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# Synthesis of Zinc Chlorin–Spiropyran Dyads and Their Self-Aggregation Properties

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### **Graphical abstract**

### Highlights

- Photochromic spiropyran was appended to self-aggregative chlorophyll derivatives.
- Spiropyran moiety in the chlorophyll derivatives reversibly isomerized by photoirradiation.
- Open form of spiropyran, merocyanine form, quenched fluorescence emission of the chlorophyll moiety.
- Self-aggregation properties of zinc 3<sup>1</sup>-hydroxy-chlorins were affected by isomerization of spiropyran moiety.
- Photo-triggered reversible self-aggregation of zinc 3<sup>1</sup>-methoxy-chlorin was observed.

#### Abstract

A photochromic spiropyran moiety has been covalently linked to a self-aggregative zinc analogue of chlorophyllous pigments. Semi-synthetic zinc chlorins possessing a  $3^1$ -hydroxy- or  $3^1$ -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.

*Keywords:* Chlorophyll, Light-harvesting antenna, Photochromism, Photosynthesis, Self-aggregation, Spiropyran

### 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 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 are promising functional building blocks providing photoresponsible compounds 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], photoswitched 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 section

#### 2.1. Apparatuses and materials

Visible absorption and fluorescence spectra were recorded by Shimadzu UV-3100 spectrophotometer and Hitachi F-4500 fluorescence spectrophotometer, respectively. <sup>1</sup>H 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 GCmateII 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 μm, 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°C. The reaction mixture was stirred at 50°C for 2 days and poured into ice-chilled water. The product was extracted with DCM and washed with saturated aqueous NaHCO<sub>3</sub>, water and dried with anhydrous Na<sub>2</sub>SO4. The product was purified with FCC (10% Et<sub>2</sub>O / 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°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<sub>3</sub>, water and dried with Na<sub>2</sub>SO<sub>4</sub>. The product was purified with FCC (12–16% Et<sub>2</sub>O / DCM) and recrystallization (DCM and hexane) to give the corresponding spiropyran-appended chlorin.

### 2.5. Transesterification of methyl ester group of chlorin with alcoholic spiropyran 1

Chlorins with a methyl ester group at the 17-propionic side chain (42.0  $\mu$ mol) were dissolved in distilled toluene (15 mL), and **1** (63.0  $\mu$ mol, 22.1 mg) and bis(di-*n*-butylchlorotin) oxide (126 mmol, 69.7 mg) were added. The mixture was refluxed for 18 h after which the solvent was evaporated. The crude reaction mixture was purified with FCC (16% Et<sub>2</sub>O / DCM) and recrystallization (DCM and hexane) to give the corresponding spiropyran-appended chlorin.

### 2.6. Spectral Data

### 2.6.1. Spiropyran-appended 3-devinyl-3-hydroxymethyl-pyropheophorbide-a (2)

Esterification and reduction of the 3-formyl group gave black solids of **2** in 49% yield (FCC 16% Et<sub>2</sub>O/CH<sub>2</sub>Cl<sub>2</sub>). Mp 159–163°C; vis (CH<sub>2</sub>Cl<sub>2</sub>)  $\lambda_{max}$  662 (relative intensity, 0.47), 605 (0.11), 537 (0.12), 505 (0.13), 410 nm (1.00); <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta(R/S)$  9.48/9.44, 9.46/9.43, 8.55/8.54 (each 1H, s, chlorin (Chl)-5-,10-,20-H), 7.91/7.90 (1H, dd, J = 3, 9 Hz, benzopyran (Bp)-7-H), 7.82/7.68 (1H, d, J = 3 Hz, Bp-5-H), 7.06/6.91 (1H, dt, J = 1, 8 Hz, indoline (In)-6-H), 6.98/6.97 (1H, dt, J = 7, 1 Hz, In-4'-H), 6.80/6.69 (1H, dt, J = 1, 7 Hz, In-5'-H), 6.61/6.60 (1H, d, J = 9 Hz, In-7-H), 6.57/6.30 (1H, d, J = 10 Hz, Bp-4-H), 6.45/6.40 (1H, d, J = 8 Hz, Bp-8-H), 5.90/5.88 (2H, s, Chl-3-CH<sub>2</sub>), 5.58/5.37 (1H, d, J = 1, 7 Hz, Chl-18-H), 5.05/5.04 (each 1H, d, J = 20 Hz, Chl-13<sup>2</sup>-H<sub>2</sub>), 4.40/4.38 (1H, dt, J = 1, 7 Hz, Chl-18-H),

4.28–4.21 (1H, m, Chl-17-H), 4.12-3.90 (2H, m, -COOCH<sub>2</sub>), 3.68/3.66 (2H, q, J = 8 Hz, Chl-8-CH<sub>2</sub>), 3.64/3.62, 3.42/3.41, 3.25/3.24 (each 3H, s, Chl-2-, 7-, 12-CH<sub>3</sub>), 3.16–2.97 (2H, m, -NCH<sub>2</sub>), 2.62–2.49, 2.44–1.97 (1H+3H, m, Chl-17-CH<sub>2</sub>CH<sub>2</sub>), 1.77/1.75 (3H, d, J = 7 Hz, Chl-18-CH<sub>3</sub>), 1.68/1.67 (3H, t, J = 8 Hz, Chl-8<sup>1</sup>-CH<sub>3</sub>), 1.15/1.12, 1.00./0.94 (each 3H, s, In-3-CH<sub>3</sub>), 0.30 (1H, br, Chl-NH), -1.80/–1.81 (1H, s, Chl-NH); MS (FAB) found: m/z = 873. Calcd for C<sub>52</sub>H<sub>53</sub>N<sub>6</sub>O<sub>7</sub>: MH<sup>+</sup>, 873.

