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# Synthesis of Self-Aggregative Zinc Chlorophylls Possessing Polymerizable Esters as a Stable Model Compound for Main Light-Harvesting Antennas of Green Photosynthetic Bacteria

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Zinc bacteriochlorophyll-*d* derivatives possessing a polymerizable moiety at the 17-propionate were prepared as model compounds of natural occurring chlorophylls in the main peripheral antennas of green photosynthetic bacteria (chlorosomes). The synthetic compounds self-aggregated in nonpolar organic solvents as well as in the solid state to give large oligomers similar to chlorosomal J-aggregates. Such introduction of the polymerizable groups in the ester did not suppress the ability of self-aggregation.

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## 1. INTRODUCTION

Green photosynthetic bacteria have extramembranous peripheral antenna systems, called chlorosomes. Chlorosomes are main light-harvesting antennas in the cell and are different from any other antennas in the structural motif. Chlorosomal core parts are built by self-aggregation of composite chlorophyllous pigments [1–5], while the others are based on specific interaction of (bacterio)chlorophylls with peptides. In chlorosomes of *Chloroflexus aurantiacus*, one of the green nonsulfur (filamentous or gliding/sliding) bacteria, bacteriochlorophyll(BChl)*s-c* possessing ethyl and methyl groups at the 8- and 12-positions, respectively, (see Figure 1(a)) are the light-absorbing chlorophyllous pigments. A large number of the molecules self-aggregate to form oligomers in a hydrophobic environment surrounded by a chlorosomal lipid monolayer. The J-aggregates with their unique ability of fast light energy migration are assumed to make rod structures in a chlorosome. In the rod model, the propionate ester group at the 17-position is situated at the surface. This location was first proposed from molecular calculation (MM+/PM3) [6] and is supported using synthetic models (Figure 1(b)) [2, 7–10]. Recently, atomic force microscopic observation showed that self-aggregates of the model compound indeed made rod structures [11].

Chlorosomal self-aggregates are fragile and dissociate readily to monomers by addition of coordinatable species.

In natural systems, the surface monolayer of lipids is reinforced by membranous additives including proteins [12] in order to suppress such deaggregation. In artificial micelle systems, amphiphilic compounds surrounding self-aggregates were cross-linked to overcome the instability of supramolecules [13–15]. Here we report synthesis of zinc bacteriochlorophyll-*d* derivatives **3** possessing polymerizable substituents at the ester group of the 17-propionate and their self-aggregation in a nonpolar organic solvent as chlorosomal hydrophobic environments. These functional groups are assumed to be situated at the surface of the self-aggregated supramolecules and would be polymerized via C–C bondings to stabilize the noncovalently self-assembled, large oligomeric J-aggregates [16, 17], which is promising for construction of photoactive nanodevices.

## 2. EXPERIMENTAL

### 2.1. General

All the apparatuses and solvents used were described previously [9]. Pyropheophorbide-*d* (**6**) was prepared according to the previous report [18]. 3-Acetyl-3-devinylpyropheophorbide-*a* (**9**) was synthesized by similar acidic hydrolysis of the corresponding methyl ester **8** [19, 20] (94% yield) as in preparation of **5** → **6** [18, 21]. 10,12-Pentacosadiyn-1-ol, tetracosanol, and 4-hydroxybutyl acrylate were

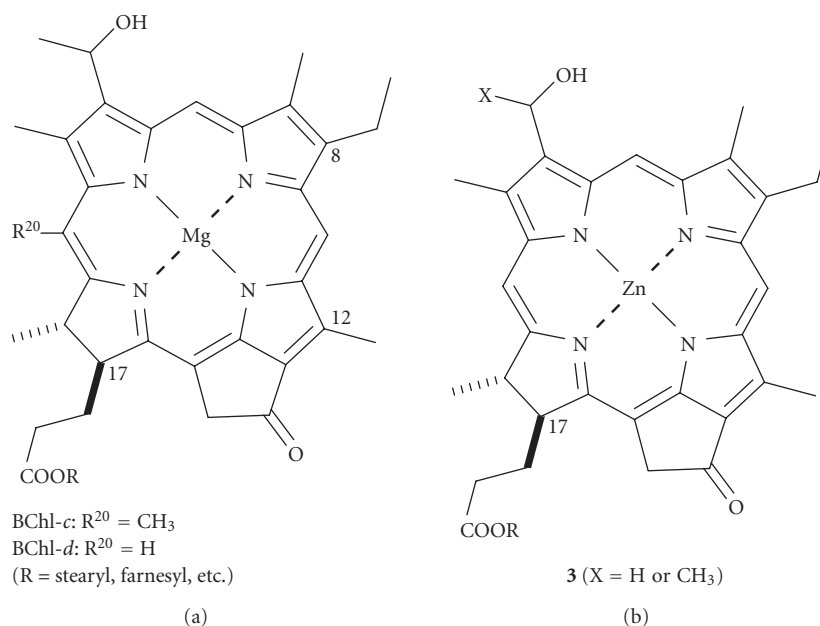


FIGURE 1: (a) Naturally occurring chlorosomal chlorophylls and (b) their synthetic models **3**.

purchased from Tokyo Chemical Ind. All the reactions were done in the dark under nitrogen. TLC and flash column chromatography (FCC) were performed on 0.25 mm pre-coated silica gel 60 F<sub>254</sub> (Merck) and silica gel, Kieselgel 60 (Merck, 40–63  $\mu$ m), respectively.

## 2.2. Synthetic procedures

### 2.2.1. Esterification

A primary alcohol (0.3 mmol) was added to an ice-chilled dry CH<sub>2</sub>Cl<sub>2</sub> solution (30 mL) of 3-carbonyl-17<sup>2</sup>-carboxy-chlorin **6** or **9** (0.1 mmol) with stirring. After further addition of 3-ethyl-1-[3-(*N,N*-dimethylamino)propyl]carbodiimide hydrochloride (EDC · HCl, 0.5 mmol) and 4-(*N,N*-dimethylamino)pyridine (DMAP, 1 mmol), the solution was stirred at 0°C for 30 minutes and at room temperature overnight. The reaction was monitored by TLC and the complete disappearance of the starting carboxylic acid was confirmed. The reaction mixture was washed with aqueous 1% HCl, 4% NaHCO<sub>3</sub> and water, and dried over Na<sub>2</sub>SO<sub>4</sub>. The mixture was purified with FCC and recrystallization to afford the desired ester **1** as a dark brown solid.

