

Preparation of (ruthenium (II) complex)-bound cellulose derivative for photocurrent generation system

Yasuko Saito¹ · Hiroshi Kamitakahara¹ · Toshiyuki Takano¹

Received: 9 December 2015 / Accepted: 24 February 2016 / Published online: 25 March 2016
© The Japan Wood Research Society 2016

Abstract 6-*O*-[Acetylacetonato-bis(2,2'-bipyridine)ruthenium(II)]-2,3-di-*O*-myristyl cellulose (**3**) was prepared from 2,3-di-*O*-myristyl cellulose (**1**) by two reaction steps in 37.7 % total yield. The LB monolayer film of compound **3** was successfully deposited onto an indium tin oxide electrode by a vertical dipping method and showed photocurrent generation performance in the range of 400–600 nm. Compound **3** was expected as a complementary material of porphyrin-bound cellulose derivative for biomaterial-based solar cells.

Keywords Cellulose · Langmuir–Blodgett film · Photo-electro conversion · Photosensitizer · Ruthenium complex

Introduction

Cellulose is the main component of wood. Numerous functional cellulose derivatives have been proposed for new applications [1–3]. However, attention is still focused on the development of the high-value added utilization for cellulose and its derivatives. From this point of the view, our group has reported that Langmuir–Blodgett (LB) films constructed from porphyrin-bound cellulose derivatives exhibited high photocurrent generation performances, suggesting that such cellulose derivatives are promising materials with potential applications in biomaterials-based solar cells [4, 5]. 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 to 420 nm as shown by spectrum (a) in Fig. 1, although the target wavelength range for an ideal solar cell should be considered from 300 to 1200 nm [6]. Therefore, other photosensitizer-bound cellulose derivatives which generate photocurrent at the unused region of solar light were strongly desired for the combination of the porphyrin-bound cellulose derivatives. In the previous papers, phthalocyanine- and squaraine-bound cellulose derivatives which covered photocurrent generation at the range from 650 to 720 nm [spectrum (b) in Fig. 1] and the range from 550 to 680 nm [spectrum (c) in Fig. 1] have been reported as the complementary materials of the porphyrin-bound cellulose derivatives (from 400 to 420 nm), respectively [7–9]. However, the new photosensitizer-bound cellulose derivative was still required for the photocurrent generation performance at the range from 420 to 600 nm (Fig. 1).

Polypyridyl ruthenium (II) complexes, which are ruthenium coordination compounds with 2,2'-bipyridine ligands (bpy), are well-known as the panchromatic sensitizers for dye-sensitized solar cells (DSSCs) [10–12]. Indeed, LB films consist of tris(2,2'-bipyridine) ruthenium complex for photocurrent generation systems around 450 nm have been reported [13]. Then, (ruthenium (II) complex)-bound cellulose derivative seemed to be an attractive as a new complementary material of the porphyrin-bound cellulose derivatives.

In this paper, acetylacetonato-bis(bipyridyl)-ruthenium (II) [acac(bpy)₂Ru (II)] complex-bound cellulose derivative (**3**) was selected as a target material for the photocurrent generation performance in the range of 420–600 nm. This was inspired by a report that the coordination reaction of acetoacetyl groups of the polyester with 2,2'-bipyridine complex of ruthenium dichloride (*cis*-(bpy)₂ RuCl₂) formed [acac(bpy)₂Ru (II)] complexes [14] and by another report that acetoacetyl cellulose

✉ Toshiyuki Takano
takatmys@kais.kyoto-u.ac.jp

¹ Division of Forest and Biomaterials Science, Graduate School of Agriculture, Kyoto University, Kitashirakawa-Oiwake-cho, Sakyo-ku, Kyoto 606-8502, Japan