### 2.6.2. Spiropyran-appended $(3^{1}R)$ 3-devinyl-3-(1-hydroxyethyl)-pyropheophorbide-a (3R)

Transesterification gave black solids of **3R** in 41% yield (FCC 16% Et<sub>2</sub>O/CH<sub>2</sub>Cl<sub>2</sub>). Mp 128–132°C; vis (CH<sub>2</sub>Cl<sub>2</sub>)  $\lambda_{max}$  661 (relative intensity, 0.38), 605 (0.17), 537 (0.12), 505 (0.12), 410 (0.90), 347 nm (1.00); <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta(R/S)$  9.69/9.68, 9.52/9.50, 8.52/8.51 (each 1H, s, Chl-5-, 10-, 20-H), 7.90/7.91 (1H, dd, J = 3, 9 Hz, Bp-7-H), 7.81/7.68 (1H, d, J = 3 Hz, Bp-5-H), 7.06/6.91 (1H, dt, J = 1, 8 Hz, In-6-H), 6.98/6.98 (1H, dd, J = 1, 7 Hz, In-4-H), 6.80/6.70 (1H, dt, J = 1, 7 Hz, In-5-H), 6.61/6.60 (1H, d, J = 9 Hz, Bp-8-H), 6.55/6.29 (1H, d, J = 10 Hz, Bp-4-H), 6.45 (1H, m, Chl-3-CH), 6.45/6.40 (1H, d, J = 8 Hz, In-7-H), 5.58/5.37 (1H, d, J = 10 Hz, Bp-3-H), 5.20/5.07, 5.15/5.06 (each 1H, d, J = 20 Hz, Chl-13<sup>2</sup>-H<sub>2</sub>), 4.39 (1H, dq, J = 1, 7 Hz, Chl-18-H), 4.27 (1H, m, Chl-17-H), 4.10–3.84 (2H, m, COOCH<sub>2</sub>), 3.69/3.68 (2H, q, J = 8 Hz, Chl-8-CH<sub>2</sub>), 3.67/3.65, 3.42/3.43, 3.26/3.26 (each 3H, s, Chl-2-, 7-, 12-CH<sub>3</sub>), 3.20–2.97 (2H, m, NCH<sub>2</sub>), 2.63–1.96 (4H, m, Chl-17-CH<sub>2</sub>CH<sub>2</sub>), 2.15/2.14 (3H, d, J = 7 Hz, Chl-3<sup>1</sup>-CH<sub>3</sub>), 1.78/1.76 (3H, d, J = 7 Hz, Chl-18-CH<sub>3</sub>), 0.39 (1H, br, Chl-NH), -1.79/-1.80 (1H, s, Chl-NH); MS (FAB) found: m/z = 887. Calcd for C<sub>53</sub>H<sub>55</sub>N<sub>6</sub>O<sub>7</sub>: MH<sup>+</sup>, 887.

### 2.6.3. Spiropyran-appended $(3^{1}S)$ 3-devinyl-3-(1-hydroxyethyl)-pyropheophorbide-a (3S)

Transesterification gave black solids of 3S in 45% yield (FCC 16% Et<sub>2</sub>O/CH<sub>2</sub>Cl<sub>2</sub>). Mp

125–128°C; vis (CH<sub>2</sub>Cl<sub>2</sub>)  $\lambda_{max}$  661 (relative intensity, 0.38), 605 (0.17), 537 (0.12), 505 (0.12), 410 (0.90), 347 nm (1.00); <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ(*R/S*) 9.69/9.66, 9.46/9.44, 8.49/8.49 (each 1H, s, Chl-5-, 10-, 20-H), 7.91/7.89 (1H, dd, *J* = 3, 9 Hz, Bp-7-H), 7.81/7.67 (1H, d, *J* = 3 Hz, Bp-5-H), 7.07/6.92 (1H, dt, *J* = 1, 8 Hz, In-6-H), 6.98/6.98 (1H, dd, *J* = 1, 7 Hz, In-4-H), 6.81/6.70 (1H, dt, *J* = 1, 7 Hz, In-5-H), 6.61/6.59 (1H, d, *J* = 9 Hz, Bp-8-H), 6.56/6.29 (1H, d, *J* = 10 Hz, Bp-4-H), 6.46/6.38 (1H, d, *J* = 8 Hz, In-7-H), 6.36/6.36 (1H, q, *J* = 7 Hz, Chl-3-CH), 5.55/5.38 (1H, d, *J* = 10 Hz, Bp-3-H), 5.17/5.04, 5.12/5.05 (each 1H, d, *J* = 20 Hz, Chl-13<sup>2</sup>-H<sub>2</sub>), 4.38 (1H, dq, *J* = 1, 7 Hz, Chl-18-H), 4.23 (1H, m, Chl-17-H), 4.11–3.90 (2H, m, COOCH<sub>2</sub>), 3.68/3.66 (2H, q, *J* = 8 Hz, Chl-8-CH<sub>2</sub>), 3.63/3.61, 3.39/3.38, 3.24/3.23 (each 3H, s, Chl-2-, 7-, 12-CH<sub>3</sub>), 3.11–2.97 (2H, m, NCH<sub>2</sub>), 2.65–1.96 (4H, m, Chl-17-CH<sub>2</sub>CH<sub>2</sub>), 2.13/2.12 (3H, d, *J* = 7 Hz, Chl-3<sup>1</sup>-CH<sub>3</sub>), 1.75/1.73 (3H, d, *J* = 7 Hz, Chl-18-CH<sub>3</sub>), 1.68/1.67 (3H, t, *J* = 8 Hz, Chl-8<sup>1</sup>-CH<sub>3</sub>), 1.15/1.12, 1.00./0.94 (each 3H, s, In-3-CH<sub>3</sub>), 0.32 (1H, br, Chl-NH), -1.83/–1.84 (1H, s, Chl-NH); MS (FAB) found: *m*/*z* = 887. Calcd for C<sub>53</sub>H<sub>55</sub>N<sub>6</sub>O<sub>7</sub>: MH<sup>+</sup>, 887.