### 2.2.2. Reduction of 3-formyl group

*Tert*-Butylamine borane complex (0.25 mmol) was added to an ice-chilled dry CH<sub>2</sub>Cl<sub>2</sub> solution (30 mL) of 3-formyl-13<sup>1</sup>-oxo-chlorin **1a/b/d** (0.1 mmol), which was stirred at 0°C for 15 minutes and at room temperature for a few hours. The reaction was monitored by visible absorption spectra: a blue shift of Q<sub>y</sub>-band from 695 to 661 nm. After the complete shift (usually with 2-hour stirring), the reaction mixture was stirred with aqueous 2% HCl solution (10 mL). The sepa-

rated CH<sub>2</sub>Cl<sub>2</sub> phase was washed with aqueous 4% NaHCO<sub>3</sub> and water, and dried over Na<sub>2</sub>SO<sub>4</sub>. The mixture was purified with FCC (5% Et<sub>2</sub>O–CH<sub>2</sub>Cl<sub>2</sub>) and recrystallization (CH<sub>2</sub>Cl<sub>2</sub>–hexane) to afford the desired 3<sup>1</sup>-hydroxy-13<sup>1</sup>-oxo-chlorin **2a/b/d** (black solid) as a selectively reduced product.

### 2.2.3. Reduction of 3-acetyl group

A methanol solution (1 mL) of sodium borohydride (0.15 mmol) was added to an ice-chilled dry CH<sub>2</sub>Cl<sub>2</sub> solution (30 mL) of 3-acetyl-13<sup>1</sup>-oxo-chlorin **1c** (0.1 mmol) with stirring. The reaction was monitored by visible absorption spectra: a blue shift of Q<sub>y</sub>-band from 683 to 661 nm. [Caution] Prolonged reaction induced an undesired reduction of the 13-keto carbonyl group. After the complete shift (usually with 10-minute stirring), the reaction was quenched by addition of acetone, washed with water, and dried over Na<sub>2</sub>SO<sub>4</sub>. The mixture was purified with FCC (5% Et<sub>2</sub>O–CH<sub>2</sub>Cl<sub>2</sub>) and recrystallization (CH<sub>2</sub>Cl<sub>2</sub>–MeOH) to afford the desired 3<sup>1</sup>-hydroxy-13<sup>1</sup>-oxo-chlorin **2c** (black solid) as a selectively reduced product.

### 2.2.4. Zinc metallation

A methanol solution (4 mL) saturated with zinc acetate dihydrate was added to a dry CH<sub>2</sub>Cl<sub>2</sub> solution (30 mL) of metal-free chlorin **2** (0.1 mmol), which was stirred at room temperature for 90 minutes. The reaction was monitored by TLC and the complete disappearance of the starting free base was confirmed. The reaction mixture was stirred with aqueous 4% NaHCO<sub>3</sub> solution (10 mL) for 20 minutes. The separated CH<sub>2</sub>Cl<sub>2</sub> phase was washed with aqueous 4%

NaHCO<sub>3</sub> and water, and dried over Na<sub>2</sub>SO<sub>4</sub>. The mixture was purified with FCC (10% Et<sub>2</sub>O–CH<sub>2</sub>Cl<sub>2</sub>) and recrystallization (CH<sub>2</sub>Cl<sub>2</sub>–MeOH) to afford the desired zinc complex **3** as a dark green solid.

### 2.3. Synthesis of chlorins

#### 2.3.1. Synthesis of 10,12-pentacosadiyn-1-yl pyropheophorbide-**d** (**1a**)

Esterification of **6** with 10,12-pentacosadiyn-1-ol gave **1a** (61% yield) after FCC (1% Et<sub>2</sub>O–CH<sub>2</sub>Cl<sub>2</sub>) and recrystallization (CH<sub>2</sub>Cl<sub>2</sub>–hexane); VIS (CH<sub>2</sub>Cl<sub>2</sub>) λ<sub>max</sub> = 694 (relative intensity, 0.80), 633 (0.08), 554 (0.16), 522 (0.14), 429 (1.00), 388 nm (0.83); IR (KBr) ν = 1732 (17<sup>2</sup>-C=O), 1701 (13-C=O), 1678 (3-C=O), 1618 cm<sup>-1</sup>; <sup>1</sup>H-NMR (CDCl<sub>3</sub>) δ = 11.56 (1H, s, CHO), 10.33, 9.63, 8.85 (each 1H, s, 5-, 10-, 20-H), 5.36, 5.20 (each 1H, d, J = 20 Hz, 13<sup>1</sup>-CH<sub>2</sub>), 4.58 (1H, br-q, J = 7 Hz, 18-H), 4.40 (1H, br-d, J = 8 Hz, 17-H), 3.98, 3.91 (each 1H, dt, J = 11, 7 Hz, COOCH<sub>2</sub>), 3.74 (2H, q, J = 7.5 Hz, 8-CH<sub>2</sub>), 3.79, 3.73, 3.33 (each 3H, s, 2-, 7-, 12-CH<sub>3</sub>), 2.67–2.78, 2.52–2.62, 2.24–2.39 (1H + 1H + 2H, m, 17-CH<sub>2</sub>CH<sub>2</sub>), 2.20, 2.18 (each 2H, t, J = 7 Hz, CH<sub>2</sub>C≡C–C≡CCH<sub>2</sub>), 1.85 (3H, d, J = 7 Hz, 18-CH<sub>3</sub>), 1.72 (3H, t, J = 7.5 Hz, 8<sup>1</sup>-CH<sub>3</sub>), 1.38–1.50 (6H, m, COOCCH<sub>2</sub>, CH<sub>2</sub>CC≡C–C≡CCCH<sub>2</sub>), 1.16–1.30 (28H, m, 17<sup>6–10,19–27</sup>-CH<sub>2</sub>), 0.86 (3H, t, J = 6.5 Hz, 17<sup>28</sup>-CH<sub>3</sub>), 0.12, –2.05 (each 1H, s, NH). MS (FAB) found: *m/z* 879. Calculated for C<sub>57</sub>H<sub>75</sub>N<sub>4</sub>O<sub>4</sub>: MH<sup>+</sup>, 879.