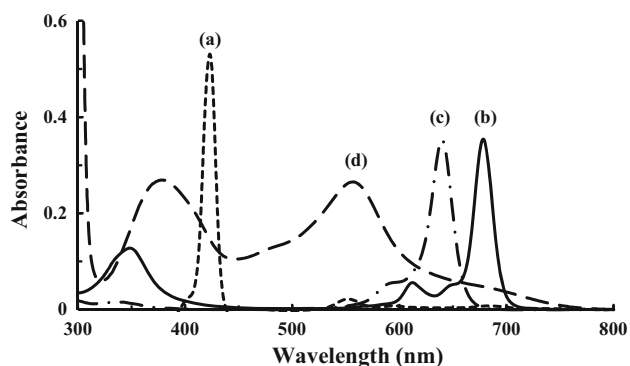


Fig. 1 Target UV–Vis spectra of porphyrin- (a), phthalocyanine- (b), squaraine- (c), and ruthenium (II) complex- (d) bound cellulose derivatives

acted as a metal absorbent [15]. The present paper describes the preparation of compound **3** as shown in Fig. 2, the fabrication of its LB monolayer film, and evaluation for photocurrent generation performance of the film.

Materials and methods

Materials

2,3-Di-*O*-myristyl cellulose (**1**) with degree of substitution of myristyl group (DS_{myristyl}) of 1.70 (determined by ^1H NMR method) and degree of polymerization (DP_n) of 39 ($M_w/M_n = 1.7$) was prepared according to the reported procedure [7]. 2,2'-Bipyridine complex of ruthenium dichloride dihydrate (*cis*-(bpy) $_2$ RuCl $_2$ ·2H $_2$ O) was prepared by the known method [16]. Diketene was distilled from CaH $_2$ under reduced pressure before use. All other

chemicals were purchased from commercial sources and used without further purification.

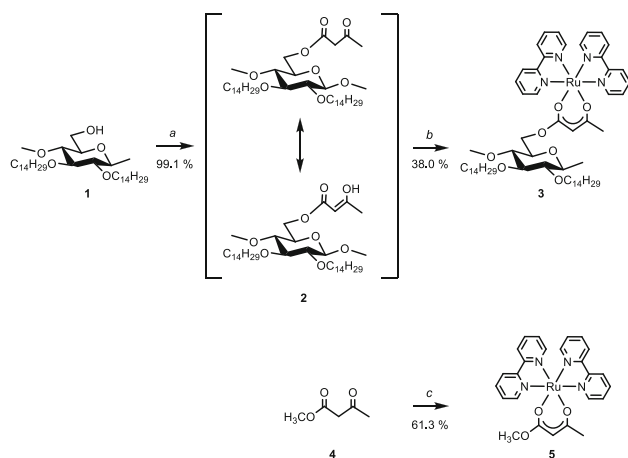
Measurements

The ^1H and ^{13}C nuclear magnetic resonance (NMR) spectra were recorded on a Varian 500 MHz FT-NMR (500 MHz) spectrometer (Agilent Technologies, Santa Clara, CA, USA) in CDCl $_3$. The chemical shift (δ) values were given in parts per million (ppm). The Fourier transform infrared (FT-IR) spectra were recorded from KBr pellets using a Shimadzu IRPrestige-21 spectrophotometer (Shimadzu Co., Kyoto, Japan). The UV–vis spectra were recorded on a Jasco V-560 UV–vis spectrophotometer (Jasco, Tokyo, Japan) in CHCl $_3$. Gel permeation chromatography (GPC) was performed on a Shimadzu LC-10 system equipped with a Shimadzu UV–vis 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: CHCl $_3$; flow rate: 1.0 mL/min; standards: polystyrene standards (Shodex, Showa Denko K.K.).