#### 2.6.4. Spiropyran-appended 3-devinyl-3-methoxymethyl-pyropheophorbide-a (4)

Esterification gave black solids of **4** in 71% yield (FCC 12% Et<sub>2</sub>O/CH<sub>2</sub>Cl<sub>2</sub>). Mp 132–136°C; vis (CH<sub>2</sub>Cl<sub>2</sub>)  $\lambda_{max}$  661 (relative intensity, 0.44), 603 (0.07), 535 (0.09), 502 (0.09), 410 nm (1.00); <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta(R/S)$  9.55/9.52, 9.47/9.46, 8.56/8.54 (each 1H, s, Chl-5-, 10-, 20-H), 7.92/7.92 (1H, dd, J = 3, 9 Hz, Bp-7-H), 7.83/7.73 (1H, d, J = 3 Hz, Bp-5-H), 7.06/6.91 (1H, dt, J = 1, 8 Hz, In-6-H), 6.98/6.97 (1H, dd, J = 1, 8 Hz, In-4-H), 6.80/6.69 (1H, dt, J = 1, 7 Hz, In-5-H), 6.63/6.61 (1H, d, J = 9 Hz, Bp-8-H), 6.58/6.35 (1H, d, J = 10 Hz, Bp-4-H), 6.46/6.44 (1H, d, J = 8 Hz, In-7-H), 5.72/5.71 (2H, s, Chl-3-CH<sub>2</sub>), 5.62/5.38 (1H, d, J = 10 Hz, Bp-3-H), 5.22/5.17, 5.09/5.07 (each 1H, d, J = 20 Hz, Chl-13<sup>2</sup>-H<sub>2</sub>), 4.40 (1H, dq, J = 1, 7 Hz Chl-18-H), 4.28 (1H, m, Chl-17-H), 4.15–3.90 (2H, m, COOCH<sub>2</sub>), 3.71/3.71 (2H, q, J = 8 Hz, Chl-8-CH<sub>2</sub>), 3.70/3.70, 3.69/3.67, 3.42/3.41, 3.27/3.27 (each 3H, s, Chl-2-, 7-, 12-CH<sub>3</sub>)

3-COCH<sub>3</sub>), 3.24–2.95 (2H, m, NCH<sub>2</sub>), 2.58–1.95 (4H, m, Chl-17-CH<sub>2</sub>CH<sub>2</sub>), 1.79/1.77 (3H, d, J = 7 Hz, Chl-18-CH<sub>3</sub>), 1.70/1.69 (3H, t, J = 8 Hz, Chl-8<sup>1</sup>-CH<sub>3</sub>), 1.16/1.13, 1.00./0.93 (each 3H, s, In-3-CH<sub>3</sub>), 0.41 (1H, br, Chl-NH), -1.72 (1H, s, Chl-NH); MS (FAB) found: m/z = 887. Calcd for C<sub>53</sub>H<sub>55</sub>N<sub>6</sub>O<sub>7</sub>: MH<sup>+</sup>, 887.

#### 2.6.5. Spiropyran-appended zinc 3-devinyl-3-hydroxymethyl-pyropheophorbide-a (**Zn2**)

Zinc metalation gave dark green solids of **Zn2** in 93% yield (HPLC: retention time was 6.6 min.). Mp 235–238°C; vis (CH<sub>2</sub>Cl<sub>2</sub>)  $\lambda_{max}$  650 (relative intensity, 0.72), 604 (0.10), 564 (0.07), 520 (0.05), 424 nm (1.00); <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta(R/S)$  9.53/9.50, 9.32/9.29, 9.37/9.35 (each 1H, s, Chl-5-, 10-, 20-H), 7.92/7.90 (1H, dd, *J* = 3, 9 Hz, Bp-7-H), 7.79/7.65 (1H, d, *J* = 3 Hz, Bp-5-H), 7.03/6.92 (1H, dt, *J* = 1, 8 Hz, In-6-H), 6.98/6.97 (1H, dd, *J* = 1, 8 Hz, In-4-H), 6.78/6.70 (1H, dt, *J* = 1, 7 Hz, In-5-H), 6.61/6.59 (1H, d, *J* = 9 Hz, Bp-8-H), 6.41/6.41 (1H, d, *J* = 8 Hz, In-7-H), 6.40/6.06 (1H, d, *J* = 10 Hz, Bp-4-H), 5.76/5.75 (2H, s, 3-CH<sub>2</sub>), 5.76/5.50 (1H, d, *J* = 10 Hz, Bp-3-H), 5.16/5.13, 5.11/5.07 (each 1H, d, *J* = 20 Hz, Chl-13<sup>2</sup>-H<sub>2</sub>), 4.36 (1H, m, Chl-18-H), 4.23 (1H, m, Chl-17-H), 4.05–3.82 (2H, m, COOCH<sub>2</sub>), 3.74/3.76 (2H, q, *J* = 8 Hz, Chl-8-CH<sub>2</sub>), 3.65/3.62, 3.35/3.34, 3.31/3.27 (each 3H, s, Chl-2-, 7-, 12-CH<sub>3</sub>), 3.21–3.08 (2H, m, NCH<sub>2</sub>), 2.58–1.99 (4H, m, Chl-17-CH<sub>2</sub>CH<sub>2</sub>), 1.80 (3H, d, *J* = 7 Hz, Chl-18-CH<sub>3</sub>), 1.71/1.69 (3H, t, *J* = 8 Hz, Chl-8<sup>1</sup>-CH<sub>3</sub>), 1.13/1.08, 0.95/0.85 (each 3H, s, In-3-CH<sub>3</sub>); MS (FAB) found: *m*/z = 935. Calcd for C<sub>52</sub>H<sub>51</sub>N<sub>6</sub>O<sub>7</sub>Zn: MH<sup>+</sup>, 935.