#### 2.3.2. Synthesis of 10,12-pentacosadiyn-1-yl 3-hydroxymethyl-3-devinyl-pyropheophorbide-**a** (**2a**)

Reduction of **1a** with t-BuNH<sub>2</sub>BH<sub>3</sub> gave **2a** (92% yield); VIS (CH<sub>2</sub>Cl<sub>2</sub>) λ<sub>max</sub> = 661 (rel., 0.48), 605 (0.08), 535 (0.09), 504 (0.10), 409 nm (1.00); IR (KBr) ν = 3350 (3<sup>1</sup>-O–H), 1732 (17<sup>2</sup>-C=O), 1692 (13-C=O), 1622 cm<sup>-1</sup>; <sup>1</sup>H-NMR (CDCl<sub>3</sub>) δ = 9.51, 9.45, 8.57 (each 1H, s, 5-, 10-, 20-H), 5.92 (2H, s, 3-CH<sub>2</sub>), 5.26, 5.10 (each 1H, d, J = 20 Hz, 13<sup>1</sup>-CH<sub>2</sub>), 4.49 (1H, br-q, J = 7 Hz, 18-H), 4.30 (1H, br-d, J = 8 Hz, 17-H), 3.99, 3.93 (each 1H, dt, J = 11, 7 Hz, COOCH<sub>2</sub>), 3.70 (2H, q, J = 7.5 Hz, 8-CH<sub>2</sub>), 3.67, 3.49, 3.43 (each 3H, s, 2-, 7-, 12-CH<sub>3</sub>), 2.62–2.73, 2.49–2.59, 2.18–2.36 (1H + 1H + 2H, m, 17-CH<sub>2</sub>CH<sub>2</sub>), 2.21, 2.17 (each 2H, t, J = 7 Hz, CH<sub>2</sub>C≡C–C≡CCH<sub>2</sub>), 1.81 (3H, d, J = 7 Hz, 18-CH<sub>3</sub>), 1.70 (3H, t, J = 7.5 Hz, 8<sup>1</sup>-CH<sub>3</sub>), 1.38–1.50 (6H, m, COOCCH<sub>2</sub>, CH<sub>2</sub>CC≡C–C≡CCCH<sub>2</sub>), 1.17–1.31 (28H, m, 17<sup>6–10,19–27</sup>-CH<sub>2</sub>), 0.87 (3H, t, J = 6.5 Hz, 17<sup>28</sup>-CH<sub>3</sub>), 0.29, –1.79 (each 1H, s, NH). MS (FAB) found: *m/z* 881. Calculated for C<sub>57</sub>H<sub>77</sub>N<sub>4</sub>O<sub>4</sub>: MH<sup>+</sup>, 881.

#### 2.3.3. Synthesis of zinc 10,12-pentacosadiyn-1-yl 3-hydroxymethyl-3-devinyl-pyropheophorbide-**a** (**3a**)

Zinc-metallation of **2a** gave **3a** (92% yield); mp > 300°C; VIS (THF) λ<sub>max</sub> = 646 (rel., 0.74), 602 (0.10), 565 (0.05), 520

(0.03), 424 (1.00), 404 nm (0.57); IR (KBr) ν = 3150 (3<sup>1</sup>-O–H), 1732 (17<sup>2</sup>-C=O), 1664 (13-C=O), 1620 cm<sup>-1</sup>; <sup>1</sup>H-NMR (CDCl<sub>3</sub>–1% C<sub>5</sub>D<sub>5</sub>N) δ = 9.57, 9.31, 8.36 (each 1H, s, 5-, 10-, 20-H), 5.83 (2H, s, 3-CH<sub>2</sub>), 5.19, 5.05 (each 1H, d, J = 20 Hz, 13<sup>1</sup>-CH<sub>2</sub>), 4.40 (1H, br-q, J = 7 Hz, 18-H), 4.20 (1H, br-d, J = 8 Hz, 17-H), 3.95 (2H, m, COOCH<sub>2</sub>), 3.76 (2H, q, J = 7.5 Hz, 8-CH<sub>2</sub>), 3.69, 3.35, 3.26 (each 3H, s, 2-, 7-, 12-CH<sub>3</sub>), 2.48–2.62, 2.29–2.42 (each 2H, m, 17-CH<sub>2</sub>CH<sub>2</sub>), 2.20 (4H, m, CH<sub>2</sub>C≡C–C≡CCH<sub>2</sub>), 1.72 (3H, d, J = 7 Hz, 18-CH<sub>3</sub>), 1.70 (3H, t, J = 7.5 Hz, 8<sup>1</sup>-CH<sub>3</sub>), 1.41–1.50 (6H, m, COOCCH<sub>2</sub>, CH<sub>2</sub>CC≡C–C≡CCCH<sub>2</sub>), 1.20–1.30 (28H, m, 17<sup>6–10,19–27</sup>-CH<sub>2</sub>), 0.87 (3H, t, J = 6.5 Hz, 17<sup>28</sup>-CH<sub>3</sub>). MS (FAB) found: *m/z* 942. Calculated for C<sub>57</sub>H<sub>74</sub>N<sub>4</sub>O<sub>4</sub><sup>64</sup>Zn: M<sup>+</sup>, 942.

#### 2.3.4. Synthesis of tetracosanyl pyropheophorbide-**d** (**1b**)

Esterification of **6** with tetracosanol gave **1b** (76% yield) after FCC (1% Et<sub>2</sub>O–CH<sub>2</sub>Cl<sub>2</sub>) and recrystallization (CH<sub>2</sub>Cl<sub>2</sub>–hexane); <sup>1</sup>H-NMR (CDCl<sub>3</sub>) δ = 11.57 (1H, s, 3-CHO), 10.33, 9.64, 8.85 (each 1H, s, 5-, 10-, 20-H), 5.35, 5.20 (each 1H, d, J = 20 Hz, 13<sup>1</sup>-CH<sub>2</sub>), 4.58 (1H, br-q, J = 7 Hz, 18-H), 4.40 (1H, br-d, J = 8 Hz, 17-H), 3.88–4.01 (2H, m, COOCH<sub>2</sub>), 3.79, 3.73, 3.34 (each 3H, s, 2-, 7-, 12-CH<sub>3</sub>), 3.74 (2H, q, J = 7 Hz, 8-CH<sub>2</sub>), 2.62–2.80, 2.62–2.50, 2.20–2.40 (1H + 1H + 2H, m, 17-CH<sub>2</sub>CH<sub>2</sub>), 1.85 (3H, d, J = 7 Hz, 18-CH<sub>3</sub>), 1.73 (3H, t, J = 7 Hz, 8<sup>1</sup>-CH<sub>3</sub>), 1.44 (2H, m, COOCCH<sub>2</sub>), 1.05–1.36 (42H, m, 17<sup>6–26</sup>-CH<sub>2</sub>), 0.87 (3H, t, J = 6 Hz, 17<sup>27</sup>-CH<sub>3</sub>), –0.11, –2.04 (each 1H, s, NH).

