



Contents lists available at ScienceDirect

# Journal of Photochemistry and Photobiology A: Chemistry

journal homepage: [www.elsevier.com/locate/jphotochem](http://www.elsevier.com/locate/jphotochem)

## Synthesis of zinc chlorin–spiropyran dyads and their self-aggregation properties

Tomohiro Miyatake<sup>a,b,\*</sup>, Yuki Takamori<sup>a</sup>, Kanae Yamaguchi<sup>a</sup><sup>a</sup> Department of Materials Chemistry, Ryukoku University, Otsu, Shiga 520-2194, Japan<sup>b</sup> Innovative Materials and Processing Research Center, Ryukoku University, Otsu, Shiga 520-2194, Japan

## ARTICLE INFO

## Article history:

Received 16 March 2015

Received in revised form 12 June 2015

Accepted 16 June 2015

Available online 26 June 2015

## Keywords:

Chlorophyll

Light-harvesting antenna

Photochromism

Photosynthesis

Self-aggregation

Spiropyran

## ABSTRACT

A photochromic spiropyran moiety has been covalently linked to a self-aggregative zinc analog of chlorophyllous pigments. Semi-synthetic zinc chlorins possessing a 3<sup>1</sup>-hydroxy- or 3<sup>1</sup>-methoxy group were used as the chlorophyll model, and the spiropyran part was introduced at the 17-position of the chlorin macrocycle. The spiropyran moiety reversibly isomerized to its opened merocyanine form in the dyads. The photoisomerization induced drastic change in electric dipole moment of the side chain, and photoswitchable chlorophyll aggregation was found in the pigment conjugates.

© 2015 Elsevier B.V. All rights reserved.

### 1. Introduction

Chlorophylls are metallo-tetrapyrrolic compounds that work in light-harvesting and energy conversion in early events of photosynthesis [1]. In light-harvesting antennas and reaction centers chlorophyll molecules are adequately arranged for efficient intermolecular energy or electron transfers [2]. Generally, chlorophyll molecules formed pigment–protein complexes in the photosynthetic apparatuses, and the proteins contribute to the organization of the photosynthetic pigments. Apart from such pigment–protein complexes, self-aggregates of chlorophyllous pigments were found in a light-harvesting antenna system of green photosynthetic bacteria [3–5]. The supramolecular antenna system is called a chlorosome, in which a number of bacteriochlorophyll(BChl) s-c, d, e and f molecules self-aggregate without any assistance of proteins (left drawing of Fig. 1). The chlorosomal chlorophylls possess a hydroxy group at the 3<sup>1</sup>-position, and the functional group makes an intermolecular hydrogen bond with the 13<sup>1</sup>-oxo group of the neighboring chlorophyll and a coordination bond with the central magnesium of the third molecule [3,4,6]. The specific intermolecular interactions as well as the  $\pi$ – $\pi$  stacking result in the formation of J-aggregate with showing largely red-

shifted Qy absorption band at around 720–740 nm compared to their original Qy band at around 650–660 nm. Interestingly, the chlorosomal aggregate can be reproduced in non-polar organic solvent such as hexane [7,8]. The in vitro model studies of BChl aggregate encouraged us to make artificial chlorophyllous aggregate by using synthetic model pigments possessing a hydroxy group. Semi-synthetic model pigments, zinc chlorins with 3<sup>1</sup>-hydroxy group (right drawing of Fig. 1), successfully gave a chlorosomal model with the red-shifted Qy absorption band as well as exciton coupled circular dichroism (CD) signals [8–17]. In addition, the artificial aggregates actually acted as an effective light-harvesting system showing fast energy transfer among the assembled pigments [12,13]. The in vitro studies of chlorosomal chlorophyll models [14–17] as well as pigment modification studies on in vivo aggregates [18] indicated that the side chain at the 17-propionate group affects the supramolecular structure of the chlorosomal aggregate. The molecular modeling [19–21] and solid state NMR [22] studies on the BChl aggregates suggest that chlorosomal BChls form inverse micelle like rod structure in which the side chain at the 17-position oriented toward the outside of the assembly. The modified chlorophyll molecules with a hydrophilic oligooxyethylene group were prepared, and the amphiphilic zinc chlorins formed stable micelle like aggregate in aqueous media [9,23]. The hydrophilic oxyethylene group might be oriented toward the outside of the aggregate, and the length of the oxyethylene chain affected the self-aggregation of the chlorophyllous pigments. Therefore, the chemical structure of the 17-side