2.6.6. Spiropyran-appended zinc  $(3^{1}R)$  3-devinyl-3-(1-hydroxyethyl)-pyropheophorbide-a (Zn3R)

Zinc metalation gave dark green solids of **Zn3R** in 92% yield (HPLC: retention time was 6.4 min.). Mp 193–196°C; vis (CH<sub>2</sub>Cl<sub>2</sub>)  $\lambda_{max}$  648 (relative intensity, 0.75), 601 (0.17), 554 (0.11), 512 (0.10), 421 nm (1.00); <sup>1</sup>H NMR (10%CD<sub>3</sub>OD/CDCl<sub>3</sub>)  $\delta$ (*R/S*) 9.54/9.53, 9.45/9.44,

8.31/8.30 (each 1H, s, Chl-5-, 10-, 20-H), 7.92/7.91 (1H, dd, J = 3, 9 Hz, Bp-7-H), 7.83/7.72 (1H, d, J = 3 Hz, Bp-5-H), 7.04/6.94 (1H, dt, J = 1, 8 Hz, In-6-H), 6.98/6.98 (1H, dd, J = 1, 7 Hz, In-4-H), 6.80/6.73 (1H, dt, J = 1, 7 Hz, In-5-H), 6.61/6.61 (1H, d, J = 9 Hz, Bp-8-H), 6.57/6.34 (1H, d, J = 10 Hz, Bp-4-H), 6.43/6.39 (1H, d, J = 8 Hz, In-7-H), 6.19 (1H, m, Chl-3-CH), 5.60/5.43 (1H, d, J = 10 Hz, Bp-3-H), 5.12/5.04, 5.10/5.03 (each 1H, d, J = 20 Hz, Chl-13<sup>2</sup>-H<sub>2</sub>), 4.35/4.35 (1H, dq, J = 1, 7 Hz, Chl-18-H), 4.22 (1H, m, Chl-17-H), 4.04–3.84 (2H, m, COOCH<sub>2</sub>), 3.75/3.75 (2H, q, J = 8 Hz, Chl-8-CH<sub>2</sub>), 3.66/3.64, 3.64/3.63, 3.41/3.41 (each 3H, s, Chl-2-, 7-, 12-CH<sub>3</sub>), 3.23–2.99 (2H, m, NCH<sub>2</sub>), 2.57–1.89 (4H, m, Chl-17-CH<sub>2</sub>CH<sub>2</sub>), 2.07/2.06 (3H, d, J = 7 Hz, Chl-3<sup>1</sup>-CH<sub>3</sub>), 1.79/1.77 (3H, d, J = 7 Hz, Chl-18-CH<sub>3</sub>), 1.72/1.70 (3H, t, J = 8 Hz, Chl-8<sup>1</sup>-CH<sub>3</sub>), 1.16/1.14, 1.00./0.97 (each 3H, s, In-3-CH<sub>3</sub>); MS (FAB) found: m/z = 949. Calcd for C<sub>53</sub>H<sub>53</sub>N<sub>6</sub>O<sub>7</sub>Zn: MH<sup>+</sup>, 949.

