Electronic Supplementary Material (ESI) for Photochemical & Photobiological Sciences. This journal is © The Royal Society of Chemistry and Owner Societies 2019

# **Electronic Supplementary Information**

# Heterodimers of zinc and free-base chlorophyll derivatives co-assembled in biomimetic chlorosomal J-aggregates

Sunao Shoji,\* Yosaku Nomura and Hitoshi Tamiaki\*

Graduate School of Life Sciences, Ritsumeikan University, Kusatsu, Shiga 525-8577,

Japan

# **Table of Contents**

- 1. Synthesis and spectral data of (B)Chl-a derivatives
- 2. Optical data of (B)Chl-a derivatives in THF
- 3. Optical data of co-assemblies of chlorosomal J-aggregates with heterodimers

4. References

#### 1. Synthesis and spectral data of (B)Chl-a derivatives

Methyl pyrobacteriopheophorbide-*a* (H<sub>2</sub>B-ME)

**H<sub>2</sub>B-ME** was synthesized according to the reported procedure (see ref. S1): UV-Vis (THF)  $\lambda_{max}$  751 (rel., 0.64), 680 (0.08), 623 (0.03), 530 (0.25), 497 (0.05), 385 (0.51), 359 nm (1.00); <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 9.00 (1H, s, 5-H), 8.47 (1H, s, 10-H), 8.42 (1H, s, 20-H), 5.11, 4.94 (each 1H, d, J = 19 Hz, 13<sup>1</sup>-CH<sub>2</sub>), 4.30<sub>2</sub> (1H, dq, J = 3, 7 Hz, 18-H), 4.29<sub>7</sub> (1H, dq, J = 3, 7 Hz, 7-H), 4.13 (1H, dt, J = 8, 3 Hz, 17-H), 4.03 (1H, dt, J = 8, 3 Hz, 8-H), 3.62 (3H, s, 17<sup>2</sup>-COOCH<sub>3</sub>), 3.50 (3H, s, 2-CH<sub>3</sub>), 3.45 (3H, s, 12-CH<sub>3</sub>), 3.17 (3H, s, 3-COCH<sub>3</sub>), 2.60, 2.53, 2.25 (1H+1H+2H, m, 17-CH<sub>2</sub>CH<sub>2</sub>), 2.36, 2.09 (each 1H, m, 8-CH<sub>2</sub>), 1.80 (3H, d, J = 7 Hz, 7-CH<sub>3</sub>), 1.73 (3H, d, J = 7 Hz, 18-CH<sub>3</sub>), 1.11 (3H, t, J = 7 Hz, 8<sup>1</sup>-CH<sub>3</sub>), 0.36, -1.03 (each 1H, s, NH×2); MS (LDI) found: *m/z* 566.6. Calcd. for C<sub>34</sub>H<sub>38</sub>N<sub>4</sub>O<sub>4</sub>: M<sup>+</sup>, 566.3. See also ref. S1–S3 for its spectral data.

# Methyl 3-acetyl-3-devinyl-pyropheophorbide-a (H<sub>2</sub>C-ME)

**H**<sub>2</sub>**C-ME** was synthesized according to the reported procedure (see ref. S1): UV-Vis (THF)  $\lambda_{max}$  682 (rel., 0.55), 622 (0.07), 546 (0.11), 514 (0.12), 416 (1.00), 383 nm (0.75); <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 9.98 (1H, s, 5-H), 9.57 (1H, s, 10-H), 8.77 (1H, s, 20-H), 5.32, 5.17 (each 1H, d, J = 19 Hz, 13<sup>1</sup>-CH<sub>2</sub>), 4.55 (1H, dq, J = 2, 7 Hz, 18-H), 4.36 (1H, dt, J = 8, 2 Hz, 17-H), 3.70 (2H, q, J = 8 Hz, 8-CH<sub>2</sub>), 3.69 (3H, s, 12-CH<sub>3</sub>), 3.65 (3H, s, 2-CH<sub>3</sub>), 3.61 (3H, s, 17<sup>2</sup>-COOCH<sub>3</sub>), 3.29 (3H, s, 3-COCH<sub>3</sub>), 3.28 (3H, s, 7-CH<sub>3</sub>), 2.71, 2.59, 2.32 (1H+1H+2H, m, 17-CH<sub>2</sub>CH<sub>2</sub>), 1.84 (3H, d, J = 7 Hz, 18-CH<sub>3</sub>), 1.70 (3H, t, J = 8 Hz, 8<sup>1</sup>-CH<sub>3</sub>), -0.03, -2.03 (each 1H, s, NH×2); MS (LDI) found: *m/z* 564.6. Calcd. for C<sub>34</sub>H<sub>36</sub>N<sub>4</sub>O<sub>4</sub>: M<sup>+</sup>, 564.3. See also ref. S1, S4, and S5 for its spectral data.