6-*O*-Acetoacetyl-2,3-di-*O*-myristyl cellulose (**2**)

To a solution of 2,3-di-*O*-myristyl cellulose (**1**) (0.400 g, 0.807 mmol) in tetrahydrofuran (THF, 7 mL), pyridine (0.33 mL, 4.03 mmol) and diketene (0.32 mL, 4.03 mmol) were added. The reaction mixture was stirred at 80 °C for 6 h. MeOH (0.2 mL) was added to the mixture to stop acetoacetylation. The mixture was then concentrated in vacuo to give a residue. The residue was extracted with CH $_2$ Cl $_2$. The organic-layer was washed with distilled water twice, dried with anhydrous Na $_2$ SO $_4$, and concentrated to give a yellow residue. The solution of the residue in CH $_2$ Cl $_2$ (5 mL) was added to MeOH (100 mL) in a drop-wise manner, and the resulting precipitate was collected by centrifugation (14,000×*g*, 10 min), washed with MeOH twice, and dissolved in CHCl $_3$ (5 mL). The solution was added to MeOH (100 mL) in a drop-wise manner, and the resulting precipitate was collected by centrifugation (14,000×*g*, 10 min), washed with MeOH twice, and dried in vacuo at 70 °C overnight to afford compound **2** (0.470 g, 99.1 % yield). The degree of substitution of acetoacetyl groups (DS_{acac}) of compound **2** was calculated based on the area of the methyl groups of acetoacetyl groups (from 2.32 to 2.10 ppm) and that of the ring-proton of cellulose and the methylene group of myristyl groups (from 5.28 to 2.80 ppm) in the ^1H NMR spectrum.

Compound **2**; DS_{acac} : 1.13; DP_n : 32 ($M_w/M_n = 1.94$); ^1H NMR (CDCl $_3$): δ 12.05–11.92 (acac-COCHC(OH)CH $_3$ (enol form)), 6.20–5.95 (acac-COCHC(OH)CH $_3$ (enol



a: diketene/pyridine/THF, 80 °C, 6 h. b: *cis*-bis(bpy) $_2$ RuCl $_2$ /Et $_3$ N/THF-MeOH (1:2, v/v), reflux, 48 h. c: *cis*-bis(bpy) $_2$ RuCl $_2$ /Et $_3$ N/MeOH, reflux, 8 h

Fig. 2 Synthetic route for 6-*O*-[acac(bpy) $_2$ Ru (II)]-2,3-di-*O*-myristyl cellulose (**3**) and methyl [acac(bpy) $_2$ Ru (II)] complex (**5**)

form)), 5.38–2.80 (CELL ring-H, myristyl-OCH₂–, acac-COCH₂COCH₃ (keto form)), 2.32–2.10 (acac-CH₃), 1.60–1.38 (myristyl-OCH₂CH₂–), 1.38–1.04 (myristyl-CH₂–), 0.96–0.80 (myristyl-CH₃) ppm; ¹³C NMR (CDCl₃): δ 199.9 (acac-C=O), 166.4 (acac-O-C=O), 102.6 (C-1), 82.7 (C-3), 81.9 (C-2), 78.8–70.6 (C-4, myristyl-OCH₂–, C-5), 63.6 (C-6), 49.9, 49.6 (acac-CH₂–), 31.9, 30.3, 29.7, 29.3, 26.3, 26.2, 26.0, 22.6, 22.5 (myristyl-CH₂–, acac-CH₃), 14.1 (myristyl-CH₃) ppm; FT-IR (KBr): ν 3435, 2926, 2854, 1751, 1720, 1668, 1635, 1462, 1409, 1361, 1315, 1259, 1236, 1151, 1091, 1062, 918, 721, 540 cm⁻¹.

6-*O*-[Acetylacetonato-bis(2,2'-bipyridine)ruthenium(II)]-2,3-di-*O*-myristyl cellulose (6-*O*-[acac(bpy)₂Ru(II)]-2,3-di-*O*-myristyl cellulose) (3)

To a suspension of 6-*O*-acetoacetyl-2,3-di-*O*-myristyl cellulose (**2**) (34.2 g, 0.581 mmol) in THF/MeOH (1/2, v/v, 15 mL), *cis*-bis(bpy)₂RuCl₂·2H₂O (92.5 mg, 0.191 mmol) and Et₃N (180 μL, 1.29 mmol) were added. The reaction mixture was refluxed for 48 h, and added into EtOH (100 mL) in a drop-wise manner. The resulting precipitate was removed by centrifugation (14,000×g, 10 min). The supernatant was dialyzed by Spectra/Por dialysis tube (MWCO = 1000) (Spectrum Laboratories Inc., Rancho Dominguez, CA, USA) against EtOH for 8 days, and concentrated in vacuo to afford compound **3** as a red solid (16.8 mg, 38.0 % yield). The DS_{Ru-complex} of compound **3** was estimated by UV-Vis method (UV detection: 522 nm) with calibration curves from compound **5**.