#### 2.3.5. Synthesis of tetracosanyl 3-hydroxymethyl-3-devinyl-pyropheophorbide-**a** (**2b**)

Reduction of **2a** with t-BuNH<sub>2</sub>BH<sub>3</sub> gave **2b** (65% yield); <sup>1</sup>H-NMR (CDCl<sub>3</sub>) δ = 9.51, 9.45, 8.57 (each 1H, s, 5-, 10-, 20-H), 5.92 (2H, d, J = 5 Hz, 3-CH<sub>2</sub>), 5.25, 5.10 (each 1H, d, J = 20 Hz, 13<sup>1</sup>-CH<sub>2</sub>), 4.73 (1H, br-q, J = 7 Hz, 18-H), 4.29 (1H, br-d, J = 8 Hz, 17-H), 3.90–4.04 (2H, m, COOCH<sub>2</sub>), 3.70 (2H, q, J = 7 Hz, 8-CH<sub>2</sub>), 3.66, 3.43, 3.27 (each 3H, s, 2-, 7-, 12-CH<sub>3</sub>), 2.62–2.74, 2.47–2.61, 2.20–2.39, 2.10–2.19 (each 1H, m, 17-CH<sub>2</sub>CH<sub>2</sub>), 1.80 (3H, d, J = 7 Hz, 18-CH<sub>3</sub>), 1.70 (3H, t, J = 7 Hz, 8<sup>1</sup>-CH<sub>3</sub>), 1.46 (2H, m, COOCCH<sub>2</sub>), 1.10–1.31 (42H, m, 17<sup>6–26</sup>-CH<sub>2</sub>), 0.87 (3H, t, J = 6 Hz, 17<sup>27</sup>-CH<sub>3</sub>), 0.30, –1.79 (each 1H, s, NH).

#### 2.3.6. Synthesis of zinc tetracosanyl 3-hydroxymethyl-3-devinyl-pyropheophorbide-**a** (**3b**)

Zinc-metallation of **2b** gave **3b** (66% yield); <sup>1</sup>H-NMR (CDCl<sub>3</sub>–1% C<sub>5</sub>D<sub>5</sub>N) δ = 9.56, 9.31, 8.33 (each 1H, s, 5-, 10-, 20-H), 5.82 (2H, s, 3-CH<sub>2</sub>), 5.17, 5.05 (each 1H, d, J = 20 Hz, 13<sup>1</sup>-CH<sub>2</sub>), 4.38 (1H, br-q, J = 8 Hz, 18-H), 4.19 (1H, br-d, J = 7 Hz, 17-H), 3.96–3.91 (2H, m, COOCH<sub>2</sub>), 3.74 (2H, q, J = 8 Hz, 8-CH<sub>2</sub>), 3.68, 3.32, 3.23 (each 3H, s, 2-, 7-, 12-CH<sub>3</sub>), 2.43–2.61, 1.89–2.43 (1H + 3H, m, 17-CH<sub>2</sub>CH<sub>2</sub>), 1.70

(3H, d,  $J = 8$  Hz, 18-CH<sub>3</sub>), 1.69 (3H, t,  $J = 8$  Hz, 8<sup>1</sup>-CH<sub>3</sub>), 1.47 (2H, m, COOCCH<sub>2</sub>), 1.10–1.31 (42H, m, 17<sup>6–26</sup>-CH<sub>2</sub>), 0.86 (3H, t,  $J = 6$  Hz, 17<sup>27</sup>-CH<sub>3</sub>). MS (FAB) found:  $m/z$  936. Calculated for C<sub>56</sub>H<sub>80</sub>N<sub>4</sub>O<sub>4</sub>Zn : M<sup>+</sup>, 936.

### 2.3.7. Synthesis of 10,12-pentacosadiyn-1-yl 3-acetyl-3-devinyl-pyropheophorbide-**a** (**1c**)

Esterification of **9** with 10,12-pentacosadiyn-1-ol gave **1c** (93% yield) after FCC (3% Et<sub>2</sub>O–CH<sub>2</sub>Cl<sub>2</sub>) and recrystallization (CH<sub>2</sub>Cl<sub>2</sub>–MeOH); <sup>1</sup>H-NMR (CDCl<sub>3</sub>)  $\delta = 10.08$ , 9.61, 8.78 (each 1H, s, 5-, 10-, 20-H), 5.33, 5.18 (each 1H, d,  $J = 20$  Hz, 13<sup>1</sup>-CH<sub>2</sub>), 4.57 (1H, br-q,  $J = 7$  Hz, 18-H), 4.38 (1H, br-d,  $J = 8$  Hz, 17-H), 3.90–4.01 (2H, m, COOCH<sub>2</sub>), 3.73 (2H, q,  $J = 7$  Hz, 8-CH<sub>2</sub>), 3.72, 3.66, 3.30 (3H + 3H + 6H, s, 2-, 3<sup>1</sup>-, 7-, 12-CH<sub>3</sub>), 2.65–2.78, 2.50–2.62, 2.40–2.23 (1H + 1H + 2H, m, 17-CH<sub>2</sub>CH<sub>2</sub>), 2.21, 2.18 (each 2H, t,  $J = 7$  Hz, CH<sub>2</sub>C≡C–C≡CCH<sub>2</sub>), 1.84 (3H, d,  $J = 7$  Hz, 18-CH<sub>3</sub>), 1.72 (3H, t,  $J = 7$  Hz, 8<sup>1</sup>-CH<sub>3</sub>), 1.39–1.52 (6H, m, COOCCH<sub>2</sub>, CH<sub>2</sub>CC≡C–C≡CCCH<sub>2</sub>), 1.17–1.31 (28H, m, 17<sup>6–10,19–27</sup>-CH<sub>2</sub>), 0.87 (3H, t,  $J = 6$  Hz, 17<sup>28</sup>-CH<sub>3</sub>), –0.01, –2.01 (each 1H, s, NH).