# Methyl 3-acetyl-devinyl-pyroprotopheophorbide-*a* (H<sub>2</sub>P-ME)

H<sub>2</sub>P-ME was synthesized according to the reported procedure (see ref. S1): UV-Vis

(THF)  $\lambda_{\text{max}}$  648 (rel., 0.02), 596 (0.05), 569 (0.08), 526 (0.03), 429 (0.52), 419 nm (1.00); <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  10.43 (1H, s, 5-H), 9.49 (1H, s, 10-H), 9.21 (1H, s, 20-H), 4.89 (2H, d, J = 3 Hz, 13<sup>1</sup>-CH<sub>2</sub>), 3.93 (2H, q, J = 8 Hz, 8-CH<sub>2</sub>), 3.70 (3H, s, 2-CH<sub>3</sub>), 3.69 (3H, s, 17<sup>2</sup>-COOCH<sub>3</sub>), 3.63 (3H, s, 12-CH<sub>3</sub>), 3.59 (3H, s, 7-CH<sub>3</sub>), 3.46 (2H, t, J = 8 Hz, 17-CH<sub>2</sub>), 3.30 (3H, s, 3-COCH<sub>3</sub>), 3.14 (3H, s, 18-CH<sub>3</sub>), 2.61 (2H, t, J = 8 Hz, 17<sup>1</sup>-CH<sub>2</sub>), 1.80 (3H, t, J = 8 Hz, 8<sup>1</sup>-CH<sub>3</sub>), -4.24, -5.67 (each 1H, s, NH×2); MS (LDI) found: m/z 562.7. Calcd. for C<sub>34</sub>H<sub>34</sub>N<sub>4</sub>O<sub>4</sub>: M<sup>+</sup>, 562.3. See also ref. S1 for its spectral data.

Zinc methyl pyrobacteriopheophorbide-a (ZnB-ME)

**ZnB-ME** was synthesized according to the reported procedure (see ref. S5): UV-Vis (THF)  $\lambda_{\text{max}}$  766 (rel., 1.00), 701 (0.10), 568 (0.22), 390 (0.47), 356 nm (0.75); <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  8.74 (1H, s, 5-H), 8.37 (1H, s, 10-H), 8.28 (1H, s, 20-H), 4.50, 4.37 (each 1H, d, J = 19 Hz, 13<sup>1</sup>-CH<sub>2</sub>), 4.28 (1H, dq, J = 3, 7 Hz, 7-H), 4.17 (1H, dq, J = 2, 7 Hz, 18-H), 4.02 (1H, dt, J = 8, 3 Hz, 8-H), 3.99 (1H, dt, J = 8, 2 Hz, 17-H), 3.40 (3H, s, 2-CH<sub>3</sub>), 3.18 (3H, s, 17<sup>2</sup>-COOCH<sub>3</sub>), 3.17 (3H, s, 12-CH<sub>3</sub>), 2.97 (3H, s, 3-COCH<sub>3</sub>), 2.38, 2.31, 2.16 (1H+2H+3H, m, 17-CH<sub>2</sub>CH<sub>2</sub>, 8-CH<sub>2</sub>), 1.76 (3H, d, J = 7 Hz, 7-CH<sub>3</sub>), 1.69 (3H, d, J = 7 Hz, 18-CH<sub>3</sub>), 1.15 (3H, t, J = 8 Hz, 8<sup>1</sup>-CH<sub>3</sub>); MS (LDI) found: *m*/*z* 628.3. Calcd. for C<sub>34</sub>H<sub>36</sub>N<sub>4</sub>O<sub>4</sub>Zn: M<sup>+</sup>, 628.2. See also ref. S5 for its spectral data.