Compound **3**; DS_{Ru-complex}: 0.42; DP_n: 4 (*M_w*/*M_n* = 1.44); ¹H NMR (CDCl₃): δ 9.08–6.84 (2-2'-bipyridine-H), 6.19–5.92 (acac-COCH(OH)CH₃ (enol form)), 5.20–2.65 (CELL ring-H, myristyl-OCH₂–, acac-COCH₂COCH₃ (keto form)), 2.45–1.70 (acac-CH₃), 1.70–1.42 (myristyl-OCH₂-CH₂–), 1.42–1.00 (myristyl-CH₂–), 1.00–0.80 (myristyl-CH₃) ppm; FT-IR (KBr): ν 3425, 2924, 2852, 1741, 1716, 1668, 1627, 1597, 1560, 1541, 1506, 1462, 1419, 1367, 1311, 1265, 1153, 1068, 798, 767, 725 cm⁻¹; UV-Vis (in CHCl₃): λ (log ε) 522 (3.6), 370 (3.6), 297 (4.3), 250 (4.2) nm.

Methyl acetylacetonato bis(2,2'-bipyridine)ruthenium (II) complex (5)

To a suspension of *cis*-bis(bpy)₂RuCl₂ (32.1 mg, 0.0663 mmol) in MeOH (10 mL), methyl acetoacetate (**4**) (27 μL, 0.247 mmol) and Et₃N (61 μL, 0.438 mmol) were added. The reaction mixture was refluxed for 8 h, and concentrated in vacuo to give a crude product. The product was purified by silica gel column chromatography using 10 % MeOH/CH₂Cl₂ (v/v) as an eluent, followed by preparative

thin-layer chromatography developed with 10 % MeOH/CH₂Cl₂ to yield compound **5** as a red solid (21.5 mg, 61.3 %).

Compound **5**; ¹H NMR (CDCl₃): δ 8.84 (d, 1H, *J* = 8.0), 8.77 (d, 1H, *J* = 4.5), 8.75–8.67 (m, 3H), 8.52 (d, 1H, *J* = 8.0), 8.18–8.10 (m, 2H), 7.84 (t, 1H, *J* = 7.5), 7.76 (t, 1H, *J* = 7.5), 7.66–7.60 (m, 4H), 7.14 (t, 1H, *J* = 6.2), 7.09 (t, 1H, *J* = 6.5) (2,2'-pyridinyl-H), 4.75 (s, 1H, CH), 3.34 (s, 3H, -OCH₃), 1.82 (s, 3H, -CH₃) ppm; ¹³C NMR (CDCl₃): δ 188.4 (C = O), 170.2 (-C=C(OH)-), 159.7, 159.3, 158.18, 158.15, 153.1, 152.6, 150.3, 149.9, 136.7, 136.3, 135.3, 134.7, 126.1, 126.0, 125.5, 125.4, 124.0, 123.8, 123.7, 123.5 (2,2'-bipyridinyl-C), 83.5 (CH), 51.6 (-OCH₃), 27.8 (-CH₃) ppm; FT-IR (KBr): ν 3429, 3061, 3010, 2949, 2760, 2659, 2482, 1595, 1508, 1456, 1419, 1274, 1180, 1064, 1014, 804, 767, 731, 657, 638 cm⁻¹; UV-Vis (in CHCl₃): λ (log ε) 527 (3.8), 372 (3.9), 297 (4.6), 250 (4.4) nm.