2.6.7. Spiropyran-appended zinc (3<sup>1</sup>S) 3-devinyl-3-(1-hydroxyethyl)-pyropheophorbide-a (**Zn3S**)

Zinc metalation gave dark green solids of **Zn3S** in 94% yield (HPLC: retention time was 6.6 min.). Mp 192–195°C; vis (CH<sub>2</sub>Cl<sub>2</sub>)  $\lambda_{max}$  648 (relative intensity, 0.75), 601 (0.17), 554 (0.11), 512 (0.10), 421 nm (1.00); <sup>1</sup>H NMR (10%CD<sub>3</sub>OD/CDCl<sub>3</sub>)  $\delta(R/S)$  9.52/9.52, 9.51/9.51, 8.30/8.29 (each 1H, s, Chl-5-, 10-, 20-H), 7.93/7.92 (1H, dd, J = 3, 9 Hz, Bp-7-H), 7.85/7.75 (1H, d, J = 3 Hz, Bp-5-H), 7.07/6.97 (1H, dt, J = 1, 8 Hz, In-6-H), 7.00/7.00 (1H, dd, J = 1, 7 Hz, In-4-H), 6.81/6.76 (1H, dt, J = 1, 7 Hz, In-5-H), 6.64/6.64 (1H, d, J = 9 Hz, Bp-8-H), 6.61/6.40 (1H, d, J = 10 Hz, Bp-4-H), 6.47/6.42 (1H, d, J = 8 Hz, In-7-H), 6.30/6.29 (1H, q, J = 7 Hz, Chl-3-CH), 5.64/5.48 (1H, d, J = 10 Hz, Bp-3-H), 5.13/5.04, 5.11/5.03 (each 1H, d, J = 20 Hz, Chl-13<sup>2</sup>-H<sub>2</sub>), 4.35 (1H, m, Chl-18-H), 4.20 (1H, m, Chl-17-H), 4.09–3.89 (2H, m, COOCH<sub>2</sub>), 3.74/3.74 (2H, q, J = 8 Hz, Chl-8-CH<sub>2</sub>), 3.65/3.65, 3.64/3.63, 3.38/3.38 (each 3H, s, Chl-2-, 7-, 12-CH<sub>3</sub>), 3.21–3.04 (2H, m, NCH<sub>2</sub>), 2.58–1.94 (4H, m, Chl-17-CH<sub>2</sub>CH<sub>2</sub>), 2.12/2.11

(3H, d, J = 7 Hz, Chl-3<sup>1</sup>-CH<sub>3</sub>), 1.76/1.74 (3H, d, J = 7 Hz, Chl-18-CH<sub>3</sub>), 1.71/1.69 (3H, t, J = 8 Hz, Chl-8<sup>1</sup>-CH<sub>3</sub>), 1.17/1.16, 1.02./0.98 (each 3H, s, In-3-CH<sub>3</sub>); MS (FAB) found: m/z = 949. Calcd for C<sub>53</sub>H<sub>53</sub>N<sub>6</sub>O<sub>7</sub>Zn: MH<sup>+</sup>, 949.

#### 2.6.8. Spiropyran-appended zinc 3-devinyl-3-methoxymethyl-pyropheophorbide-a (Zn4)

Zinc metalation gave dark green solids of **Zn4** in 93% yield (HPLC: retention time was 8.5 min.). Mp 200–202°C; vis (CH<sub>2</sub>Cl<sub>2</sub>)  $\lambda_{max}$  648 (relative intensity, 0.73), 600 (0.12), 553 (0.07), 512 (0.05), 422 nm (1.00); <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta(R/S)$  9.55/9.54, 9.28/9.27, 8.36/8.35 (each 1H, s, Chl-5-, 10-, 20-H), 7.93/7.92 (1H, dd, *J* = 3, 9 Hz, Bp-7-H), 7.85/7.74 (1H, d, *J* = 3 Hz, Bp-5-H), 7.06/6.96 (1H, dt, *J* = 1, 8 Hz, In-6-H), 6.98/6.98 (1H, dd, *J* = 1, 8 Hz, In-4-H), 6.80/6.74 (1H, dt, *J* = 1, 7 Hz, In-5-H), 6.63/6.62 (1H, d, *J* = 9 Hz, Bp-8-H), 6.57/6.33 (1H, d, *J* = 10 Hz, Bp-4-H), 6.46/6.43 (1H, d, *J* = 7 Hz, In-7-H), 5.61/5.60 (2H, s, Chl-3-CH<sub>2</sub>), 5.61/5.41 (1H, d, *J* = 10 Hz, Bp-3-H), 5.15/5.12, 5.10/5.06 (each 1H, d, *J* = 20 Hz, Chl-13<sup>2</sup>-H<sub>2</sub>), 4.36 (1H, m, Chl-18-H), 4.23 (1H, m, Chl-17-H), 4.03–3.87 (2H, m, COOCH<sub>2</sub>), 3.75/3.74 (2H, q, *J* = 8 Hz, Chl-8-CH<sub>2</sub>), 3.75/3.74, 3.65/3.64, 3.40/3.39, 3.32/3.31 (each 3H, s, Chl-2-, 7-, 12-CH<sub>3</sub>, 3-COCH<sub>3</sub>), 3.22–2.95 (m, 2H, NCH<sub>2</sub>), 2.40–1.90 (4H, m, Chl-17-CH<sub>2</sub>CH<sub>2</sub>), 1.78/1.78 (3H, d, *J* = 7 Hz, Chl-18-CH<sub>3</sub>), 1.68/1.67 (3H, t, *J* = 8 Hz, Chl-8<sup>1</sup>-CH<sub>3</sub>), 1.16/1.13, 1.00./0.94 (each 3H, s, In-3-CH<sub>3</sub>); MS (FAB) found: *m*/z = 949. Calcd for C<sub>53</sub>H<sub>53</sub>N<sub>6</sub>O<sub>7</sub>Zn: MH<sup>+</sup>, 949.