Zinc methyl 3-acetyl-3-devinyl-pyropheophorbide-*a* (ZnC-ME)

**ZnC-ME** was synthesized according to the reported procedure (see ref. S5): UV-Vis (THF)  $\lambda_{\text{max}}$  670 (rel., 0.74), 621 (0.12), 580 (0.07), 534 (0.04), 435 (1.00), 386 nm (0.45); <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  9.87 (1H, s, 5-H), 9.63 (1H, s, 10-H), 8.53 (1H, s, 20-H), 5.22, 5.11 (each 1H, d, *J* = 19 Hz, 13<sup>1</sup>-CH<sub>2</sub>), 4.46 (1H, dq, *J* = 2, 7 Hz, 18-H), 4.25 (1H, dt, *J* = 8, 2 Hz, 17-H), 3.77 (2H, q, *J* = 8 Hz, 8-CH<sub>2</sub>), 3.71 (3H, s, 12-CH<sub>3</sub>), 3.58<sub>4</sub> (3H, s, 2-CH<sub>3</sub>), 3.57<sub>6</sub> (3H, s, 17<sup>2</sup>-COOCH<sub>3</sub>), 3.29 (3H, s, 7-CH<sub>3</sub>), 3.22 (3H, s, 3-COCH<sub>3</sub>), 2.58,

2.42, 2.28, 1.99 (each 1H, m, 17-CH<sub>2</sub>CH<sub>2</sub>), 1.74 (3H, d, J = 7 Hz, 18-CH<sub>3</sub>), 1.71 (3H, t, J = 8 Hz,  $8^{1}$ -CH<sub>3</sub>); MS (LDI) found: m/z 626.7. Calcd. for C<sub>34</sub>H<sub>34</sub>N<sub>4</sub>O<sub>4</sub>Zn: M<sup>+</sup>, 626.2. See also ref. S5 for its spectral data.

#### Zinc methyl 3-acetyl-devinyl-pyroprotopheophorbide-a (ZnP-ME)

**ZnP-ME** was synthesized according to the reported procedure (see ref. S5): UV-Vis (THF)  $\lambda_{\text{max}}$  623 (rel., 0.10), 570 (0.03), 531 (0.02), 432 nm (1.00); <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  10.39 (1H, s, 5-H), 9.87 (1H, s, 10-H), 9.66 (1H, s, 20-H), 5.54 (2H, d, J = 1 Hz, 13<sup>1</sup>-CH<sub>2</sub>), 3.95 (2H, q, J = 8 Hz, 8-CH<sub>2</sub>), 3.87 (2H, tt, J = 1, 8 Hz, 17-CH<sub>2</sub>), 3.84 (3H, s, 12-CH<sub>3</sub>), 3.81 (3H, s, 2-CH<sub>3</sub>), 3.73 (3H, s, 17<sup>2</sup>-COOCH<sub>3</sub>), 3.51 (3H, s, 7-CH<sub>3</sub>), 3.36 (3H, s, 18-CH<sub>3</sub>), 3.30 (3H, s, 3-COCH<sub>3</sub>), 2.92 (2H, t, J = 8 Hz, 17<sup>1</sup>-CH<sub>2</sub>), 1.83 (3H, t, J = 8 Hz, 8<sup>1</sup>-CH<sub>3</sub>); MS (LDI) found: *m*/*z* 624.7. Calcd. for C<sub>34</sub>H<sub>32</sub>N<sub>4</sub>O<sub>4</sub>Zn: M<sup>+</sup>, 624.2. See also ref. S5 for its spectral data.

#### 2-Hydroxyethyl 3-acetyl-3-devinyl-pyropheophorbide-*a* (H<sub>2</sub>C-EE)

H<sub>2</sub>C-EE was synthesized according to the reported procedure (see ref. S6). To an ice-chilled mixture of ethylene glycol (10 mL) and methyl ester H<sub>2</sub>C-ME (53.5 mg, 94.7  $\mu$ mol) was added concentrated H<sub>2</sub>SO<sub>4</sub> (1 mL). The reaction mixture was stirred at room temperature for overnight, poured into ice water and extracted with dichloromethane. The organic layer was washed with aqueous 4% NaHCO<sub>3</sub> and water, dried over Na<sub>2</sub>SO<sub>4</sub>, filtered and evaporated. The residue was dissolved in acetone (10 mL) and treated with aqueous 5% HCl (10 mL) for 2 h at room temperature for deprotection of its partially produced acetal. The reaction mixture was extracted with dichloromethane and the organic layer was washed with aqueous 4% NaHCO<sub>3</sub> and water, dried over Na<sub>2</sub>SO<sub>4</sub>, and filtered. After evaporation of all the solvents, the residue was purified by FCC with 0.5–2% methanol and dichloromethane and successively recrystallized from dichloromethane and hexane to give ethylene glycol ester H<sub>2</sub>C-EE