### 2.3.8. Synthesis of 10,12-pentacosadiyn-1-yl bacteriopheophorbide-**d** (**2c**)

Reduction of **1c** with NaBH<sub>4</sub> gave **2c** (56% yield); <sup>1</sup>H-NMR (CDCl<sub>3</sub>)  $\delta$  (3<sup>1</sup>R/S = 1/1) = 9.64/66, 9.44, 8.50/51 (each 1H, s, 5-, 10-, 20-H), 6.39 (1H, m, 3-CH), 5.20/22, 5.07/08, (each 1H, d,  $J = 20$  Hz, 13<sup>1</sup>-CH<sub>2</sub>), 4.46 (1H, br-q,  $J = 7$  Hz, 18-H), 4.25 (1H, m, 17-H), 3.93–4.01 (2H, m, COOCH<sub>2</sub>), 3.68 (2H, q,  $J = 7$  Hz, 8-CH<sub>2</sub>), 3.63, 3.39/40, 3.24 (each 3H, s, 2-, 7-, 12-CH<sub>3</sub>), 2.57–2.75, 2.45–2.57, 2.17–2.35 (2H + 1H + 2H, m, 3<sup>1</sup>-OH, 17-CH<sub>2</sub>CH<sub>2</sub>), 2.14–2.31 (4H, m, CH<sub>2</sub>C≡C–C≡CCH<sub>2</sub>), 2.13 (3H, d,  $J = 7$  Hz, 3<sup>1</sup>-CH<sub>3</sub>), 1.77/79 (3H, d,  $J = 7$  Hz, 18-CH<sub>3</sub>), 1.66 (3H, t,  $J = 7$  Hz, 8<sup>1</sup>-CH<sub>3</sub>), 1.41–1.50 (6H, m, COOCCH<sub>2</sub>, CH<sub>2</sub>CC≡C–C≡CCCH<sub>2</sub>), 1.18–1.38 (28H, m, 17<sup>6–10,19–27</sup>-CH<sub>2</sub>), 0.87 (3H, t,  $J = 6$  Hz, 17<sup>28</sup>-CH<sub>3</sub>), 0.28, –1.85/84 (each 1H, s, NH).

### 2.3.9. Synthesis of zinc 10,12-pentacosadiyn-1-yl bacteriopheophorbide-**d** (**3c**)

Zinc metallation of **2c** gave **3c** (80% yield); VIS (THF)  $\lambda_{\max} = 645$  (rel., 0.59), 606 (0.11), 564 (0.06), 520 (0.04), 424 nm (1.00); <sup>1</sup>H-NMR (CDCl<sub>3</sub>–1% C<sub>5</sub>D<sub>5</sub>N)  $\delta$  (3<sup>1</sup>R/S = 1/1) = 9.53/56, 9.49/53, 8.28 (each 1H, s, 5-, 10-, 20-H) 6.41–6.32 (1H, m, 3-CH), 5.15, 5.03 (each 1H, d,  $J = 20$  Hz, 13<sup>1</sup>-CH<sub>2</sub>), 4.37 (1H, br-q,  $J = 7$  Hz, 18-H), 4.17 (1H, br-d,  $J = 7$  Hz, 17-H), 3.87–3.96 (2H, m, COOCH<sub>2</sub>), 3.73 (2H, q,  $J = 7$  Hz, 8-CH<sub>2</sub>), 3.66, 3.31/33, 3.23 (each 3H, s, 2-, 7-, 12-CH<sub>3</sub>), 2.45–2.60, 1.86–2.00 (each 2H, m, 17-CH<sub>2</sub>CH<sub>2</sub>), 2.13–2.24 (4H, m, CH<sub>2</sub>C≡C–C≡CCH<sub>2</sub>), 2.12 (3H, d,  $J = 6$  Hz, 3<sup>1</sup>-CH<sub>3</sub>), 1.65–1.80 (6H, m, 8<sup>1</sup>-CH<sub>3</sub>, 18-CH<sub>3</sub>), 1.38–1.50 (6H, m, COOCCH<sub>2</sub>, CH<sub>2</sub>CC≡C–C≡CCCH<sub>2</sub>), 1.20–1.33 (28H, m, 17<sup>6–10,19–27</sup>-CH<sub>2</sub>), 0.85 (3H, t,  $J = 6$  Hz,

17<sup>28</sup>-CH<sub>3</sub>). MS (FAB) found:  $m/z$  956. Calculated for C<sub>58</sub>H<sub>76</sub>N<sub>4</sub>O<sub>4</sub>Zn : M<sup>+</sup>, 956.

### 2.3.10. Synthesis of 4-(vinylcarbonyloxy)butyl pyropheophorbide-**d** (**1d**)

Esterification of **6** with 4-hydroxybutyl acrylate gave **1d** (69% yield) after FCC (1% Et<sub>2</sub>O–CH<sub>2</sub>Cl<sub>2</sub>) and recrystallization (CH<sub>2</sub>Cl<sub>2</sub>–hexane); VIS (CH<sub>2</sub>Cl<sub>2</sub>)  $\lambda_{\max} = 694$  (rel., 0.81), 633 (0.09), 554 (0.16), 521 (0.15), 428 (1.00), 388 nm (0.84); <sup>1</sup>H-NMR (CDCl<sub>3</sub>)  $\delta = 11.56$  (1H, s, 3-CHO), 10.32, 9.63, 8.85 (each 1H, s, 5-, 10-, 20-H), 6.32 (1H, dd,  $J = 1$ , 17 Hz, COC=CH *trans* to C–H), 6.03 (1H, dd,  $J = 10$ , 17 Hz, COCH=C), 5.75 (1H, dd,  $J = 1$ , 10 Hz, COC=CH *cis* to C–H), 5.42, 5.13 (each 1H, d,  $J = 20$  Hz, 13<sup>1</sup>-CH<sub>2</sub>), 4.58 (1H, br-q,  $J = 7$  Hz, 18-H), 4.40 (1H, br-d,  $J = 8$  Hz, 17-H), 3.93–4.06 (4H, m, COOCH<sub>2</sub>C<sub>2</sub>CH<sub>2</sub>), 3.70–3.78 (2H, m, 8-CH<sub>2</sub>), 3.78, 3.73, 3.33 (each 3H, s, 2-, 7-, 12-CH<sub>3</sub>), 2.65–2.74, 2.42–2.58, 2.17–2.36 (1H + 1H + 2H, m, 17-CH<sub>2</sub>CH<sub>2</sub>), 1.85 (3H, d,  $J = 7$  Hz, 18-CH<sub>3</sub>), 1.72 (3H, t,  $J = 7$  Hz, 8<sup>1</sup>-CH<sub>3</sub>) 1.54–1.65 (4H, m, COOCCH<sub>2</sub>CH<sub>2</sub>), 0.24, –1.83 (each 1H, s, NH). MS (FAB) found;  $m/z$  662. Calculated for C<sub>39</sub>H<sub>42</sub>N<sub>4</sub>O<sub>6</sub> : M<sup>+</sup>, 662.