#### 3. Results and discussion

#### 3.1. Synthesis of spiropyran-appended zinc chlorins

Spiropyran-appended zinc chlorins were prepared from methyl pyropheophorbide-a which was obtained by modification of natural chlorophyll-a (Scheme 1). The 3-vinyl group was

oxidized to a formyl group, and the 3-formyl group was transferred to a 3-methoxymethyl group by reduction and acid-catalyzed condensation with methanol. The 17-propionic methyl esters of the 3-formyl and 3-methoxymethyl chlorins were hydrolyzed to carboxylic acids, and esterified with alcoholic spiropyran 1 to afford the corresponding spiropyran-appended chlorins. Reduction of the 3-formylchlorin was performed, and the 3-hydroxymethyl- (2) and 3-methoxymethyl (4) chlorins were zinc metalized to give zinc chlorin-spiropyran dyads Zn2 and **Zn4**, respectively. The obtained dyads were mixtures of stereoisomers with different configuration at the chiral 2'-position of spiropyran moiety. The dyads have additional chiral carbons at the 17- and 18-positions (17S and 18S) of the chlorin macrocycle, and their <sup>1</sup>H-NMR spectra indicated that the ratios of the diastereomers were 1/1 regardless of the substituent at the 3-position. In the following experiments, we used these dyads as their diastereomeric mixtures. The other spiropyran-appended zinc chlorins 3 with 3-(1-hydroxyethyl) group were prepared by non-stereoselective hydration of the 3-vinyl group. The obtained 3<sup>1</sup>-hydroxy product was a 1:1 mixture of  $3^{1}R$  and  $3^{1}S$  epimers. The diastereometric mixture was zinc metalated, and the  $3^{1}R$ and  $3^{1}S$  diastereomers were separated by a single reversed phase HPLC run with a packed ODS column. The epimerically pure zinc chlorins were demetalated by acid treatment, and the free base chlorins transesterified with the spiropyran 1 followed by zinc metalation to afford the  $3^{1}R$ isomer (**Zn3R**) and the  $3^{1}S$  isomer (**Zn3S**).

#### 3.2. Spectroscopic properties of spiropyran-appended (zinc) chlorins

UV-Visible absorption spectra of the closed form of zinc chlorin–spiropyran dyad **Zn2***c* in methanol showed 653- and 427-nm maxima of Qy and Soret bands, respectively (dashed line of Fig. 3A). These bands are identical to those of the corresponding zinc 3-hydroxymethyl-chlorin. An additional weak absorption band at around 330 nm appeared in the spectrum due to the

contribution of closed form of spiropyran moiety. When the methanol solution of **Zn2***c* was irradiated by UV light (352 nm) for 3 min, a new absorption band appeared at around 500–600 nm with a little decrease in absorption band at around 330 nm (solid line of Fig. 3A). The spectral change is ascribed to the ring-opening reaction of the spiropyran moiety to afford merocyanine appended zinc chlorin, **Zn2***o*. The formation of merocyanine chromophore accompanied a slight decrease in Qy absorption band of the zinc chlorin, suggesting that a little interaction between the two chromophoric units appeared in the dyad. The merocyanine moiety of **Zn2***o* was re-isomerized to the original spiropyran form **Zn2***c* by irradiation of visible light (540 nm) for 15 min, and the initial absorption spectrum of **Zn2***c* was completely recovered. A relatively slow thermal ring closing reaction of the merocyanine form **Zn2***o* to the spiro form was also observed in about 1 h in the dark at room temperature. The other (zinc) chlorin–spiropyran dyads **Zn3**, **Zn4** and **2–4** showed the similar reversible isomerization of the spiropyran moiety, i.e. the photochromic isomerization of spiropyran was not disturbed by the covalently linked (zinc) chlorin moiety.

Fluorescence emission spectra of the dyads Zn2c and Zn2o were measured upon excitation at 430 nm where the zinc chlorin chromophore was selectively excited. The corrected fluorescence spectrum of Zn2c measured in methanol showed a strong emission band at 658 nm (dashed line of Fig. 3B). The shape and amplitude of the spectrum is essentially identical to those of the fluorescence spectrum of methyl ester form of zinc 3-hydroxymethyl-chlorin (R=CH<sub>3</sub> in the right drawing of Fig. 1) solution with the same concentration. Therefore, the covalently connected spiropyran moiety in Zn2c did not disturb the fluorescence emission of the zinc chlorin moiety. The Zn2c solution was UV-irradiated to convert the Zn2o solution, and fluorescence spectrum was recorded with 430-nm excitation (solid line of Fig. 3B). A fluorescence emission band of the merocyanine chromophore might be expected at around 640

nm, and the amplitude of the merocyanine emission was too small to be found in the spectrum. The fluorescence emission band of zinc chlorin moiety similarly appeared at 658 nm, but its intensity decreased to 45% of the **Zn2***c* emission. The strong fluorescence emission of zinc chlorin moiety was recovered, when the opened merocyanine form was converted to the closed spiropyran form by visible light irradiation. These results showed that the opened merocyanine form quenched the singlet excited state of the zinc chlorin chromophore. The similar photoswitchable fluorescence quenching of a tetrapyrrolic chromophore was reported in spiropyran-appended porphyrins. The mechanism of quenching is considered to be singlet energy transfer from the photo-excited porphyrin to merocyanine moiety [36]. In our zinc chlorin–merocyanine dyad, quenching of zinc chlorin singlet excited state ( $\lambda_{em} = 658$  nm) by opened merocyanine moiety ( $\lambda_{abs} = 530$  nm) is thermodynamically unfavorable. Therefore, the quenching might be assigned to other photochemical pathways such as intramolecular electron transfer.