(35.1 mg, 59.0 µmol, 62%) as a black solid: UV-Vis (THF)  $\lambda_{max}$  682 (rel., 0.55), 623 (0.07), 546 (0.10), 514 (0.12), 416 (1.00), 383 nm (0.75); <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  9.96 (1H, s, 5-H), 9.47 (1H, s, 10-H), 8.76 (1H, s, 20-H), 5.32, 5.17 (each 1H, d, J = 19 Hz, 13<sup>1</sup>-CH<sub>2</sub>), 4.55 (1H, dq, J = 2, 8 Hz, 18-H), 4.37 (1H, dt, J = 8, 2 Hz, 17-H), 4.12, 4.09 (each 1H, ddd, J = 3, 6, 12 Hz, 17<sup>2</sup>-COOCH<sub>2</sub>), 3.66 (2H, q, J = 8 Hz, 8-CH<sub>2</sub>), 3.65 (2H, m, 17<sup>2</sup>-COOCCH<sub>2</sub>), 3.65 (3H, s, 2-CH<sub>3</sub>), 3.60 (3H, s, 12-CH<sub>3</sub>), 3.28 (3H, s, 3-COCH<sub>3</sub>), 3.26 (3H, s, 7-CH<sub>3</sub>), 2.71, 2.59, 2.36 (1H+1H+2H, m, 17-CH<sub>2</sub>CH<sub>2</sub>), 1.87 (1H, s, 17<sup>2</sup>-COOC<sub>2</sub>OH), 1.83 (3H, d, J = 8 Hz, 18-CH<sub>3</sub>), 1.67 (3H, t, J = 8 Hz, 8<sup>1</sup>-CH<sub>3</sub>), -0.07, -2.05 (each 1H, s, NH×2); MS (LDI) found: *m*/*z* 594.4. Calcd. for C<sub>35</sub>H<sub>38</sub>N<sub>4</sub>O<sub>5</sub>: M<sup>+</sup>, 594.3. See also ref. S6 for its spectral data.

# 2-Hydroxyethyl 3-acetyl-3-devinyl-pyroprotopheophorbide-a (H<sub>2</sub>P-EE)

Similar to the synthesis of H<sub>2</sub>C-EE, transesterification of methyl ester H<sub>2</sub>P-ME (99.5 mg, 177 µmol), purification by FCC (0.5–2% methanol and dichloromethane) and recrystallization (dichloromethane and hexane) gave ethylene glycol ester H<sub>2</sub>P-EE (70.0 mg, 118 µmol, 67%) as a black solid: UV-Vis (THF)  $\lambda_{max}$  648 (rel., 0.02), 595 (0.05), 570 (0.08), 526 (0.03), 430 (0.52), 419 nm (1.00); <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  10.57 (1H, s, 5-H), 9.76 (1H, s, 10-H), 9.63 (1H, s, 20-H), 5.44 (2H, d, *J* = 3 Hz, 13<sup>1</sup>-CH<sub>2</sub>), 4.32 (2H, t, *J* = 5 Hz, 17<sup>2</sup>-COOCH<sub>2</sub>), 4.00 (2H, q, *J* = 8 Hz, 8-CH<sub>2</sub>), 3.93 (2H, t, *J* = 8 Hz, 17<sup>-</sup>COOCH<sub>2</sub>), 3.81 (3H, s, 2-CH<sub>3</sub>), 3.63 (3H, s, 7-CH<sub>3</sub>), 3.41 (3H, s, 18-CH<sub>3</sub>), 3.32 (3H, s, 3-COCH<sub>3</sub>), 2.93 (2H, t, *J* = 8 Hz, 17<sup>1</sup>-CH<sub>2</sub>), 2.54 (1H, t, *J* = 5 Hz, 17<sup>2</sup>-COOC<sub>2</sub>OH), 1.83 (3H, t, *J* = 8 Hz, 8<sup>1</sup>-CH<sub>3</sub>), -3.42, -4.58 (each 1H, s, NH×2); MS (LDI) found: *m*/*z* 592.4. Calcd. for C<sub>35</sub>H<sub>36</sub>N<sub>4</sub>O<sub>5</sub>: M<sup>+</sup>, 592.3.

