

**Studies on regio-selectively substituted cellulose and chitosan
derivatives for organic light emitting diodes**

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Introduction

Cellulose is the main component of the plant cell wall and the most abundant biopolymers in nature. It is a linear homopolymer consisting of regio- and stereo-specific β -1,4-glycosidic bonded D-glucopyranose, and has three hydroxyl groups at C-2, C-3 and C-6 positions in anhydro glucose units. On the other hand, chitosan is a product derived from *N*-deacetylation of chitin which is the second most abundant natural biopolymer derived from exoskeletons of crustaceans, fungi and insects. It is a linear homopolymer consisting of regio- and stereo-specific β -1,4-glycosidic bonded D-glucosamine, and could be considered as cellulose analogue (2-amino-2-deoxy-cellulose). Much attention has been still paid for high value-added utilization of cellulose and chitin from the viewpoints of renewable resources, although they are widely used in our daily life. One of the important approaches for cellulose and chitosan-based advance materials is the utilization of their well-defined chemical structures, that is, regio-selectively substituted cellulose and chitosan derivatives as a scaffold for good arrangement of functional groups, in other words, inhibition of aggregation of functional groups. For example, Langmuir–Blodgett films of photosensitizer dye- regio-selectively bound cellulose derivatives have been reported to show good photoelectric conversion performance for biomaterial-based solar cells.²⁻⁵ However, there are a few reports about the application of regio-selectively substituted cellulose and chitosan derivatives to advance materials.

Alternative candidate of application of regio-selectively substituted cellulose and chitosan derivatives is the scaffold in organic light emitting diode (OLED) elements. Since Tang et al. reported a first multilayer OLED in 1987,⁷ OLEDs have attracted much attentions because of their potential as next generation flat-panel display. OLEDs have a simple structure in which very thin organic layers are sandwiched between metal electrodes, and when OLEDs are applied a voltage, holes and electrons are injected from cathode and anode, respectively. The injected charges are transferred into an emitting layer through each layer and recombine to form excitons, resulting the emission assigned to radiative transition of excitons occurs. Generally, an emitting layer of OLEDs consists of emitters (guest materials) and matrix materials (host materials) to disperse the emitters for inhibiting concentration quenching.⁸ As host materials, electron-donating compounds such as carbazole⁹ and triphenylamine derivatives¹⁰ are mainly used, whereas guest materials are classified into three types¹¹; fluorescence materials used in first generation fluorescence OLEDs,¹² phosphorescence materials used in second generation phosphorescence OLEDs,¹³ and thermally activated delayed fluorescence (TADF) materials used in third generation TADF OLEDs.¹⁴ Host and guest materials form aggregation easily because they are π -conjugated compounds. However, the aggregation causes the reduction of OLEDs performance.¹⁵⁻¹⁷ In other words, inhibiting aggregation of host and guest

materials is essential to OLEDs with high performance. Therefore, regio-selectively substituted cellulose and chitosan derivatives are expected as a scaffold material for OLEDs. Indeed, 6-*O*-[4-(9H-carbazol-9-yl)butyl]-2,3-di-*O*-methyl cellulose has been reported for OLED applications.¹⁸ However, the performance of such devices is far from satisfactory, and there are no reports of chitosan derivatives application to my knowledge.

Then, the thesis describes new synthetic methods of cellulose and chitosan isothiocyanate derivatives which are useful intermediates for the synthesis of regio-selectively substituted cellulose and chitosan derivatives (Chapter 1 and 2), and the preparation and evaluation of OLEDs element-bound cellulose and chitosan derivatives towards OLEDs using cellulose and chitosan derivatives (Chapter 3, 4 and 5). Furthermore, as the derived studies, the preparation and evaluation of new TADF emitter for OLEDs (Chapter 6) and photosensitizer-bound chitosan derivative for dye-sensitizer solar cells (Chapter 7).

Abstract

Chapter 1

Synthetic method of cellulose isothiocyanate derivatives for regio-selectively substituted cellulose derivatives

6-Isothiocyanato-2,3-di-*O*-decanoyl-6-deoxycellulose (**1**) was prepared from 6-azido-2,3-di-*O*-decanoyl-6-deoxycellulose (**2**) by tandem Staudinger/aza-Witting reaction using CS₂ and triphenylphosphine. Compound **1** was a useful reaction intermediate for regio-selectively substituted cellulose derivative, because it had high reactivity with amine. Indeed, the reaction of compound **1** with 4-aminobenzo-15-crown-5-ether proceeded to afford 6-*N*-((benzo-15-crown-5)-4'-yl)thioureido-2,3-di-*O*-decanoyl-6-deoxycellulose (**3**) which was one of the functional cellulose derivatives. Furthermore, compound **3** was also obtained by the one pot reaction with compound **2** with 4-aminobenzo-15-crown-5-ether using CS₂ and triphenylphosphine.

Chapter 2

Synthetic method for chitosan isothiocyanate derivatives for regio-selectively substituted chitosan derivatives

A facile and safe synthetic method for 3,6-di-*O*-acyl chitosan isothiocyanate (**4**) from chitosan by two

reaction steps (*N*-phenylcarbaoylation, and the following acylation) was established. Amino groups of chitosan was converted to *N*-phenylthioureido groups in the former reaction, and the *N*-phenylthioureido groups was further done to isothiocyanate groups via *N,N*-(acyl)phenylthioureido groups in the latter reaction. Compound **4** was a useful reaction intermediate for regio-selectively substituted chitosan derivative, because it reacted with various amine (aniline, *n*-propylamine, piperidine) easily.

Chapter 3

Triphenylamine-bound chitosan derivative for a host material of OLEDs

Triphenylamine (TPA) -bound chitosan derivative (**5**) with DS_{TPA} of 0.70 was designed and prepared by the reaction of hexanoyl chitosan isothiocyanate (**2a**) with 4-aminotriphenylamine for a host material of solution-processed OLEDs. The spin-coated film from compound **5** (host material) and Ir(*ppy*)₃ (guest material) showed efficient Förster energy transfer from compound **5** to Ir(*ppy*)₃. OLED device using compound **5** and Ir(*ppy*)₃ in the emitting layer showed green emission when the voltage was applied to that. This is a first application of chitosan derivative to OLED elements.

Chapter 4, 5, 6

The details will be published latter.

Chapter 7

Porphyrin-bound chitosan derivative for a sensitizer of dye sensitized solar cells

Porphyrin-bound chitosan derivative (**6**) was prepared from decanoyl chitosan isothiocyanate (**2b**). The LB monolayer film of compound **6** exhibited a good photon-to-electron conversion performance in the range from 400 to 450 nm. This result suggested that compound **6** could be used as a promising photon-to-electron conversion material.

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