Preparation and characterization of LB monolayer film of compound 3

The LB monolayer films of compound **3** were prepared according to the reported procedure [7]. The photocurrent measurements were performed according to the method reported by Sakakibara and Nakatsubo [5].

Results and discussion

Synthesis of 6-*O*-[acac(bpy)₂Ru(II)]-2,3-di-*O*-myristyl cellulose (3)

Acetoacetylation of 2,3-di-*O*-myristyl cellulose (**1**) was carried out using the method for wood meal [17] to give compound **2** in 99 % yield. The characteristic β-ketoester bands at 1751 and 1720 cm⁻¹ [18] appeared in the FT-IR spectrum of compound **2** (Fig. 3b), suggesting that acetoacetylation of compound **1** proceeded smoothly. The signals derived from acetoacetyl groups around 2.20 ppm in the ¹H NMR spectrum of compound **2** and those derived from carbonyl groups at 199.9 and 166.4 ppm [15] in the ¹³C NMR spectrum also supported successful synthesis of compound **2**. The equilibrium between the enol and keto forms of the β-diketones has been reported [19]. Indeed, the equilibrium was found in the ¹H NMR spectrum of compound **2**, that is, the signals assigned to hydroxyl groups (-OH) and vinyl protons (-CH=) of the enol structure of acetoacetyl groups around 12.0 and 6.10 ppm [14, 19] were clearly found, although the signals assigned to methylene protons (-CH₂-) of the keto structure of acetoacetyl groups overlapped with the signals of cellulose ring protons and methylene groups (-OCH₂-) of myristyl groups. The DS_{acac} of compound **2** was calculated to be

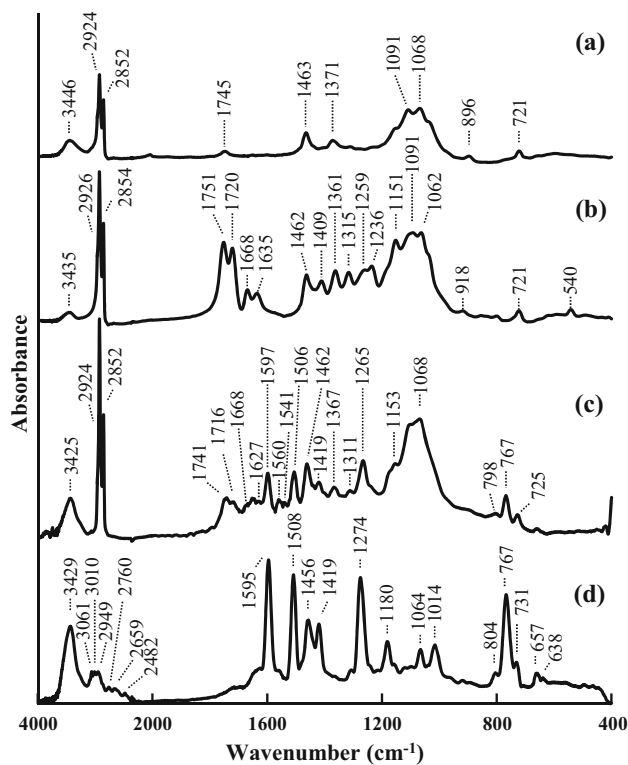


Fig. 3 FT-IR spectra of compounds (a) **1**, (b) **2**, (c) **3** and (d) **5**

1.13 by ^1H NMR method. Compound **2** was soluble in CHCl_3 , CH_2Cl_2 , $\text{ClCH}_2\text{CH}_2\text{Cl}$ and THF, but insoluble in MeOH, DMSO and DMF.

