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Title

Synthesis of (zinc(II) phthalocyanine)-containing cellulose derivative using phthalocyanine-ring formation reaction

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Abstract

2,3-Di-*O*-myristyl-6-*O*-(zinc(II) phthalocyaninyl) cellulose (**5**) was synthesized from cellulose (**1**) by five reaction steps via 6-*O*-(3',4'-dicyanophenyl)-2,3-di-*O*-myristyl cellulose (**4**). The key reaction was phthalocyanine-ring formation on a cellulose backbone, that is, the reaction of compound **4** with *o*-phthalodinitrile in the presence of hexamethyldisilazane (HMDS) and zinc acetate in DMF afforded to compound **5** in 35.4 % yield. Consequently, the degree of substitution with phthalocyanine moieties of compound **5** was 0.38. The LB monolayer film of compound **5** on an Indium Tin Oxide (ITO) electrode was found to show photocurrent generation performance at 680 nm.

Keywords

Introduction

Cellulose is the most abundant and important renewable biopolymer in nature. Recently, much attention

has been paid to new applications of cellulose derivatives as advanced materials such as shape

memory-recovery material (Aoki et al. 2007), material for memory device (Karakawa et al. 2007) and

photoactive materials (Wondraczek et al. 2011). One of the proposed applications is the photocurrent

generation system using porphyrin-containing cellulose derivatives (Sakakibara et al. 2007; Sakakibara

and Nakatsubo 2008, 2010). Sakakibara and Nakatsubo (2010) have reported the fabrication of

Langmuir-Blodgett (LB) films using 6-*O*-porphyrin-2,3-di-*O*-stearoyl cellulose or

6-*O*-porphyrin-2,3-di-*O*-myristoyl cellulose with high photocurrent generation performance. The

cellulose backbone played an important role in the inhibition the porphyrin self-aggregation as a scaffold

of porphyrin 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 nm to 450 nm

(Sakakibara et al. 2007). The target wavelength range for a solar cell should be considered from 400 nm

to 920 nm (Nazeeruddin et al. 2001). To expand the range of wavelength at which light is absorbed by the

LB films, a new photosensitive dye-bearing cellulose derivative is required for the combination of the

above porphyrin-containing cellulose derivatives in the films. One of the candidates for the derivative is a

phthalocyanine-containing cellulose derivative, because the main adsorption band of phthalocyanine (Q

bands) ranges from 600 nm to 700 nm (Mack et al. 1995). There are several reports concerning

phthalocyanine-containing celluloses. For example, cotton covalently linked copper phthalocyanine trisulphonate, which is named "blue cotton" (Hayatsu et al. 1992), cotton reacted with copper phthalocyanine (Okada et al. 1998) and cellulose nanofiber modified with cobalt tetraaminophthalocyanine (Chen et al. 2011) have been reported. However, they were surface modified celluloses with phthalocyanines, and could not be directly applied to the LB films for the photocurrent generation system. Then, 2,3-di-*O*-myristyl-6-*O*-(zinc(II) phthalocyaninyl) cellulose (**5**) was selected as a target material in our study. In target material **5**, the myristyl group (C14 alkyl group) was chosen as the *O*-2 and *O*-3 substituent groups by the following four reasons. (1) It was found in preliminary experiments, which will be published elsewhere, that the acyl groups more than fourteen carbons long were essential to good solubility in common organic solvents and formability of LB films in 6-*O*-porphyrin-2,3-di-*O*-acyl cellulose derivatives with various acyl groups from acetyl group (C2) to stearoyl group (C18). (2) The photocurrent performance of 6-*O*-porphyrin-2,3-di-*O*-myristoyl cellulose (C14 chain) has been found to be higher than that of 6-*O*-porphyrin-2,3-di-*O*-stearoyl cellulose (C18 chain) (Sakakibara and Nakatsubo. 2010). (3) The alkyl group which is fourteen carbons long (C14 chain) was thought to be preferable in the combination of 6-*O*-porphyrin-2,3-di-*O*-myristoyl cellulose with C14 acyl groups to prepare a new LB film. (4) The substituent groups at *O*-2 and *O*-3 positions should be stable under alkali conditions in the synthetic route described below (Scheme 1).

There are two general methods to prepare target material **5**. One is direct introduction of

mono-substituted phthalocyanine derivative to a cellulose backbone, and another is phthalocyanine-ring

formation on a cellulose backbone using a precursor-bound cellulose derivative. In the former method,

preparation of a *mono*-substituted phthalocyanine derivative is known to be time-consuming (Erdem et al.

2008), and the poor solubility of phthalocyanine derivative in common organic solvents (Allcock and

Neenan. 1986) may be inconvenient to homogeneous reaction for high yield synthesis of compound **5**. In

the latter method, these problems may be avoided. Then, this paper describes the preparation of

2,3-di-*O*-myristyl-6-*O*-(zinc(II) phthalocyaninyl) cellulose (**5**) using the latter method, the preparation

of LB monolayer films of compound **5** and preliminary evaluation of photocurrent generation

performance of the LB films.

Experimental

Materials

6-*O*-(4-Methoxytrityl) cellulose (**2**) was prepared from cellulose (**1**) [Microcrystalline cellulose (Avicel[®],

DP_n = 141, Merck (Darmstadt, Germany))] by the conventional method (Camacho Gómez et al. 1996).

The degree of substitution of 4-methoxytrityl group ($DS_{4-meO-Tr}$) and the degree of polymerization (DP_n)

of compound **2** was 1.00 (determined by elementary analysis) and 138 (M_w/M_n= 3.29), respectively.