### 2.3.11. Synthesis of 4-(vinylcarbonyloxy)butyl 3-hydroxymethyl-3-devinyl-pyropheophorbide-**a** (**2d**)

Reduction of **1d** with t-BuNH<sub>2</sub>BH<sub>3</sub> gave **2d** (86% yield); VIS (CH<sub>2</sub>Cl<sub>2</sub>)  $\lambda_{\max} = 662$  (rel., 0.48), 605 (0.08), 535 (0.09), 505 (0.10), 410 nm (1.00); <sup>1</sup>H-NMR (CDCl<sub>3</sub>)  $\delta = 9.45$ , 9.43, 8.56 (each 1H, s, 5-, 10-, 20-H), 6.31 (1H, dd,  $J = 2$ , 17 Hz, COC=CH *trans* to C–H), 6.01 (1H, dd,  $J = 10$ , 17 Hz, COCH=C), 5.90, 5.87 (each 1H, d,  $J = 13$  Hz, 3-CH<sub>2</sub>) 5.74 (1H, dd,  $J = 2$ , 10 Hz, COC=CH *cis* to C–H), 5.22, 5.08 (each 1H, d,  $J = 19$  Hz, 13<sup>1</sup>-CH<sub>2</sub>), 4.47 (1H, dq,  $J = 2$ , 8 Hz, 18-H), 4.28 (1H, dt,  $J = 8$ , 2 Hz, 17-H), 3.90–3.95, 3.78–3.79 (3H + 1H, m, COOCH<sub>2</sub>C<sub>2</sub>CH<sub>2</sub>), 3.68 (2H, q,  $J = 8$  Hz, 8-CH<sub>2</sub>), 3.63, 3.41, 3.25 (each 3H, s, 2-, 7-, 12-CH<sub>3</sub>), 2.62–2.67, 2.44–2.49, 2.30–2.36, 2.17–2.24 (1H + 1H + 2H + 1H, m, 3<sup>1</sup>-OH, 17-CH<sub>2</sub>CH<sub>2</sub>), 1.80 (3H, d,  $J = 8$  Hz, 18-CH<sub>3</sub>), 1.68 (3H, t,  $J = 8$  Hz, 8<sup>1</sup>-CH<sub>3</sub>), 1.39–1.41 (4H, m, COOCCH<sub>2</sub>CH<sub>2</sub>), 0.24, –1.83 (each 1H, s, NH). MS (FAB) found;  $m/z$  664. Calculated for C<sub>39</sub>H<sub>44</sub>N<sub>4</sub>O<sub>6</sub> : M<sup>+</sup>, 664.

### 2.3.12. Synthesis of zinc 4-(vinylcarbonyloxy)butyl 3-hydroxymethyl-3-devinyl-pyropheophorbide-**a** (**3d**)

Zinc metallation of **2d** gave **3d** (83% yield); VIS (THF)  $\lambda_{\max} = 646$  (rel., 0.75), 600 (0.10), 566 (0.05), 521 (0.03), 424 (1.00), 404 nm (0.56); <sup>1</sup>H-NMR (CDCl<sub>3</sub>–1% C<sub>5</sub>D<sub>5</sub>N)  $\delta = 9.55$ , 9.32, 8.33 (each 1H, s, 5-, 10-, 20-H), 6.31 (1H, dd,  $J = 2$ , 17 Hz, COC=CH *trans* to C–H), 6.02 (1H, dd,  $J = 10$ , 17 Hz, COCH=C), 5.82 (2H, s, 3-CH<sub>2</sub>) 5.76 (1H, dd,  $J = 2$ , 10 Hz, COC=CH *cis* to C–H), 5.16, 5.05 (each 1H, d,  $J = 19$  Hz, 13<sup>1</sup>-CH<sub>2</sub>), 4.39 (1H, dd,  $J = 2$ , 7 Hz, 18-H), 4.19 (1H, dt,  $J = 7$ , 2 Hz, 17-H), 4.00–4.02, 3.93–3.96, 3.85–3.89 (2H + 1H + 1H, m, COOCH<sub>2</sub>C<sub>2</sub>CH<sub>2</sub>), 3.73 (2H, q,  $J = 8$  Hz, 8-CH<sub>2</sub>), 3.67, 3.32, 3.22 (each 3H, s, 2-, 7-, 12-CH<sub>3</sub>), 2.51–2.55, 2.27–2.35, 1.92–1.96, (1H + 2H + 1H,



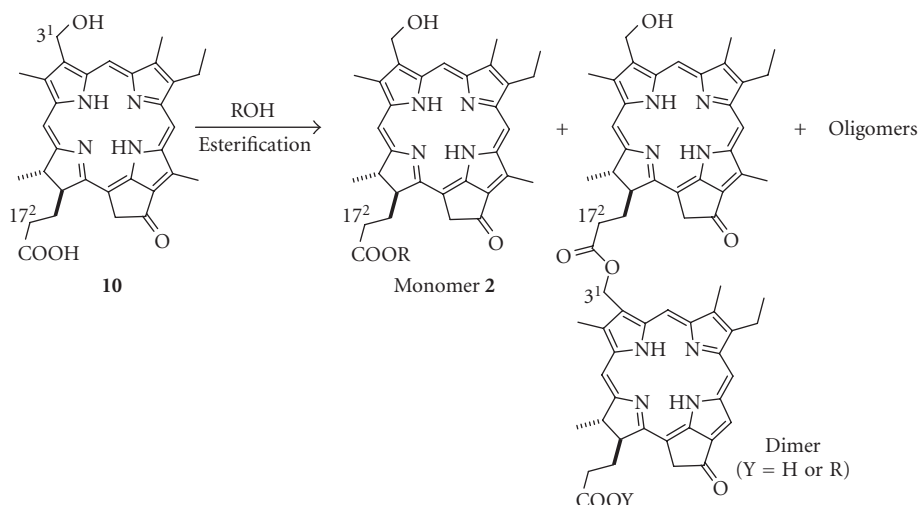


FIGURE 2: Esterification of 3<sup>1</sup>-hydroxy-17<sup>2</sup>-carboxy-chlorin **10** with alcohol (ROH).

m, 17-CH<sub>2</sub>CH<sub>2</sub>), 1.70 (3H, d,  $J = 8$  Hz, 18-CH<sub>3</sub>), 1.68 (3H, t,  $J = 8$  Hz, 8<sup>1</sup>-CH<sub>3</sub>), 1.47–1.53 (4H, m, COOCCH<sub>2</sub>CH<sub>2</sub>). MS (FAB) found;  $m/z$  726. Calculated for C<sub>39</sub>H<sub>42</sub>N<sub>4</sub>O<sub>6</sub><sup>64</sup>Zn : M<sup>+</sup>, 726.