First, the coordination reaction of compound **2** with *cis*-bis(bpy) $_2$ RuCl $_2$ ·2H $_2$ O was performed under the reaction conditions (Et_3N /THF/reflux/48 h) [14]. However, compound **3** could not be obtained. The reason might be caused by poor solubility of *cis*-bis(bpy) $_2$ RuCl $_2$ ·2H $_2$ O in THF. Then, the coordination reaction of compound **2** was performed in THF-MeOH (1:2, v/v) in the presence of Et_3N under reflux for 48 h to give compound **3** as a red solid in 38.0 % yield, although the purification was a tedious and time-consuming work. Compound **5** was also prepared as an authentic sample by the reaction of methyl acetoacetate (**4**) with *cis*-bis(bpy) $_2$ RuCl $_2$ in $\text{ClCH}_2\text{CH}_2\text{Cl}$ in the presence of Et_3N . Compound **3** was subjected to FT-IR, NMR, UV-Vis and GPC measurements. The characteristic enol-form bands at 1597 1506, 1265 and 767 cm^{-1} [20] were clearly observed in the FT-IR spectrum of compound **3** (Fig. 3c). The presence of bipyridyl groups was confirmed by the ^1H NMR spectrum of compound **3**. Furthermore, the UV-Vis spectrum of compound **3** had the same profile as that of compound **5** (Fig. 4). These results suggested that the coordination reaction proceeded successfully. However, the DP of compound **2** decreased significantly during

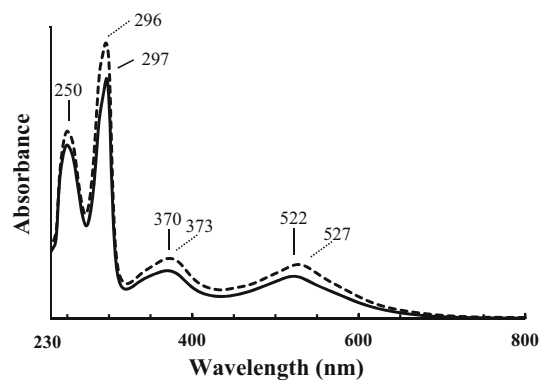


Fig. 4 UV-Vis spectra of compounds **3** (solid line) and **5** (dotted line) in CHCl_3

the coordination reaction. The $\text{DS}_{\text{Ru-complex}}$ was calculated to be 0.42 by UV-Vis method with calibration curves made by compound **5**.

Preparation and characterization of LB monolayer film of compound **3**

The surface pressure (π)-area (*A*) isotherms of compounds **1** and **3** at the air-water surface at 20 $^\circ\text{C}$ are shown in Fig. 5. The degree of slope and collapsed pressure in the isotherm of compound **3** was similar to the corresponding degree and pressure in that of compound **1**, although the limiting area of compound **3** (0.83 nm^2/AGU) was somewhat larger than that of compound **1** (0.60 nm^2/AGU), but was smaller than that of phthalocyanine-bound cellulose derivative (1.11 nm^2/AGU) reported in the previous paper [8]. These results suggested the low DP of compound **3** did not significantly influence the LB film fabrication. Indeed, LB monolayer film of compound **3** could be successfully deposited onto an indium tin oxide (ITO) electrode by a vertical dipping method at a surface pressure at deposition of 10 mN/m . The transfer ratio of the LB monolayer film was 0/1.38 (downward/upward strokes), indicating that the film is a Z-type film.

The photoelectrochemical response of the LB monolayer film of compound **3** when irradiated by the light at 510 nm is shown in Fig. 6a. A steady-state anodic photocurrent appeared upon light illumination. The action spectrum (the relationship between generating photocurrent and wavelength of the irradiated light) of film **3** from 400 to 800 nm is also shown in Fig. 6b; the spectrum at less than 400 nm could not be measured because of lack of interference filters (less than 400 nm) in our laboratory. The action spectrum was similar to the absorption spectrum of compound **3** in CHCl_3 , indicating that the ruthenium complex moieties in compound **3** serves as the photoactive species for the photocurrent generation in the region of 400–600 nm. The photocurrent density (photocurrent per