[2(3),9(10),16(17),23(24)-Tetrakis(*tert*-butyl)phthalocyaninato]zinc(II) (Zn*t*BPc) was prepared according

to the method of Mori et al. (2010) as a reference sample in UV-vis measurements. Zinc(II)

phthalocyanine (ZnPc) was purchased from Tokyo Chemical Industry (Tokyo, Japan) as a reference

sample in FTIR measurements. All other chemicals were purchased from commercial sources and used

without further purification, unless otherwise specified. Tetrahydrofuran (THF) was distilled from

potassium, and K_2CO_3 was dried in vacuo at 105 °C overnight before use.

2,3-Di-*O*-myristyl cellulose (**3**)

6-*O*-(4-Methoxytrityl) cellulose (**2**) (0.500 g, 1.15 mmol) was dissolved in DMSO (13 ml).

1-Bromotetradecane (1.9 ml, 6.99 mmol) was added to the solution. After the suspension was stirred at

room temperature (r.t.) for 2 h, powdered NaOH (1.38 g, 34.5 mmol) and DMSO (10 ml) were added to

the suspension. The reaction mixture was stirred at r.t. for 1 h and at 70 °C for 20 h. Distilled water (40

ml) was added at r.t. to dissolve the residual NaOH, and 35% HCl (1.1 ml) was added for neutralization.

The reaction mixture was extracted with $CHCl_3$. The organic layer was washed with distilled water, a

saturated $NaHCO_3$ aqueous solution, distilled water, dried with Na_2SO_4, and concentrated to give an oil.

The oil was added dropwise to MeOH (250 ml). The resulting precipitates were collected by

centrifugation (7,300 × g, 10 min), and dried in vacuo at 70 °C to give crude products (0.956 g).

To the solution of the products in $CHCl_3$ (10 ml), *p*-toluenesulfonic acid monohydrate (*p*-TsOH)

(0.438 g, 2.30 mmol) was added. The reaction solution was stirred at r.t. for 12 h, and added dropwise to

EtOH (175 ml). The resulting precipitates were collected by centrifugation (14,000 × g, 10 min), dried in

vacuo at r.t., and dissolved in $CHCl_3$ (6 ml). After addition of p-TsOH (0.218 g, 1.15 mmol) to the solution, the reaction mixture was kept at r.t. for 1.6 h, and added dropwise to EtOH (150 ml). The resulting precipitates were collected by centrifugation (410 $\times$ g, 10 min), and dissolved in a small amount of $CHCl_3$. The solution was added dropwise in acetone (150 ml). The resulting precipitates were collected by centrifugation (14,000 $\times$ g, 10 min), washed with acetone and EtOH, and dried in vacuo at 65 °C overnight to afford compound **3** (0.444 g, 79.1 % yield).

Compound **3**; $DS_{myristyl}$: 1.66 (determined by elementary analysis); DP_n: 38 (M_w/M_n= 1.69); ^{1}H NMR ($CDCl_3$): δ 4.31 (H-1), 3.93 (H-6a), 3.88-3.42 (H-6b, myristyl $-O-CH_2-$, H-4), 3.26 (H-3, H-5), 2.96 (H-2), 1.52 (myristyl $-OCH_2-CH_2-$), 1.14-1.31 (myristyl $-CH_2-$), 0.83-0.91 (myristyl $-CH_3$) ppm; ^{13}C NMR ($CDCl_3$), δ 102.9 (C-1), 83.0 (C-3), 82.2 (C-2), 78.1 (C-4), 75.1 (C-5), 73.9, 73.5 (myristyl $-OCH_2-$), 61.6 (C-6), 31.9, 30.4, 30.3, 29.7, 29.6, 29.3, 26.2, 22.6 (myristyl $-CH_2-$), 14.1 (myristyl $-CH_3$) ppm; FTIR (KBr): ν 3423, 2926, 2854, 1463, 1369, 1103, 1068 cm^{-1}.

6-O-(3',4'-Dicyanophenyl)-2,3-di-O-myristyl cellulose (**4**)

To the solution of 2,3-di-O-myristyl cellulose (**3**) (0.350 g, 0.718 mmol) in DMF/THF (1/4, v/v) (35 ml), 4-nitrophthalonitrile (0.546 g, 3.15 mol) and K_2CO_3 (0.872 g, 6.31 mmol) were added. The reaction mixture was stirred at 60 °C for 48 h, and was poured into EtOH (175 ml). The resulting precipitates were collected by centrifugation (14,000 $\times$ g, 12 min), and washed with EtOH, EtOH/H_2O (1/1, v/v), and EtOH to give crude products. The products were purified by the re-precipitation method from EtOH again to

give compound **4** (0.363 g, 86.5 % yield).

Compound **4**; DS$_{dicyanophenyl}$: 0.76 (determined by elementary analysis); DP$_n$: 20 (M_w/M_n= 1.28); ^{1}H NMR (CDCl$_3$): δ 7.90-7.59 (H-5'), 7.32-7.08 (H-2', H-6'), 4.80-2.83 (cellulose ring-H, myristyl -OCH$_2$-), 1.60-1.39 (myristyl-OCH$_2$-CH_2-), 1.35-1.02 (myristyl -CH$_2$-), 0.89-0.86 (myristyl -CH$_3$) ppm; ^{13}C NMR (CDCl$_3$): δ 161.5 (C-1'), 135.1 (C-5'), 119.7 (C-2', C-6'), 117.5 (C-3'), 115.5 (C4'-CN), 115.0 (C3'-CN), 108.0 (C-4'), 103.1 (C-1), 83.0 (C-3), 81.9 (C-2), 78.1(C-4), 75.2(C-5), 73.6 (myristyl-OCH$_2$-), 67.1(C-6 substituted), 61.5 (C-6 unsubstituted), 31.9, 30.4, 30.3, 29.7, 29.6, 29.3, 26.2, 22.6 (myristyl -CH$_2$-), 14.1 (myristyl -CH$_3$) ppm; FTIR (KBr): ν 3442, 2926, 2854, 2233 (CN), 1600, 1097, 1066 cm^{-1}; UV–vis (in CHCl$_3$): λ (log ε) 305 (3.5), 296 (3.5), 258 (4.1) nm.