Zinc 2-hydroxyethyl 3-acetyl-3-devinyl-pyropheophorbide-a (**ZnC-EE**) A methanol solution saturated with  $Zn(OAc)_2 \cdot 2H_2O$  (2 mL) was added to a dichloromethane solution (10 mL) of metal-free chlorin  $H_2C$ -EE (51.5 mg, 86.6 µmol) and stirred at room temperature in the dark under N<sub>2</sub> atmosphere for 2 h. After visible absorption showed the disappearance of  $H_2C$ -EE, dichloromethane (30 mL) were added to the reaction mixture, washed with aqueous 4% NaHCO<sub>3</sub> and water, dried over Na<sub>2</sub>SO<sub>4</sub> and evaporated. The resulting residue was recrystallized from dichloromethane and hexane to give the corresponding zinc complex ZnC-EE (53.4 mg, 81.1 µmol, 94%) as a dark green solid: UV-Vis (THF)  $\lambda_{max}$  670 (rel., 0.74), 622 (0.12), 581 (0.07), 535 (0.04), 435 (1.00), 386 nm (0.45); <sup>1</sup>H NMR (1% pyridine-*d*<sub>5</sub>-CDCl<sub>3</sub>)  $\delta$  9.88 (1H, s, 5-H), 9.63 (1H, s, 10-H), 8.52 (1H, s, 20-H), 5.22, 5.11 (each 1H, d, *J* = 19 Hz, 13<sup>1</sup>-CH<sub>2</sub>), 4.45 (1H, dq, *J* = 2, 7 Hz, 18-H), 4.27 (1H, dt, *J* = 7, 2 Hz, 17-H), 4.11, 4.08 (each 1H, ddd, *J* = 4, 5, 12 Hz, 17<sup>2</sup>-COOCH<sub>2</sub>), 3.77 (2H, q, *J* = 8 Hz, 8-CH<sub>2</sub>), 3.71 (3H, s, 12-CH<sub>3</sub>), 3.69, 3.68 (each 1H, br-t, *J* = 5 Hz, 17<sup>2</sup>-COOCCH<sub>2</sub>), 3.59 (3H, s, 2-CH<sub>3</sub>), 3.29 (3H, s, 7-CH<sub>3</sub>), 3.22 (3H, s, 3-COCH<sub>3</sub>), 2.74 (1H, s, 17<sup>2</sup>-COOC<sub>2</sub>OH), 2.57, 2.42, 2.31, 1.98 (each 1H, m, 17-CH<sub>2</sub>CH<sub>2</sub>), 1.83 (3H, d, *J* = 7 Hz, 18-CH<sub>3</sub>), 1.71 (3H, t, *J* = 8 Hz, 8<sup>1</sup>-CH<sub>3</sub>); MS (LDI) found: *m*/z 656.3. Calcd. for C<sub>35</sub>H<sub>36</sub>N<sub>4</sub>O<sub>5</sub>Zn: M<sup>+</sup>, 656.2.

Zinc 2-hydroxyethyl 3-acetyl-3-devinyl-pyroprotopheophorbide-*a* (**ZnP-EE**)