\* Corresponding author at: Department of Materials Chemistry, Ryukoku University, Otsu, Shiga 520-2194, Japan. Fax: +81 77 543 7483.  
E-mail address: [miyatake@rins.ryukoku.ac.jp](mailto:miyatake@rins.ryukoku.ac.jp) (T. Miyatake).

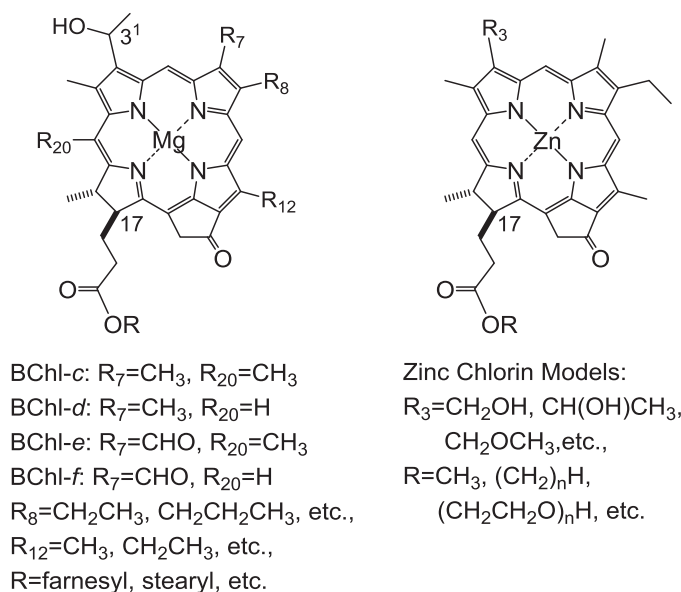


Fig. 1. Structure of bacteriochlorophylls-c, d, e, f and zinc chlorin models.

chain is one of the important factors of the chlorophyll self-assembly.

Here, we prepared novel chlorophyll derivatives possessing a photochromic spiropyran moiety at the 17-position of zinc chlorin (Scheme 1). Photochromic compounds are photofunctional materials whose colors are reversibly changeable by light irradiation. Azobenzenes [24], diarylethenes [25] and spiropyrans [26] are representative photochromic compounds, and many other kinds of photochromic compounds have been studied [27]. Photoirradiation to these photochromic compounds induces some changes in not only their optical properties but also their molecular shapes, their electronic dipole moments, etc. Therefore, photochromic compounds are promising functional building blocks providing photoresponsible supramolecular self-assemblies [28–32]. Combinations of the photochromic compounds with other kinds of pigments such as naphthalene [33], fluorescein [34], Bodipy [35], and porphyrins [36,37] were performed. These photochromic dyads showed photoswitchable physical property changes such as photo-triggered energy transfer, etc. The spiropyran photochromism (Fig. 2) was introduced in our chlorophyll conjugates. The closed form consists of indoline and benzopyran parts that are bound via spiro junction. UV irradiation of the spiropyran induces a ring opening reaction with heterolytic C–O bond cleavage to afford merocyanine structure, which has the zwitterionic or the quinoidal resonance forms. The resulting opened isomer has extended  $\pi$ -conjugation with an absorption band at around 500–600 nm, and photochemical isomerization by VIS light irradiation as well as thermal reaction gave the original closed spiropyran form. It should be pointed out that the photochromic reaction of spiropyran accompanies significant change in its electric dipole moment. The opened merocyanine form has larger dipole moment than the parent spiropyran form. The unique physicochemical character in spiropyran photochromism has been applied to functional materials such as light-triggered aggregation of gold nanoparticle [38], photoswitchable wettability changes on material surfaces [39], light-gated nanochannels [40], optical ion sensors [41], light-induced proton dissociation [42], photo-switched DNA-binding [43], etc. In our chlorophyll–spiropyran conjugate, the alcoholic spiropyran chromophore **1** was esterified at the 17-propionic side chain of the chlorin macrocycle. The polarity change at the 17-position of the chlorin is exploited for the photonic control of the self-aggregation of chlorophyllous

pigments. In the present study, the photoactive (zinc) chlorin–spiropyran dyads were synthesized and the self-aggregation properties were examined.