2,3-Di-*O*-myristyl-6-*O*-(zinc(II) phthalocyaninyl) cellulose (**5**)

6-*O*-(3',4'-Dicyanophenyl)-2,3-di-*O*-myristyl cellulose (**4**) (0.100 g, 0.172 mmol) was suspended in DMF (3.0 ml). After stirring at 100 °C for 3.3 h, 1,1,1,3,3,3-hexamethyldisilazane (HMDS) (1.3 ml, 6.23 mmol) was added. The reaction mixture was stirred at r.t. for 2.2 h and at 100 °C for 30 min. Zinc acetate (141 mg, 0.770 mmol), *o*-phthalodinitrile (376 mg, 2.94 mmol) and HMDS (0.7 ml, 3.35 mmol) were added to the mixture. The mixture was stirred under nitrogen atmosphere at 100 °C for 24 h, and was poured into MeOH (200 ml). The resulting blue precipitates were collected by centrifugation (14,000 × g, 10 min), and suspended in CHCl$_3$ (30 ml). The suspension was stirred at r.t. overnight, and filtered with CHCl$_3$ to remove by-products such as zinc(II) phthalocyanine. The filtrate was concentrated to give crude products.

The products were purified by the re-precipitation method from MeOH (150 ml) to afford the purified product. The product was further dissolved in a small amount of CHCl$_3$ and filtered with a syringe filter (0.45 μm, Minisart RC 15) to remove the insoluble fraction, and concentrated to afford compound **5** (0.0485 g, 35.4% yield). (The yield was calculated based on the assumption that the residual dicyanophenyl groups did not react with phthalodinitrile and that the residual hydroxyl groups were trimethylsilylated as described below.)

Compound **5**; DS$_{phthalocyanine}$: 0.38 (determined by UV-vis method); DP$_n$: 25 (M_w/M_n= 2.20); ^{1}H NMR (CDCl$_3$): δ 9.82-7.05 (zinc(II) phthalocyaninyl-H, dicyanophenyl-H), 4.80-2.76 (cellulose ring-H, myristyl-OCH$_2$-), 1.96-0.49 (myristyl-CH$_2$-, and –CH$_3$), 0.07 (-Si(CH$_3$)$_3$) ppm; FTIR (KBr): ν 2924, 2852, 2231 (CN), 1487, 1332, 1111, 1091, 1060, 723 cm^{-1}; UV-vis (in CHCl$_3$): λ (log ε) 676 (4.3), 617 (3.8), 339 (4.1), 243 (4.2) nm.

Preparation of Langmuir-Blodgett Films of compound **5**

A diluted solution of compound **5** in CHCl$_3$ (0.5 mg ml^{-1}) was spread onto a water subphase in a Teflon-coated trough (331 × 100 × 5 mm, USI-3-22T, USI). The ultrapure water purified by Mili-Q (Nihon Millipore) was used for the subphase. The solvent was evaporated for 30 min. The surface pressure (π)-area (A) isotherm was measured at a constant compression rater of 6 mm min^{-1}. The surface pressure was measured using a film balance of Wilhelmy type. The vertical dipping method was used to

deposit the surface monolayer onto a substrate. The upward and downward stroke rate was 6 mm min^{-1}.

During the deposition, the surface pressure was controlled to remain 10 mN m^{-1} and the surface

temperature was kept at 20 °C to prepare the LB films.

Measurements

FTIR spectra were recorded in KBr pellets with a Shimadzu IRPrestige-21 spectrophotometer. ^{1}H and ^{13}C

NMR spectra were recorded on a Varian 500 MHz NMR spectrometer in CDCl$_3$ with TMS as an internal

standard. Chemical shift (δ) was given in δ values (parts per million). UV-vis spectra were recorded on a

Jasco V-560 UV-vis spectrophotometer in CHCl$_3$. Gel permeation chromatography (GPC) was performed

using a Shimadzu LC-10 system equipped with a Shimadzu UV-vis detector (SPD-10Avp) and a

Shimadzu RI detector (RID-10A) (Conditions: columns: Shodex columns K-802, K-802.5 and K-805

(connected in series); column temperature: 40 °C; eluent: CHCl$_3$; flow rate : 1.0 ml min^{-1}; standards:

polystyrene standards (Shodex)). Wavelength of UV detection was 600 nm for compounds **4** and **5**, or 254

nm for other compounds. AFM observation of the monolayer film was performed in dynamic mode using

a Shimadzu SPM-9600 equipped with a tetrahedral shaped silicon cantilever (AC240TS-C2, Olympus).

The photocurrent measurements were performed according to the method reported by Sakakibara and

Nakatsubo (2010).

Results and discussion

Preparation of 2,3-di-*O*-myristyl-6-*O*-(zinc(II) phthalocyaninyl) cellulose (**5**)

The synthetic route of 2,3-di-*O*-myristyl-6-*O*-(zinc(II) phthalocyaninyl) cellulose (**5**) from cellulose (**1**) is

shown in Scheme 1. 6-*O*-(4-Methoxytrityl) cellulose (**2**) was prepared from cellulose (**1**) in 97.1 % yield

by the conventional method (Camacho Gómez et al. 1996).