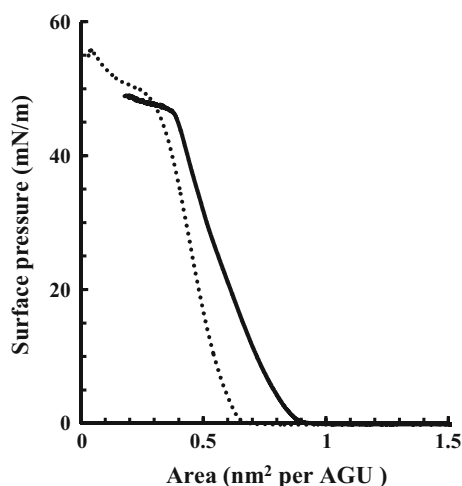


Fig. 5 Surface pressure (π)-area (A) isotherms of compounds **1** (dotted line) and **3** (solid line)

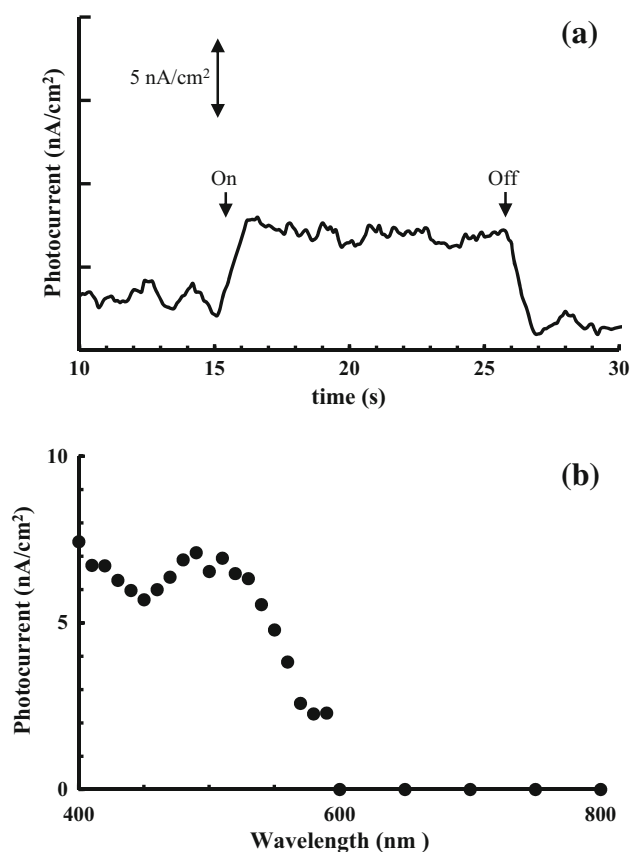


Fig. 6 **a** Photoelectrochemical response of the LB monolayer film of compound **3** with illumination at 510 nm, and **b** action spectrum of the film of compound **3**

unit area of a working electrode) of film **3** at 510 nm was found to be 7.10 nA/cm^2 , although further improvement of the photocurrent density is required.

Conclusion

6-O-[Acac(bpy)₂Ru(II)]-2,3-di-*O*-myristyl cellulose (**3**) was prepared from 2,3-di-*O*-myristyl cellulose (**1**) by two reaction steps in 37.7 % total yield. The LB monolayer film of compound **3** was successfully deposited onto ITO electrode by a vertical dipping method, suggesting the low DP of compound **3** did not influence the LB film fabrication. It showed photocurrent generation performance in the range of 400–600 nm in which LB films of other photosensitizer-bound cellulose derivatives did not generate photocurrent. Compound **3** is expected to be a third complementary material of porphyrin-bound cellulose derivative for biomaterial-based solar cells, as well as phthalocyanine-bound cellulose derivatives [7, 8] and squaraine-bound cellulose derivative [9]. It is thought that the low DP of compound **3** might be covered by the combination of other photosensitizer-bound cellulose derivatives with high DP.