## 2. Experimental

### 2.1. Apparatuses and materials

Visible absorption and fluorescence spectra were recorded by Shimadzu UV-3100 spectrophotometer and Hitachi F-4500 fluorescence spectrophotometer, respectively.  $^1H$  NMR spectra were measured with a Bruker DPX-400 spectrophotometer with tetramethylsilane as an internal standard. Fast atomic bombardment (FAB)-mass spectra (MS) were recorded with a JEOL GCmatell spectrometer. MS samples were dissolved in dichloromethane (DCM), and 3-nitrobenzyl alcohol was used as a matrix. High performance liquid chromatography (HPLC) was performed with a Shimadzu LC-10AS pump and an SPD-M10AV diode array detector. Melting points were recorded with a Yanagimoto micro melting apparatus and were uncorrected.

Methyl pyropheophorbide-*a* (3-vinyl-chlorin) was prepared according to reported procedures [8,44]. 1-(2-Hydroxyethyl)-3,3-dimethylindolino-6'-nitrobenzopyrylospiran **1** and 1-ethyl-3-(1-aminopropyl) carbodiimide hydrochloride (EDC-HCl) were purchased from Tokyo Kasei Kogyo Co., Ltd., and commercially available acetone, DCM, methanol, toluene were purchased from Nacalai Tesque. Synthetic solvents, DCM and toluene, were distilled before use. Other reaction reagents were purchased from Sigma–Aldrich. Flash column chromatography (FCC) was performed with silica gel (Merck, Kieselgel 60, 40–63  $\mu$ m, 230–400 mesh). HPLC was done with a packed ODS column (Cosmosil 5C18-ARII, Nacalai Tesque, 10  $\phi$   $\times$  250 mm). Spectroscopic-grade solvents for optical measurements were purchased from Nacalai Tesque and used without further purification.

### 2.2. General procedures

All synthetic procedures were done in the dark under nitrogen. Oxidation of the 3-vinyl group to the 3-formyl group [8], reduction of the 3-formyl group to the 3-hydroxymethyl group [8], hydration of the 3-vinyl group to the 3-(1-hydroxyethyl) group [45] and zinc metalation [8] were performed according to reported procedures.

### 2.3. Condensation of alcohols to form ether

Chlorin with the 3-hydroxymethyl group (160  $\mu$ mol) was dissolved with methanol (25 mL), and concentrated sulfuric acid (5 mL) was added to the solution at 0  $^\circ$ C. The reaction mixture was stirred at 50  $^\circ$ C for 2 days and poured into ice-chilled water. The product was extracted with DCM and washed with saturated aqueous  $NaHCO_3$ , water and dried with anhydrous  $Na_2SO_4$ . The product was purified with FCC (10%  $Et_2O/DCM$ ) and recrystallization (DCM and hexane) to give 3-methoxymethyl-chlorin.

### 2.4. Esterification of 17-propionic acid group of chlorin with alcoholic spiropyran **1**

Chlorin with the 17-propionic acid chain (100  $\mu$ mol) was dissolved with dried DCM (20 mL). EDC-HCl (1.50 mmol, 288 mg) and *N,N*-dimethyl-4-aminopyridine (DMAP: 1.50 mmol, 183 mg) were added to the solution with stirring at 0  $^\circ$ C. The excess amount (1.5 eq.) of **1** (146  $\mu$ mol, 51.2 mg) was added to the solution and stirred for 12 h. The reaction mixture was poured into 2% HCl and DCM. The organic layer was separated and washed with 4%  $NaHCO_3$ , water and dried with  $Na_2SO_4$ . The product was purified

Download English Version:

<https://daneshyari.com/en/article/26463>

Download Persian Version:

<https://daneshyari.com/article/26463>

[Daneshyari.com](https://daneshyari.com)