Kasai et al. (2005) has reported the preparation of 2,3-di-*O*-octadecylcellulose from

6-*O*-(4-methoxytrityl) cellulose with 1-bromooctadecane / NaOH powder / DMSO / a small amount of

water at 70 °C for 20 h. Myristylation of compound **2** was performed with 1-bromotetradecane / NaOH

powder / DMSO at 70 °C for 20 h, because it was found that a small amount of water was not necessary

to our reaction in a preliminary experiment. The addition order of NaOH powder and 1-bromotetradecane

was important in the myristylation. When NaOH powder was added to the solution of compound **2** at first,

the reaction mixture became to be too viscous for dispersion of 1-bromotetradecane. 1-Bromotetradecane

should be first added to the solution in the myristylation. The purification of 6-*O*-(4-methoxytrityl)
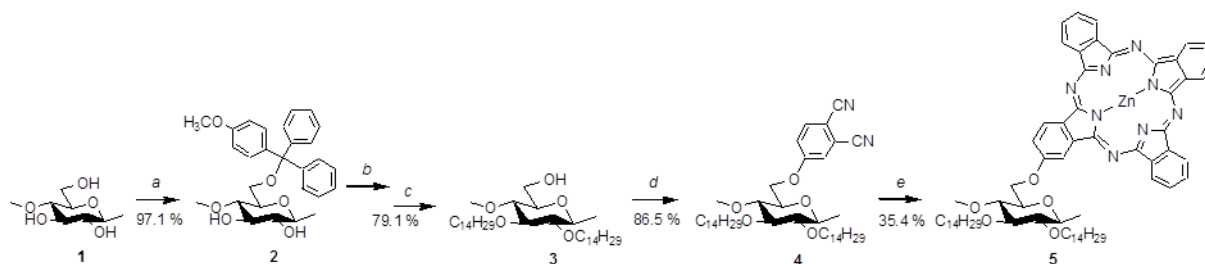
a : *p*-MeO-TrCl/Pyridine/DMAc-LiCl, 70 °C, 4h. b : C$_{14}$H$_{29}$Br/NaOH/DMSO, 70 °C, 20h. c : *p*-TsOH/CHCl$_3$/r.t. 12 h → r.t. 1.6 h.
d : NO$_2$-C$_6$H$_3$(CN)$_2$/K$_2$CO$_3$/DMF-THF (1:4, v/v), 60 °C, 48 h. e : C$_6$H$_4$(CN)$_4$/Zn(OAc)$_2$/HMDS/DMF, 100 °C, 24 h.

Scheme 1. Synthetic route for 2,3-di-*O*-myristyl-6-*O*-(zinc(II) phthalocyaninyl) cellulose (**5**)

2,3-di-*O*-myristyl cellulose was very difficult because of the similar solubility behaviors in common

organic solvents of 6-*O*-(4-methoxytrityl)-2,3-di-*O*-myristyl cellulose, the residual 1-bromotetradecane,

and the by-products from 1-bromoteradecane such as 1-tetradecanol. It has been also reported that the

purification of 6-*O*-(4-methoxytrityl)-2,3-di-*O*-octadecyl cellulose was laborious and tedious work (Kasai

et al. 2005). Indeed, the re-precipitation method was not effective for the purification of

6-*O*-(4-methoxytrityl)-2,3-di-*O*-myristyl cellulose, although several organic solvents for the

re-precipitation were tried. Then, the crude myristylated products after one re-precipitation from MeOH

were subjected to de(4-methoxy)tritylation, because de(4-methoxy)tritylation proceeded smoothly and the

purification of 2,3-di-*O*-myristyl cellulose (**3**) was relatively easy, even in the presence of the residual

1-bromotetradecane and the resulting by-products in a preliminary experiment. De(4-methoxy)tritylation

of the crude myristylation products with

p-toluenesulfonic acid in CHCl$_3$ at r.t. for 12 h afforded

the de(4-methoxy)tritylated product. However, the

^{1}H-NMR spectrum of the product showed that a small

amount of (4-methoxy)trityl group remained (data not

shown). De(4-methoxy)tritylation of the product was

conducted at r.t. for 1.6 h again to afford compound **3**

in 79.1 % yield (based on compound **2**). The bands at
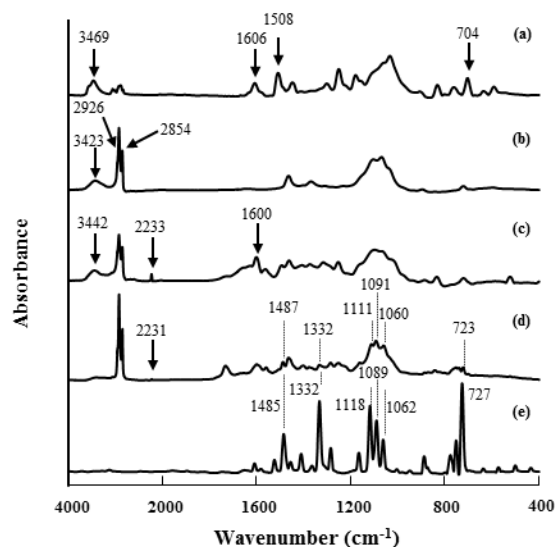
Fig. 1 FTIR spectra of compounds **2** : (a), **3** : (b), **4** : (c), **5** : (d) and ZnPc : (e)

1606 and 1508 cm^{-1} derived from (4-methoxy)trityl group were not present in the FTIR spectrum of

compound **3** (Fig. 1b) and the signals at 7.0-8.0 ppm derived from aromatic-H were not present in the ^{1}H

NMR spectrum of compound **3** (Fig. 2a), suggesting that de(4-methoxy)tritylaion completely proceeded.