### 3.3. Self-aggregation of spiropyran-appended zinc 3<sup>1</sup>-hydroxychlorins

Self-aggregates of the chlorophyllous pigments were prepared by dilution of Zn2-4 solutions with a large volume of the poor solvent. The preparation method has been widely used in making *in vitro* aggregate of BChls-*c* and their synthetic analogues. The zinc chlorin–spiropyran dyads were well soluble in polar solvents such as methanol, tetrahydrofuran, and DCM, and less soluble in non-polar organic solvents such as hexane and cyclohexane. A DCM solution of Zn2c (closed form) was diluted with a large volume of hexane to prepare the self-aggregate of the chlorophyll derivative. Visible absorption spectrum of the aggregated Zn2c in 30% DCM / hexane showed a Qy absorption band at 724 nm with a weak absorption band of the remaining monomeric zinc chlorin at 647 nm (dashed line of Fig. 4A). The ratio of

the absorption intensities was  $A_{724}$  /  $A_{650}$  = 3.19, and most of the zinc chlorin **Zn2***c* molecules self-aggregated to form oligomer in the solvent. The aggregate of **Zn2**c provided intense inverse-S type CD signals at the red-shifted wavelength. These spectroscopic features are characteristic of formation of chlorosome-type exiton-coupled J-aggregate. The freebase chlorin-spiropyran dyad 2c did not show any red-shifted absorption band in the same solvent, and formation of the chlorosome-type J-aggregate required in central zinc in the chlorin chromophore, which contributes an intermolecular coordination bond with the oxygen at the  $3^1$ -position of the neighboring molecule. The self-aggregative **Zn2***c* was converted to the merocyanine form Zn2o by UV-irradiation in DCM, and the solution was diluted with hexane. The resulting solution gave Qy absorption bands at 650 and 722 nm concomitant with the absorption band of the merocyanine chromophore at around 580 nm (solid line of Fig. 4A). The ratio of the absorption band intensities of the monomeric and aggregated zinc chlorin apparently decreased in **Zn2**o (A<sub>722</sub> / A<sub>650</sub> = 0.60). Similarly, the intensities of CD signals decreased in Zn2o solution (solid line of Fig. 4D). The merocyanine-appended chlorophyllous pigment Zn2o aggregated less than **Zn2**c possessing the hydrophobic spiropyran moiety. The polar merocyanine moiety at the 17-position of Zn2o might prevent the formation of the chlorosome-type aggregate in which the side chain at the 17-position oriented toward outside of the assembly. The miscibility of the chlorophyllous tail in non-polar organic media was changed by photoisomerization of spiropyran moiety, which affected the self-aggregation behavior of chlorophyllous pigment.

A similar photoisomerization effect on self-aggregation of zinc chlorins was found in zinc chlorins **Zn3R** and **Zn3S** with a chiral 3-(1-hydroxyethyl) group, which is found in naturally occurring chlorosomal BChls (Figs. 4B, 4C, 4E and 4F). Previous *in vitro* aggregation studies showed that the absolute configuration at the chiral 3-(1-hydroxyethyl) group affect the structure of the chlorosomal self-aggregates [10]. The closed spiropyran-appended zinc

 $(3^{1}R)$ -3-(1-hydroxyethyl)-chlorin **Zn3R***c* showed a red-shifted band at 706 nm with a small band of monomeric form at 647 nm. The ratio of the oligomeric and monomeric bands A<sub>706</sub> / A<sub>647</sub> was 1.42, which was larger than that found in the 3<sup>1</sup>S isomer **Zn3Sc** (A<sub>702</sub> / A<sub>647</sub> = 0.78). The 3<sup>1</sup>R isomers self-aggregate more easily than the corresponding 3<sup>1</sup>S isomers. However, these oligomer / monomer ratios in **Zn3***c* were smaller than that of zinc 3-hydroxymethyl-chlorin **Zn2***c*. These observations are similar as self-aggregation of BChl-*c* and their analogues. The 3<sup>1</sup>-methyl group in **Zn3** slightly disturbed the hydrogen bond and coordination bond of the neighboring 3<sup>1</sup>-hydroxy group, and the configuration of the methyl group might affect the organization of the chlorophyllous assemblies. The merocyanine form of the zinc 3-(1-hydroxyethyl)-chlorins **Zn3***o* hardly self-aggregated without showing intense CD signals at around 700 nm. The less aggregative **Zn3** showed a larger photoisomerization effect in the pigment aggregation.

Photoisomerization of the spiropyran moiety was examined in the aggregate solutions. When UV light was irradiated to the aggregated **Zn2***c* prepared in 30% DCM / hexane, a new absorption band of the merocyanine form appeared at around 580 nm. However, the absorption band of aggregated zinc chlorin chromophore at 722 nm was not affected by the irradiation. Therefore, the photoisomerization of the spiropyran to merocyanine in the dyads did not change the suprastructure of the aggregated zinc chlorin. The intermolecular interaction in aggregated zinc chlorin molecules, possibly C=O···H-O···Zn bonding as well as  $\pi$ - $\pi$  interaction, would be enough strong to maintain the suprastructure of the **Zn2***o* aggregate. In addition, visible light irradiation to the zinc chlorin-merocyanine form **Zn2***o* in 30% DCM / hexane did not show any change in absorption spectrum except decreasing the 580 nm band of the merocyanine form. Similar results were obtained in the spiropyran-appended zinc 3-(1-hydroxyethyl)chlorins **Zn3** aggregates. The suprastructures of the already prepared zinc 3<sup>1</sup>-hydroxy-chlorin aggregate were not perturbed by photoisomerization of spiropyran tail.