References

- Kang H, Liu R, Huang Y (2012) Cellulose derivatives and graft copolymers as blocks for functional materials. *Polym Int* 62:338–344
- Wondraczek H, Kotiaho A, Fardim P, Heinze T (2011) Photoactive polysaccharides. *Carbohydr Polym* 83:1048–1061
- Edgar KJ, Buchanan CM, Debenham JS, Rundquist P, Seiler BD, Shelton MC, Tindall D (2001) Advances in cellulose ester performance and application. *Progress Polym Sci* 26:1605–1688
- Sakakibara K, Ogawa Y, Nakatsubo F (2007) First cellulose Langmuir–Blodgett films towards photocurrent generation systems. *Macromol Rapid Commun* 28:1270–1275
- Sakakibara K, Nakatsubo F (2010) Effect of central metals in the porphyrin ring on photocurrent performance of cellulose Langmuir–Blodgett films. *Macromol Chem Phys* 211:2425–2433
- Burke A, Schmidt-Mende L, Ito S, Grätzel M (2007) A novel blue dye for near-IR “dye-sensitized” solar cell applications. *Chem Commun* 234–236
- Saito Y, Takano T, Sakakibara K, Kamitakahara H, Nakatsubo F (2012) Synthesis of (zinc(II) phthalocyanine)-containing cellulose derivative using phthalocyanine-ring formation reaction. *Cellulose* 19:2105–2114
- Saito Y, Kamitakahara H, Takano T (2014) 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* 21:1885–1896
- Saito Y, Kamitakahara H, Takano T (2016) Preparation of a squaraine-bounded cellulose derivative for photocurrent generation system. *Carbohydr Res* 421:40–45
- Numata Y, Zhang S, Yang X, Han L (2013) Consensitization of ruthenium-polypyridyl dyes with organic dyes in dye-sensitized solar cells. *Chem Lett* 42:1328–1335
- Yin J-F, Velayudham M, Bhattacharya D, Lin H-C, Lu K-L (2012) Structure optimization of ruthenium photosensitizers for efficient dye-sensitized solar cells – a goal toward a “bright” future. *Coord Chem Rev* 256:3008–3035

12. Vougioulakis GC, Philippopoulos A, Stergiopoulos T, Falaras P (2011) Contributions to the development of ruthenium-based sensitizers for dye-sensitized solar cells. *Coord Chem Rev* 255:2602–2621
13. Taniguchi T, Miyashita T (1997) Photoelectrochemical responses of polymer Langmuir–Blodgett films containing tris(2,2'-bipyridine)ruthenium(II) complex. *Chem Lett* 26:295–296
14. Matsumi N, Nakamura N, Aoi K (2008) Novel bio-based polyesters derived from curcumin as an inherent natural diol monomer. *Polym J* 40:400–401
15. Edgar KJ, Arnold KM, Blount WW, Lawniczak JE, Lowman DW (1995) Synthesis and properties of cellulose acetoacetates. *Macromolecules* 28:4122–4128
16. Sullivan BP, Salmon DJ, Meyer TJ (1978) Mixed phosphine 2,2'-bipyridine complexes of ruthenium. *Inorg Chem* 17:3334–3341
17. Nasuno T, Takano T, Yoshimura T, Kamitakahara H, Nakatsubo F (2006) Preparation of acetoacetylated wood meal and its properties: part 1. Preparation of parameter and preliminary evaluation of the antifungal activity. *Holzforschung* 60:201–205
18. Yoshida Y, Isogai A (2007) Preparation and characterization of cellulose β -ketoesters prepared by homogeneous reaction with alkylketene dimers: comparison with cellulose/fatty acid esters. *Cellulose* 14:481–488
19. Wallen SL, Yonker CR, Phelps CL, Wai CM (1997) Effect of fluorine substitution, pressure and temperature on the tautomeric equilibria of acetylacetonate β -diketones. *J Chem Soc Faraday Trans* 93:2391–2394
20. El-Hendawy AM, Al-Kubaisi AH, Al-Madfa HA (1997) Ruthenium (II) and (III) bipyridine complexes and their catalytic oxidation properties for organic compounds. *Polyhedron* 16:3039–3045