The completion of reaction was also supported by the ^{13}C NMR spectrum of compound **3** (Fig. 2b). The

CH stretching vibrations at 2926 cm^{-1} and 2854 cm^{-1} assigned to myristyl group were present in the FTIR

spectrum of compound **3** (Fig. 1b) and the signals at 0.83-1.52 ppm derived from myristyl group-H were

present in the ^{1}H NMR spectrum of compound **3** (Fig. 2a). The DS$_{myristyl}$ of compound **3** was calculated to

be 1.66 by elementary analysis. The DP$_n$ of compound **2** decreased from 138 to 38 during myristylation

and the following de(4-methoxy)tritylation. One of the reason is the acidic hydrolysis proceeding as a side reaction in de(4-methoxy)tritylation. Compound **3** was soluble in CHCl$_3$ and THF, but insoluble in DMSO and DMF.

The treatment of alcohol with 4-nitrophthalonitrile in the presence of K$_2$CO$_3$ in DMF gave the corresponding
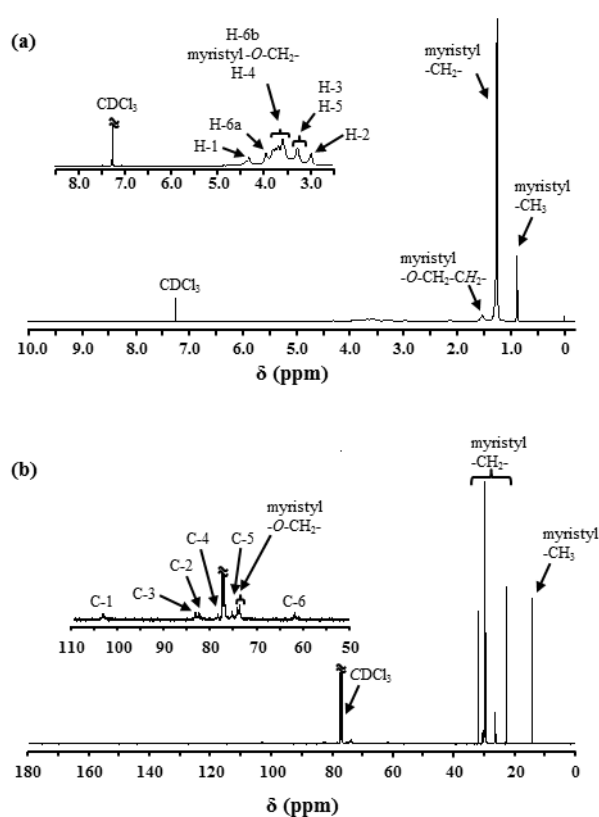
Fig. 2 NMR spectra of compound **3** (in CDCl$_3$).
^{1}H NMR : (a), ^{13}C NMR : (b)

4-alkoxyphthalonitrile (Álvarez-Micó et al. 2007; Choi et al. 2008). Then, compound **3** was treated with

the reagents in DMF at 60 °C for 24 h to give 6-*O*-(3',4'-dicyanophenyl) -2,3-di-*O*-myristyl cellulose (**4**)

in 77.0 % yield. However, the $DS_{dicyanophenyl}$ of compound **4** was 0.41, which is easily evaluated by [1]H

NMR. The low DS seemed to be due to the heterogeneous reaction in DMF. The mixed solvents of DMF

and THF with various ratios were investigated (Table 1). When DMF/THF (1/4, v/v) and THF were used, the reactions were homogeneous systems. Consequently, it was found that DMF/THF (1/4, v/v) was the best solvent to achieve a high $DS_{dycianopphenyl}$ of compound **4** (Entry 3). The characteristic band derived from the nitrile group of the dicyanophenyl group at 2233 cm^{-1} (Bilgin et al. 2008) was found in the FTIR spectrum of compound **4** (Fig. 1c). The s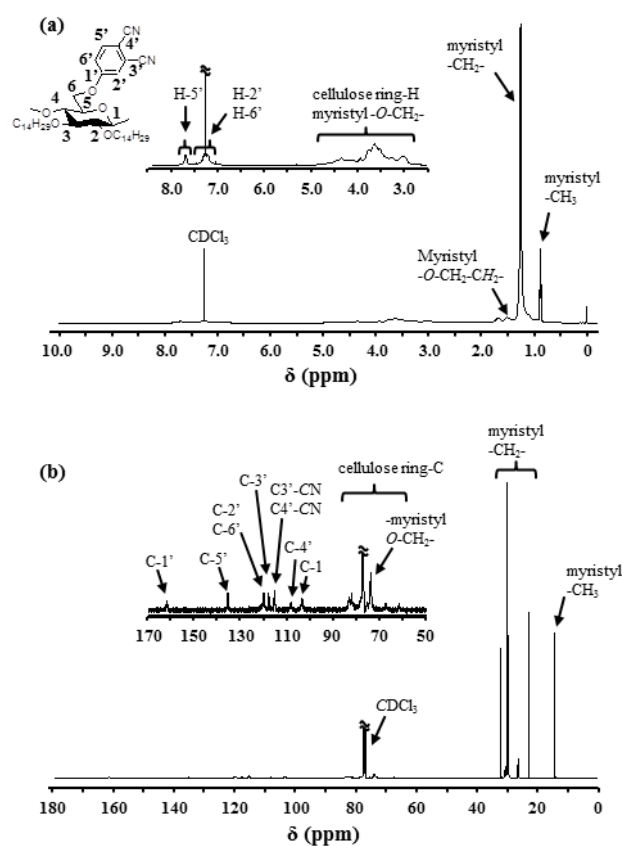ignals at 7.90-7.59 ppm and 7.32-7.08 ppm and the signals at 115.0 ppm and 115.5 ppm derived from dicyanophenyl group (Álvarez-Micó et al.