Similar to the synthesis of **ZnC-EE**, zinc metalation of **H**<sub>2</sub>**P-EE** (49.9 mg, 84.2 µmol) and successive recrystallization from dichloromethane and hexane gave the corresponding zinc complex **ZnP-EE** (54.6 mg, 83.2 µmol, 99%) as a black solid: UV-Vis (THF)  $\lambda_{max}$  623 (rel., 0.10), 570 (0.03), 532 (0.02), 432 nm (1.00); <sup>1</sup>H NMR (1% pyridine-*d*<sub>5</sub>-CDCl<sub>3</sub>)  $\delta$  10.40 (1H, s, 5-H), 9.93 (1H, s, 10-H), 9.81 (1H, s, 20-H), 5.77 (2H, d, *J* = 2 Hz, 13<sup>1</sup>-CH<sub>2</sub>), 4.32 (2H, m, 17<sup>2</sup>-COOCH<sub>2</sub>), 4.08 (2H, m, 17-CH<sub>2</sub>), 3.96 (2H, q, *J* = 8 Hz, 8-CH<sub>2</sub>), 3.88 (2H, m, 17<sup>2</sup>-COOCCH<sub>2</sub>), 3.86 (6H, s, 2-, 12-CH<sub>3</sub>), 3.50 (3H, s, 7-CH<sub>3</sub>), 3.47 (3H, s, 18-CH<sub>3</sub>), 3.33 (3H, s, 3-COCH<sub>3</sub>), 3.18 (1H, br-t, *J* = 5 Hz, 17<sup>2</sup>-COOC<sub>2</sub>OH), 3.05 (2H, m, 17<sup>1</sup>-CH<sub>2</sub>), 1.83 (3H, t, *J* = 8 Hz, 8<sup>1</sup>-CH<sub>3</sub>); MS (LDI) found: *m/z* 654.3. Calcd. for C<sub>35</sub>H<sub>34</sub>N<sub>4</sub>O<sub>5</sub>Zn: M<sup>+</sup>, 654.2.

Pyrobacteriopheophorbide-a (H<sub>2</sub>B-CA)

H<sub>2</sub>B-CA was synthesized according to the reported procedure (see ref. S6). Methyl ester  $H_2B$ -ME (21.3 mg, 37.6 µmol) was dissolved in acetone (1 mL), to which was added aqueous concentrated HCl (10 mL). The reaction mixture was stirred at room temperature for 3 h, poured into ice water and extracted with chloroform. The organic layer was washed with water, dried over Na<sub>2</sub>SO<sub>4</sub>, filtered, and evaporated. The residue was recrystallized from chloroform and hexane to give carboxy acid H<sub>2</sub>B-CA (19.3 mg, 34.9  $\mu$ mol, 93%) as a black solid: UV-Vis (THF)  $\lambda_{max}$  751 (rel., 0.64), 681 (0.08), 623 (0.03), 530 (0.25), 499 (0.05), 385 (0.52), 359 nm (1.00); <sup>1</sup>H NMR (pyridine-d<sub>5</sub>) δ 9.46 (1H, s, 5-H), 8.74 (1H, s, 20-H), 8.72 (1H, s, 10-H), 5.47, 5.15 (each 1H, d, *J* = 19 Hz,  $13^{1}$ -CH<sub>2</sub>), 4.45 (1H, dq, J = 2, 8 Hz, 18-H), 4.13 (1H, dt, J = 10, 2 Hz, 17-H), 4.24 (1H, dq, J = 3, 8 Hz, 7-H), 4.02 (1H, dt, J = 9, 3 Hz, 8-H), 3.58 (3H, s, 12-CH<sub>3</sub>), 3.50 (3H, s, 2-CH<sub>3</sub>), 3.20 (3H, s, 3-COCH<sub>3</sub>), 2.96, 2.74, 2.51 (2H+1H+1H, m, 17-CH<sub>2</sub>CH<sub>2</sub>), 2.36, 2.08 (each 1H, m, 8-CH<sub>2</sub>), 1.82 (3H, d, J = 8 Hz, 18-CH<sub>3</sub>), 1.80 (3H, d, J = 8 Hz, 7-CH<sub>3</sub>), 1.10 (3H, t, J = 7 Hz, 8<sup>1</sup>-CH<sub>3</sub>), 0.56, -0.86 (each 1H, s, NH×2) [No proton of COOH was observed]; MS (LDI) found: m/z 552.7. Calcd. for C<sub>33</sub>H<sub>36</sub>N<sub>4</sub>O<sub>4</sub>: M<sup>-</sup>, 552.3. See also ref. S6 for its spectral data.