### 3. RESULTS AND DISCUSSION

#### 3.1. Synthesis of zinc bacteriochlorophyll-*d* derivatives possessing a diacetylene moiety

Esterification of 3<sup>1</sup>-hydroxy-17<sup>2</sup>-carboxy-chlorin **10** with alcohol (ROH) gave oligomeric chlorins including dimer as byproducts besides the desired 17<sup>2</sup>-COOR ester **2** (see Figure 2). To prevent such undesired condensation affording 17<sup>2</sup>-COOC(3<sup>1</sup>) esters, the reactive 3<sup>1</sup>-hydroxy group was protected by its oxidation before esterification. Starting carboxylic acids **6** and **9** possessing the 3-carbonyl group were prepared by modifying methyl pyropheophorbide-*a* (**4**) obtained from chlorophyll-*a* (see Scheme 1). 3-Formyl-17<sup>2</sup>-carboxy-chlorin **6** was synthesized according to reported procedures [18] as in **4** → **5** → **6**: the 3-vinyl group of **4** was oxidatively cleaved to the corresponding 3-formyl group and successively the methyl ester of **5** was hydrolyzed to yield **6**. 3-Acetyl-17<sup>2</sup>-methoxycarbonyl-chlorin **8** was afforded from **4** through hydration of the 3-vinyl group in **4** and oxidation of the resulting 1-hydroxyethyl group in **7** to the 3-acetyl group in **8** [19, 20] and hydrolyzed by action of an acid [21] to give the corresponding carboxylic acid **9** (94% yield).

As a polymerizable functional group, a diacetylene moiety was first introduced in the 17<sup>2</sup>-ester. Carboxylic acids **6** and **9** reacted with 10,12-pentacosadiyn-1-ol by action of water-soluble carbodiimide (EDC) as a dehydrating condensation reagent in the presence of DMAP as a condensation promoter [9, 22] to afford esters **1a** and **1c** in good yields (see Scheme 2). The 3-formyl group in **1a** was selectively reduced by *tert*-butylamine borane complex [23] to give **2a** possessing the 3-hydroxymethyl group. The 3-acetyl group

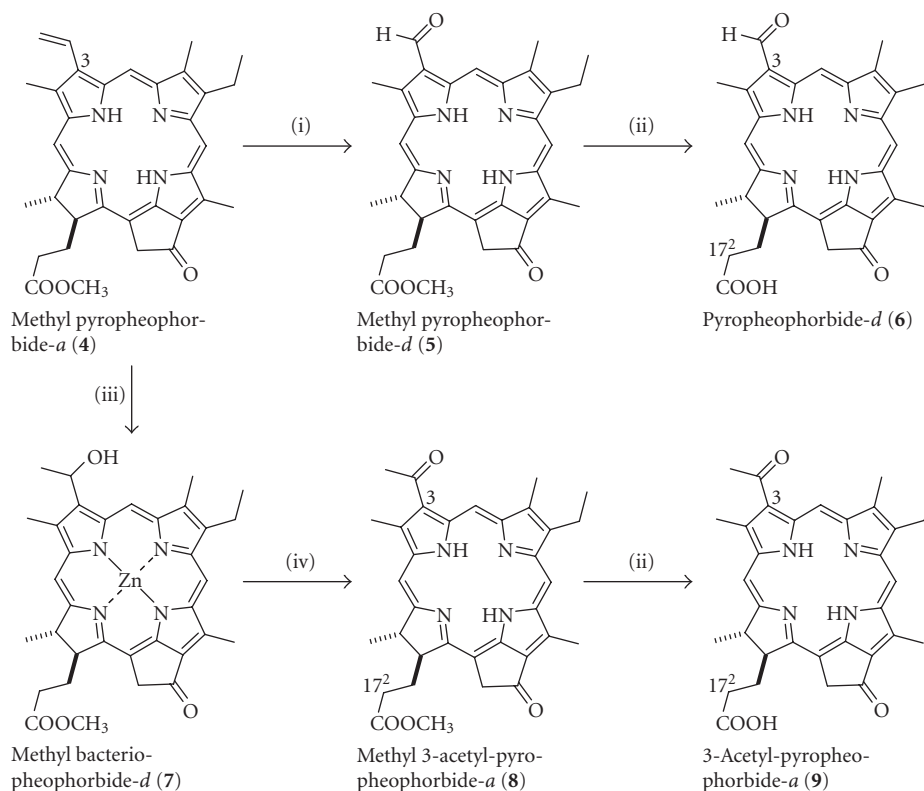
in **1c** was reduced by more reactive sodium borohydride, because a more sterically hindered keto group is less reactive than a formyl group. NaBH<sub>4</sub> can reduce the 13-C=O in a molecule and the reduction must be stopped just after visible absorption, and TLC analyses indicate a disappearance of the 3-acetyl group. It is noteworthy that the reductivity of peripheral carbonyl groups on the chlorin  $\pi$ -moiety decreases in the order, 3-CHO > 3-COCH<sub>3</sub> > 13-CO.

Zinc complexes **3a** and **3c** were obtained from free bases **2a** and **2c** by standard procedures [9]. 3-(1-Hydroxyethyl)chlorin **3c** was a 3<sup>1</sup>-epimeric mixture and the 1 : 1 mixture was used for the following experiments. As a nonpolymerizable reference compound, zinc 3-hydroxymethyl-chlorin **3b** having tetracosanyl ester was prepared similarly to the synthesis of **3a**. All the synthetic chlorins were characterized by their <sup>1</sup>H-NMR, visible, IR, and/or mass spectra.

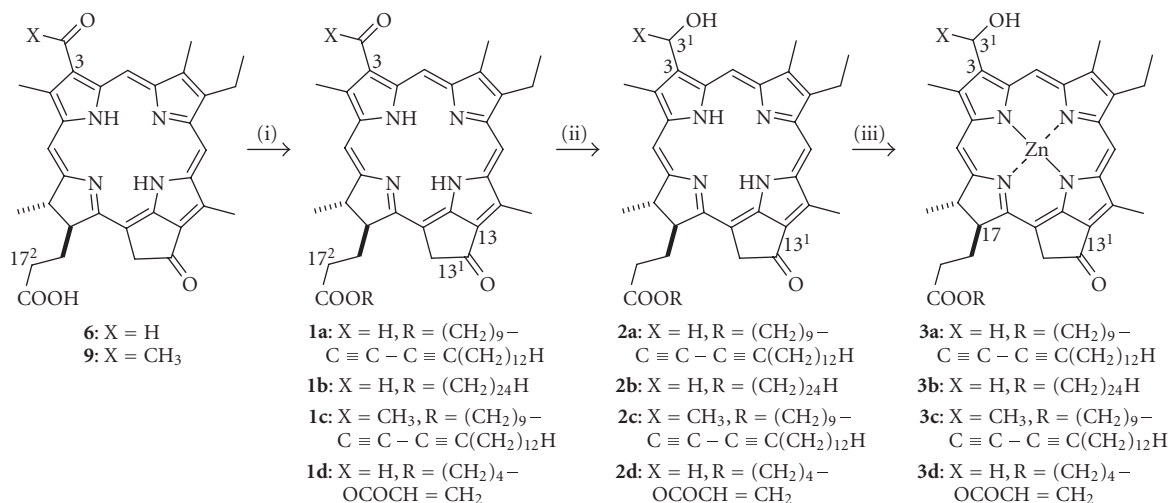
#### 3.2. Self-aggregation of zinc bacteriochlorophyll-*d* derivatives possessing a diacetylene moiety