Table 1. Results of dicyanophenylation

Entry	DMF/THF (v/v)	$DS_{dicyanophenyl}$[a]	Yield (%)
1	1/0	0.41	77
2	4/1	0.35	71
3	1/4	1.10	73
4	0/1	0.71	73

[a] determined by ^{1}H NMR method.

Fig. 3 NMR spectra of compound **4** (in CDCl₃).
^{1}H NMR : (a), ^{13}C NMR : (b)

2007) were observed in the ^{1}H NMR (Fig. 3a) and ^{13}C NMR spectra, respectively. These results suggested that dicyanophenylation proceeded as expected. The $DS_{dicyanophneyl}$ of compound **4** (Entry 3) was finally determined by elementary analysis, and found to be 0.90. The DP_n of compound **3** was decreased from 38 to 20 during dicyanophenylation. It was due to alkali hydrolysis in dicynaophenylation, although further investigation was required.
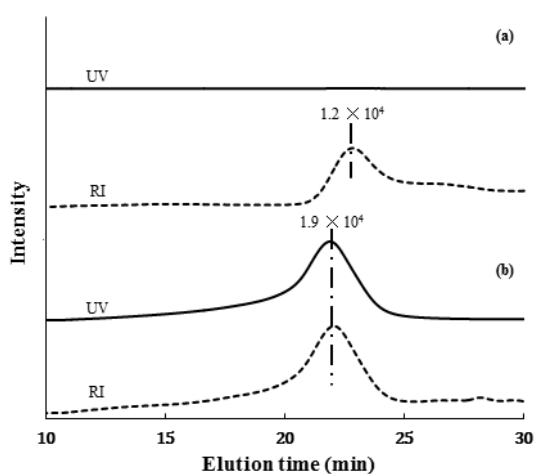
There were two problems to be considered in phthalocyanine-ring formation at C-6 position of compound **4** with phthalodinitrile. One possibility was that depolymerization of the cellulose backbone might occur simultaneously with phthalocyanine-ring formation because compound **4** should be subjected to the ring-formation reaction under hard reaction conditions. For example, the ring formations on precursor-bounded polymers with phthalodinitrile derivative / CuBr / dry DMF at 165 °C for 3.5 h (Allcock and Neenan. 1986), and that with phthalodinitrile derivative / ZnCl$_2$ / quinoline, at 210 – 230 °C for 3 h (Zhang et al. 2006) and that with phthalodinitrile derivative / [dry DMF/2-dimethylaminoethanol (1/1, v/v)] under reflux for 20 h (Leznoff and Hall 1982) have been reported. Another possibility was that
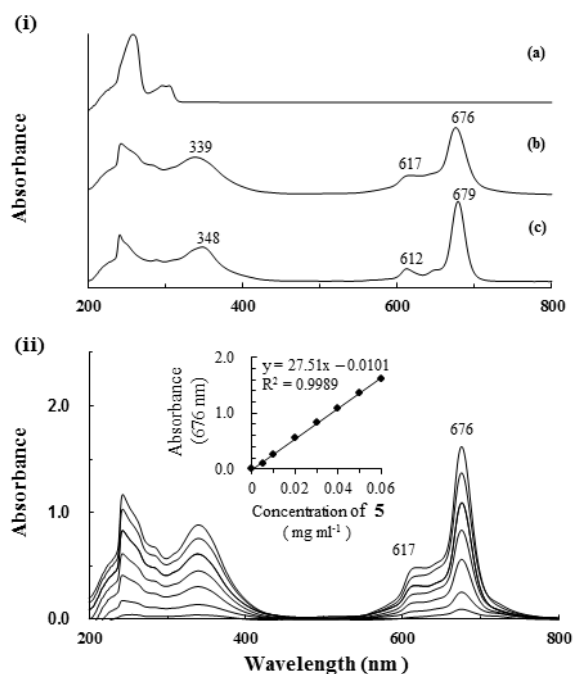
Fig. 4 (i) UV-vis spectra of compounds **4**: (a), **5** : (b) and Zn*t*BPc: (c). (ii) UV-vis spectra of compound **4** in CHCl$_3$ at different concentrations: 0.06, 0.05, 0.04, 0.03, 0.02, 0.01, 0.005 mg ml^{-1} from the top. The inset shows plot of the absorbance at 676 nm against the concentration

two or more 3,4-dicyanophenyl groups attached to the same or different cellulose chains might be incorporated into the same phthalocyanine ring. Therefore, mild conditions (especially lower reaction temperature) and dilute conditions were required in our reaction. Uchida et al. (2002) have reported that the reaction of phthalodinitrile in the presence of Zn(OAc)$_2$ and HMDS in DMF under mild conditions (at 100 °C for 10 h) afforded zinc(II) phthalocyanine in 73 % yield. The method under dilute conditions was applied to the phthalocyanine-ring formation at C-6 position of compound **4**. The reaction of compound **4** with phthalodinitrile in the presence of Zn(OAc)$_2$ and HMDS in DMF at 100 °C for 24 h gave 2,3-di-*O*-myristyl-6-*O*-(zinc(II) phthalocyaninyl) cellulose (**5**) as a dark blue product in 35.4 % yield.