#### 3-Acetyl-3-devinyl-pyropheophorbide-a (H<sub>2</sub>C-CA)

**H**<sub>2</sub>**C-CA** was synthesized according to the reported procedure (see ref. S6). Similar to the synthesis of **H**<sub>2</sub>**B-CA**, hydrolysis of methyl ester **H**<sub>2</sub>**C-ME** (31.3 mg, 55.4 μmol) and successive recrystallization from chloroform and hexane gave the corresponding carboxylic acid **H**<sub>2</sub>**C-CA** (30.0 mg, 54.5 μmol, 98%) as a black solid: UV-Vis (THF)  $\lambda_{\text{max}}$  682 (rel., 0.55), 623 (0.07), 546 (0.10), 514 (0.13), 416 (1.00), 383 nm (0.76); <sup>1</sup>H NMR (pyridine-*d*<sub>5</sub>) δ 10.54 (1H, s, 5-H), 9.98 (1H, s, 10-H), 9.07 (1H, s, 20-H), 5.64, 5.34 (each 1H, d, *J* = 19 Hz, 13<sup>1</sup>-CH<sub>2</sub>), 4.70 (1H, br-d, *J* = 6 Hz, 18-H), 4.58 (1H, br-d, *J* = 8 Hz, 17-H), 3.77 (2H, q, *J* = 8 Hz, 8-CH<sub>2</sub>), 3.74 (3H, s, 12-CH<sub>3</sub>), 3.63 (3H, s,

2-CH<sub>3</sub>), 3.31 (6H, s, 7-CH<sub>3</sub>, 3-COCH<sub>3</sub>), 3.03, 2.79, 2.53 (2H+1H+1H, m, 17-CH<sub>2</sub>CH<sub>2</sub>), 1.91 (3H, br-d, J = 6 Hz, 18-CH<sub>3</sub>), 1.70 (3H, t, J = 8 Hz,  $8^1$ -CH<sub>3</sub>), 0.29, -1.74 (each 1H, s, NH×2) [No proton of COOH was observed]; MS (LDI) found: m/z 550.7. Calcd. for C<sub>33</sub>H<sub>34</sub>N<sub>4</sub>O<sub>4</sub>: M<sup>-</sup>, 550.3. See also ref. S6 for its spectral data.

3-Acetyl-3-devinyl-pyroprotopheophorbide-a (H<sub>2</sub>P-CA)

Similar to the synthesis of H<sub>2</sub>B-CA, hydrolysis of methyl ester H<sub>2</sub>P-ME (43.5 mg, 77.3  $\mu$ mol) and successive recrystallization from chloroform and hexane gave the corresponding carboxylic acid H<sub>2</sub>P-CA (39.6 mg, 72.2  $\mu$ mol, 93%) as a black solid: UV-Vis (THF)  $\lambda_{max}$  648 (rel., 0.02), 595 (0.05), 570 (0.08), 526 (0.03), 430 (0.53), 419 nm (1.00); <sup>1</sup>H NMR (pyridine-*d*<sub>5</sub>)  $\delta$  11.12 (1H, s, 5-H), 10.27 (1H, s, 10-H), 10.06 (1H, s, 20-H), 5.99 (2H, s, 13<sup>1</sup>-CH<sub>2</sub>), 4.34 (2H, br-s, 17-CH<sub>2</sub>), 4.05 (2H, q, *J* = 8 Hz, 8-CH<sub>2</sub>), 3.88 (3H, s, 12-CH<sub>3</sub>), 3.86 (3H, s, 2-CH<sub>3</sub>), 3.58 (3H, s, 18-CH<sub>3</sub>), 3.57 (3H, s, 7-CH<sub>3</sub>), 3.36 (3H, s, 3-COCH<sub>3</sub>), 3.33 (2H, t, *J* = 8 Hz, 17<sup>1</sup>-CH<sub>2</sub>), 1.78 (3H, t, *J* = 8 Hz, 8<sup>1</sup>-CH<sub>3</sub>), -2.68, -3.84 (each 1H, s, NH×2) [No proton of COOH was observed]; MS (LDI) found: *m/z* 548.8. Calcd. for C<sub>33</sub>H<sub>32</sub>N<sub>4</sub>O<sub>4</sub>: M<sup>-</sup>, 548.2.

