃, r.t., 5 h (x 2)
 c) SQ-COOH/ EDC/ DMAP/ THF, 50°C, 5 days, d) C₁₂H₂₇OH/ EDC/ DMAP/ THF, 50°C, 5 days,

Fig. 2. Synthetic route for SQ-bounded cellulose derivative (**4**) and lauryl SQ carboxylate (**8**).

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