Compound **5** was firstly subjected to FTIR, UV-vis and NMR measurements to confirm phthalocyanine-ring formation. The characteristic bands at 1487, 1332, 1111, 1091, 1060, 723 cm^{-1} derived from zinc(II) phthalocyanine (Leznoff et al. 1991; Seoudi et al. 2005) were present (Fig. 1d).

Fig. 5 GPC elution curves of compounds **4** : (a) and **5** : (b) (UV detection wavelength was 600 nm)

Those bands were in good agreement with the bands in the FTIR spectrum of ZnPc (Fig. 1e). The band at 2231 cm^{-1} from nitrile groups was still present, although it was very small (Fig. 1d). The Q bands around 600 - 700 nm and the Soret band around 300 - 400 nm were clearly observed in the UV-vis spectrum of compound **5** as well as that of Zn*t*BPc, whereas
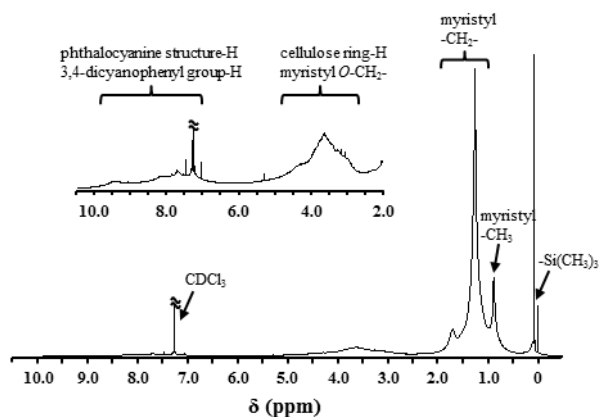
Fig. 6 ^{1}H NMR spectrum of compound **5** in CDCl$_3$

they were not observed in that of compound **4** (Fig. 4(i)). These results indicated that phthalocyanine-ring was formed as expected, although some dicyanophenyl groups did not react. On the other hand, the bands around 3400 cm^{-1} were not present in the FTIR spectrum of compound **5** (Fig. 1d). The strong peak around 0.07 ppm was observed in the spectrum of ^{1}H NMR of compound **5** (Fig. 6). Considering that HMDS is also known as a silylating agent (Deng 2011; Wang et al. 2006; Cooper et al. 1981), it was suggested that residual hydroxyl groups of compound **4** were trimethylsilylated during the phthalocyanine-ring formation. Next, compound **5** was subjected to Gel Permeation Chromatography (GPC) to confirm that phthalocyanine units were covalently attached to the cellulose backbone. Fig. 5 shows GPC elution curves by RI and UV detectors of compounds **4** and **5**. The RI and UV elution curves of compound **5** showed nearly identical elution profiles (Fig. 5b), and the peak at low molecular weight corresponding to free zinc(II) phthalocyanine, was not present in the UV elution curve of compound **5**. These results suggested that compound **5** was phthalocyanine-bearing cellulose derivative. Next, the DS$_{phthalocyanine}$ of compound **5** was investigated. Allcock and Neenan (1986) has been reported that the spectrum of monomeric copper(II) phthalocyanine consists of strong adsorption at 670 nm and the weak adsorption at 605 nm derived from

Q bands, and that of dimeric phthalocyanine consists of the two bands of almost equal intensity. Fig. 4(ii)

shows the UV-vis spectra of compound **5** in CHCl$_3$ at different concentrations in the range of 0.005 mg

ml^{-1} to 0.06 mg ml^{-1}. The strong adsorption at 676 nm was present in all UV-vis spectra. Any bands, due

to aggregation (Huang et al. 2007), were not present at the Q band, and the intensity of the Q bands

increased proportionally with an increase of concentration of compound **5**. On the other hand, the Q

bands were not present in UV-vis spectrum of compound **4** (Fig. 4(i)). Therefore, the DS$_{phthalocyanine}$ of

compound **5** could be estimated by UV-vis method (UV detection: 676 nm) with calibration curves from

ZntBPc. Consequently, the DS$_{phthalocyanine}$ was calculated to be 0.38. Finally, the DP$_n$ of compound **5** was

calculated using the following equation (1) on the assumption that the residual dicyanophenyl group did

not react with phthalodinitrile and that the residual hydroxyl groups were completely trimethylsilylated.

DP$_n$ = M$_n$ / [(a ring-formed unit (1082))*0.38 + (a not ring-formed unit with dicyanophenyl group

(639))*0.38 + (a not ring-formed unit without dicyanophenyl group (585) *0.24]   (1)

The DP$_n$ of compound **5** was estimated to be 25 whereas the DP$_n$ of compound **4** was calculated to be 20,

suggesting that cross-linking reaction proceeded to some extent during the phthalocyanine-ring formation.

Preparation of LB films of compound **5** and preliminary evaluation of photocurrent generation

  performance

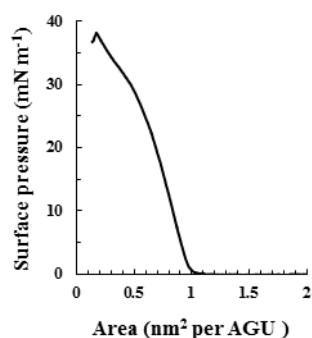Fig. 7 shows the surface pressure (π)-area (A) isotherm of compound **5** at the air-water interface at 20 °C.