### 3.4. Self-aggregation of spiropyran-appended zinc 3<sup>1</sup>-methoxychlorin

Zinc chlorins possessing a 3<sup>1</sup>-methoxy group can form aggregate with red-shifted absorption band [11,23]. The oxygen at the 3<sup>1</sup>-methoxy group would coordinate to the central zinc of another molecule, which contributes to organizing the J-aggregate. Because the modified chlorophyllous pigments miss the 3<sup>1</sup>-hydroxy group for the intermolecular hydrogen bond, the zinc 3<sup>1</sup>-methoxy-chlorins would associate loosely compared with the corresponding  $3^{1}$ -hydroxy-chlorins. The spiropyran-appended zinc 3-methoxymethyl-chlorin **Zn4***c* was dispersed in 5% DCM / hexane. The solution showed 419- and 645-nm bands characteristic of monomeric zinc chlorin (Fig. 5A). The UV-irradiation to the monomeric Zn4c solution induced red-shift in the absorption spectrum. New absorption bands appeared at 435 and 668 nm concomitant with a broad absorption band at around 580 nm of the merocyanine form of Zn4o (Fig. 5B). These red-shifted bands of zinc chlorin moiety might be ascribable to formation of a small aggregate such as dimer. Moreover, the red-shifted absorption bands of the dimeric form disappeared by visible-light irradiation (Fig. 5C). The dimerization of 3<sup>1</sup>-methoxy chlorophyll derivative Zn4 was reversibly controlled by photoirradiation, which was unambiguously caused by photoisomerization of the spiropyran tail. The formation of polar merocyanine form destabilized the monomeric zinc chlorin in the non-polar solvent, 5% DCM / hexane. The miscibility change in the chlorophyllous tail could switch on and off the aggregation behavior of weakly bound zinc  $3^1$ -methoxy-chlorin.

#### 4. Conclusion

Chlorophyll derivatives with covalently linked photochromic spiropyran showed

photoswichable properties. The spiropyran moiety was reversibly isomerized in the dyads without any perturbation of the connected chlorophyllous pigment. Therefore, the ground and excited state of the closed spiropyran and opened merocyanine forms were not affected by the photosynthetic chromophores. The freely isomerizable spiropyran unit in the dyad provided unique aggregation properties of the chlorophyllous dyads. The hydrophobic closed spiropyran tail in the chlorophyllous dyads was favorable for the aggregation of chlorosomal chlorophylls possessing a hydrophobic alkyl chain at the same position. Tunable self-aggregation activity of the chlorosomal BChl models was achieved by using the photoswichable polarity change of the appended spiropyran group. In particular, self-aggregation of weakly associated zinc 3<sup>1</sup>-methoxychlorin molecules could be controlled by the photochromic group.

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### **Figure Captions**

Scheme 1. Synthesis of spiropyran-appended zinc chlorins: (i) OsO<sub>4</sub>, NaIO<sub>4</sub>, HOAc / THF, H<sub>2</sub>O; (ii) *t*BuNH<sub>2</sub>·BH<sub>3</sub> / CH<sub>2</sub>Cl<sub>2</sub>; (iii) MeOH / H<sub>2</sub>SO<sub>4</sub> (50°C); (iv) conc. HCl; (v) 1, EDC·HCl, DMAP / CH<sub>2</sub>Cl<sub>2</sub>; (vi) Zn(OAc)<sub>2</sub>·2H<sub>2</sub>O / MeOH, CH<sub>2</sub>Cl<sub>2</sub>; (vii) HBr / HOAc (60°C), H<sub>2</sub>O, MeOH / H<sub>2</sub>SO<sub>4</sub>; (vii) reversed-phase HPLC run with ODS packed column, 2% aq. HCl; (viii) 1, (*n*BuClSn)<sub>2</sub>O / toluene, reflux.

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

Fig. 2. Photoisomerization of spiropyran 1.

**Fig. 3.** UV-Visible absorption spectra (A) and fluorescence emission (B:  $\lambda_{exc} = 430$  nm) of spiropyran-appended zinc 3-hydroxymethyl-chlorin **Zn2** before (dashed line) and after (solid line) UV irradiation at 352 nm in methanol.

**Fig. 4.** UV-Visible absorption (A–C) and CD (D–F) spectra of spiropyran-appended zinc chlorins **Zn2** (A, D), **Zn3R** (B, E) and **Zn3S** (C, F) in DCM / hexane (**Zn2**: 3 / 7, **Zn3R** and **Zn3S**: 1 / 4; v / v); dashed lines: closed spiropyran form; solid lines: open merocyanine form.

**Fig. 5.** UV-Visible absorption spectra of spiropyran-appended zinc chlorin **Zn4** in DCM / hexane (1 / 18; v / v). (A) initial state, (B) after UV irradiation, and (C) after VIS irradiation of the aggregated **Zn4**.



Scheme 1



 $\begin{array}{l} {\sf BChl-$c$:} {\sf R_7=CH_3, R_{20}=CH_3$} \\ {\sf BChl-$d$:} {\sf R_7=CH_3, R_{20}=H$} \\ {\sf BChl-$e$:} {\sf R_7=CHO, R_{20}=CH_3$} \\ {\sf BChl-$f$:} {\sf R_7=CHO, R_{20}=H$} \\ {\sf R_8=CH_2CH_3, CH_2CH_2CH_3, etc.,} \\ {\sf R_{12}=CH_3, CH_2CH_3, etc.,} \\ {\sf R=farnesyl, stearyl, etc.} \end{array}$ 



Zinc Chlorin Models:  $R_3=CH_2OH, CH(OH)CH_3,$   $CH_2OCH_3, etc.,$   $R=CH_3, (CH_2)_nH,$  $(CH_2CH_2O)_nH, etc.$ 

Fig. 1



Fig. 2







Fig. 4



Fig. 5