##### 3.2.1. In a nonpolar organic solvent

In THF, **3a** gave sharp Q<sub>y</sub> and Soret peaks at 646 and 424 nm (dashed line of Figure 3(a)). The species was monomeric and five-coordinated zinc complex with a THF molecule as an axial ligand, compared with previous data [7, 9, 21, 23]. When the solution was diluted with hexane, broadened and red-shifted absorption bands were observed. In 0.1%(v/v) THF-hexane, 739- and 450-nm bands were mainly observed and small monomeric peaks remained (solid line of Figure 3(a)), indicating that most of **3a** self-aggregated to form a similar oligomer to chlorosomal J-aggregates [7, 9, 21, 23]. In the nonpolar organic solvent, **3b** lacking a polymerizable group gave the same oligomeric absorption peaks at 739 and 450 nm. These results clearly indicate that such long hydrocarbon chains as well as the rigid diacetylene moiety in the 17-propionate did not disturb self-aggregation of zinc 3<sup>1</sup>-hydroxy-13<sup>1</sup>-oxo-chlorins.



SCHEME 1: Synthesis of pyropheophorbides: (i)  $\text{OsO}_4\text{-NaIO}_4/\text{aqueous AcOH-THF}$ ; (ii) conc.  $\text{HCl}$ ; (iii)  $\text{HBr/AcOH, H}_2\text{O, CH}_2\text{N}_2/\text{Et}_2\text{O}$ ; (iv)  $\text{Pr}_4\text{NRuO}_4\text{-Me(O)N(CH}_2\text{CH}_2)_2\text{O/CH}_2\text{Cl}_2$ .



SCHEME 2: Synthesis of zinc bacteriochlorophyll-*d* derivatives: (i)  $\text{ROH, EDC-DMAP/CH}_2\text{Cl}_2$ ; (ii)  $t\text{-BuNH}_2\text{BH}_3/\text{CH}_2\text{Cl}_2$  for X=H,  $\text{NaBH}_4/\text{MeOH-CH}_2\text{Cl}_2$  for X=CH<sub>3</sub>; (iii)  $\text{Zn(OAc)}_2 \cdot 2\text{H}_2\text{O/MeOH-CH}_2\text{Cl}_2$ .

Secondary alcohol **3c**, one of zinc 3<sup>1</sup>-hydroxy-13<sup>1</sup>-oxochlorins, self-aggregated in 0.1%(v/v) THF-hexane to give electronic absorption bands characteristic of its J-aggregates (see Figure 3(b)). The red-shift values in peak positions by self-aggregation of **3c** were smaller than those in **3a**: typically, Q<sub>y</sub>-peak shifts were 1930 and 1260 cm<sup>-1</sup> for **3a** and **3c**, respectively. This difference is ascribable to the steric effect around the 3<sup>1</sup>-OH which connected the molecules in the self-aggregates, that is, the less steric OH in primary alcohol

**3a** can coordinate to the zinc metal and hydrogen-bond with the 13-carbonyl group more tightly to give larger  $\pi\text{-}\pi$  interaction of chlorin chromophores in the supramolecule than the secondary alcoholic OH in **3c** [24].

### 3.2.2. In the solid state

The above nonpolar organic solutions containing self-aggregates of **3a-c** were cast on a quartz glass plate and all

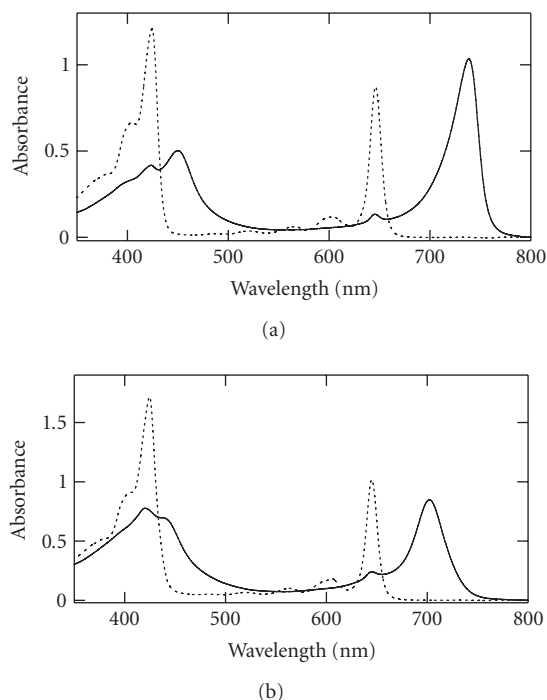


FIGURE 3: Visible absorption spectra of **3a** (a) and **3c** (b) in THF (dashed line) and 1%(v/v) THF-hexane (solid line) at 25°C (ca. 15  $\mu$ M).

the solvents were evaporated to afford the solid films. The absorption spectra of the resulting films possessing ca. 735- and 450-nm peaks were nearly the same as those in a solution (data not shown). The solid states of **3a–c** still gave their J-aggregates similarly to those in a nonpolar organic solvent.

Preliminarily, the self-aggregated films were irradiated with an ultraviolet light (254 nm) or heated at 180°C for polymerization of the diacetylene groups in **3a/c**, so that no polymers were given. The resulting films could not afford an appropriate orientation of diacetylene moieties in the solid state for their topochemical polymerization [25]. Further investigation is underway to produce poly(diacetylene) in the esters of self-aggregates.

### 3.3. Synthesis of zinc bacteriochlorophyll-*d* derivative possessing an acrylate moiety and its self-aggregation

An acrylate substituent was utilized for a polymerizable group in the 17-propionate. The synthetic route to **3d** possessing an acrylate moiety is the same as that to **3a** (see Scheme 2). During the preparation procedures (**6**  $\rightarrow$  **1d**  $\rightarrow$  **2d**  $\rightarrow$  **3d**), no polymerization of the acrylate occurred.

Synthetic compound **3d** self-aggregated in benzene ( $\lambda_{\max}$  = ca. 735/450 nm) as well as in hexane to give chlorosomal J-aggregates (data not shown). The acrylate moiety in the ester terminal did not prevent such self-aggregation. Preliminarily, radical polymerization of **3d** in benzene was examined using  $\alpha, \alpha'$ -azobisisobutyronitrile as an initiator.

After heating at 80°C for 1 hour, oligomers of **3d** were detected from gel permeation chromatography. The supramolecular structures of the resulting oligomers are being elucidated in our laboratory.

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