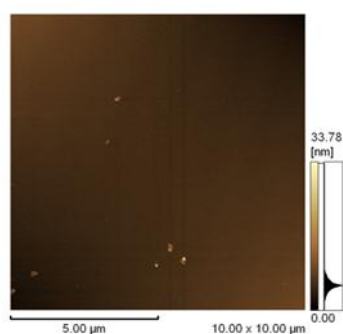Fig. 7 Surface pressure (π)-area (A) isotherm of compound **5**

Fig. 8 AFM image of the monolayer of compound **5** deposited on freshly cleaved mica at a surface pressure of 10 mN m^{-1} at 20 °C

The limiting molecular area was 0.98 nm^2 per anhydro glucose unit, obtained by the extrapolation of the steepest part of the isotherm to zero surface pressure. The cross-sectional areas of a glucopyranose ring and a phthalocyanine core are known to be ca. 0.55-0.60 nm^2 (Sakakibara et al. 2007) and ca. 1.00 nm^2 (Cook and Chambrier 2003), respectively. The average area occupied per unsubstituted phthalocyanine core is reported to be ca. 0.40 nm^2 if the molecules lie perpendicular to the water (Cook and Chambrier 2003). It was therefore suggested that the phthalocyanine units of compound **5** were oriented almost perpendicular to the water surface.

6-*O*-Porphyrin-2,3-di-*O*-stearoyl cellulose monolayer has been reported to be successfully deposited onto several substrates at surface pressure of 10 mN m^{-1} by the horizontal lifting method (Sakakibara et al. 2007). Then, the horizontal lifting method was tried to prepare of a LB monolayer film of compound **5**. The monolayer transfers with various surface pressures on various substrates, however, were unsuccessful. The vertical dipping method was applied to the LB monolayer film preparation. The monolayer of
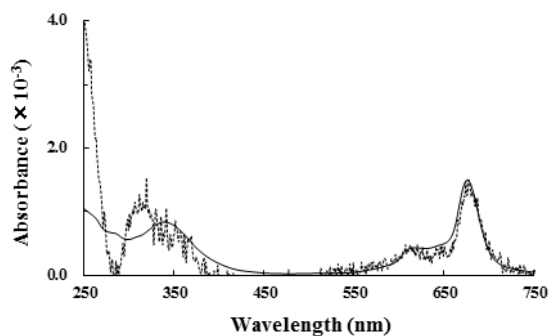
Fig. 9 UV-vis absorption spectra of the LB monolayer (solid line) and the solution in CHCl$_3$ (0.04 mg ml^{-1}) (dotted line) of compound **5** (normalized at 676 nm)
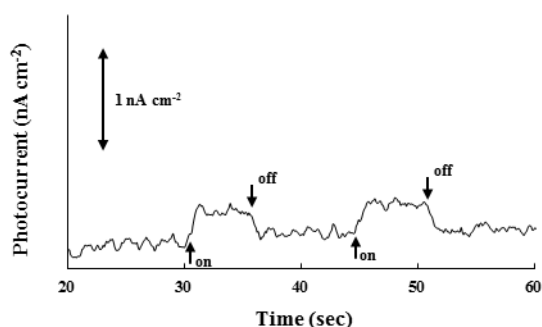
Fig. 10 Photoelectrochemical response of the monolayer of compound **5** on an ITO electrode with illumination at 680 nm

compound **5** could be transferred onto mica at surface pressure of 10 mN m^{-1} by upward stroke but not by downward stroke. Fig. 8 shows AFM image of the monolayer film of compound **5** on mica. It is shown that the surface was almost smooth and homogeneous, although some aggregates of ca. 100 nm in diameter were observed. The LB monolayer of compound **5** was also successfully transferred onto quartz and Indium Tin Oxide (ITO) electrode by the vertical dipping method. Fig. 9 shows UV-vis

spectra of the LB monolayer film of compound **5** on quartz and the solution of compound **5** in CHCl$_3$. It

has been reported that the red-sift and blue-shift of the Q bands of phthalocyanine were observed in the

J-aggregates and H-aggregates, respectively (Huang et al. 2007). The Q band of the monolayer film and

the solution of compound **5** were observed at almost same position, suggesting that the cellulose scaffold

effectively suppressed the aggregation of the phthalocyanine moieties.

Photocurrent measurement at 680 nm was performed for the LB monolayer film of compound **5** on

an ITO electrode (transfer ratio = 1.01) as a preliminary evaluation of photocurrent generation

performance. Fig. 10 shows the photocurrent generation of the LB monolayer at 680 nm. A steady state

anodic photocurrent of which photocurrent density was 0.45 nA cm^{-2} appeared during light illumination,

although the performance was low. The preparation and evaluation of the mixed LB films of compound **5**

and the porphyrin-containing cellulose derivatives without any aggregations are now investigating at the

next step of our study.

Conclusions

2,3-Di-*O*-myristyl-6-*O*-(zinc(II) phthalocyaninyl) cellulose with the DS$_{phthalocyaninse}$ of 0.38 (**5**) was

prepared from cellulose (**1**)　using phthalocyanine-ring formation on the cellulose backbone by five

reaction steps in 23.5 % overall yield. Compound **5** is the first regioselectively substituted phthalocyaine

cellulose derivative. The LB monolayer film of compound **5** on mica, quartz and ITO substrates could be

prepared by the vertical dipping method, although some aggregates were observed in AFM image of the

monlayer. The LB monolayer film of compound **5** showed photocurrent performance at 680 nm, whereas

the LB monolayer films of the porphyrin-containing celluloses generated photocurrent in the range of 400

nm to 600 nm (Sakakibara and Nakatsubo 2010). Compound **5** is expected to be a complementary

material of the porphyrin-containing cellulose derivatives for solar cell materials.

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