# ZnC-H<sub>2</sub>B

To a dry dichloromethane solution (15 mL) of carboxylic acid H<sub>2</sub>B-CA (4.2 mg, 7.6  $\mu$ mol) was added 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide hydrochloride (EDC·HCl, 2.9 mg, 15  $\mu$ mol), 4-(*N*,*N*-dimethylamino)pyridine (DMAP, 3.7 mg, 30  $\mu$ mol), and ethylene glycol ester **ZnC-EE** (5.0 mg, 7.6  $\mu$ mol) at 0 °C. The reaction mixture was stirred at room temperature for overnight, poured into ice-chilled aqueous 2% HCl and extracted with dichloromethane. The organic layer was washed with aqueous 4% NaHCO<sub>3</sub> and water, dried over Na<sub>2</sub>SO<sub>4</sub>, filtered, and evaporated. The residue was purified by normal-phase HPLC (retention time, 11.3 min): column, Cosmosil 5SL-II (10 $\phi$  × 250 mm, Nacalai Tesque); eluent, 0.5% methanol and

chloroform; flow rate 2.0 mL/min. The fraction eluted 11.3 min was dried and recrystallization from dichloromethane and hexane gave heterodimer  $ZnC-H_2B$  (5.9 mg, 4.9 µmol, 64%) as a black solid. See Experimental section in the main text for its spectral data.

#### ZnC-H<sub>2</sub>C

Similar to the synthesis of  $ZnC-H_2B$ , carboxylic acid  $H_2C-CA$  (4.2 mg, 7.6 µmol) was esterified with ethylene glycol monoester ZnC-EE (5.0 mg, 7.6 µmol) by action of EDC·HCl (2.9 mg, 15 µmol) and DMAP (3.7 mg, 30 µmol) in dry dichloromethane (15 mL), and subjected to normal-phase HPLC: column, Cosmosil 5SL-II ( $10\phi \times 250$  mm); eluent, 0.2% methanol and chloroform; flow rate 2.0 mL/min. The fraction of 19.6 min was purified by recrystallization from dichloromethane and hexane to give heterodimer **ZnC-H<sub>2</sub>C** (6.8 mg, 5.7  $\mu$ mol, 75%) as a black solid: UV-Vis (THF)  $\lambda_{max}$  674 (rel., 0.67), 622 (0.12), 578 (0.06), 545 (0.09), 514 (0.09), 422 (1.00), 383 nm (0.75); <sup>1</sup>H NMR (1% pyridine-d<sub>5</sub>-CDCl<sub>3</sub>) δ 9.94, 9.85 (each 1H, s, 5-H×2), 9.55, 9.49 (each 1H, s, 10-H×2), 8.70, 8.44 (each 1H, s, 20-H×2), 5.24, 5.15, 5.08, 5.01 (each 1H, d, J = 19 Hz,  $13^{1}$ -CH<sub>2</sub>×2), 4.49, 4.37 (each 1H, dq, J = 2, 7 Hz, 18-H×2), 4.27, 4.13 (each 1H, dt, J =8, 2 Hz, 17-H×2), 4.10 (4H, m, 17<sup>2</sup>-COOCH<sub>2</sub>×2), 3.72, 3.65 (each 2H, q, J = 8 Hz, 8-CH<sub>2</sub>×2), 3.65, 3.62 (each 3H, s, 12-CH<sub>3</sub>×2), 3.55, 3.51 (each 3H, s, 2-CH<sub>3</sub>×2), 3.26, 3.24 (each 3H, s, 7-CH<sub>3</sub>×2), 3.22, 3.17 (each 3H, s, 3-COCH<sub>3</sub>×2), 2.63, 2.55, 2.39, 2.23, 2.17, 2.04 (1H+2H+1H+2H+1H+1H, m, 17-CH<sub>2</sub>CH<sub>2</sub>×2), 1.76, 1.63 (each 3H, d, J = 7Hz, 18-CH<sub>3</sub>×2), 1.68, 1.67 (each 3H, t, J = 8 Hz,  $8^{1}$ -CH<sub>3</sub>×2), -0.01, -2.10 (each 1H, s, NH×2); MS (LDI) found: *m*/*z* 1188.4. Calcd. for C<sub>68</sub>H<sub>68</sub>N<sub>8</sub>O<sub>8</sub>Zn: M<sup>-</sup>, 1188.4; HRMS (APCI) found: m/z 1189.4527. Calcd. for C<sub>68</sub>H<sub>69</sub>N<sub>8</sub>O<sub>8</sub>Zn: MH<sup>+</sup>, 1189.4524.

# ZnP-H<sub>2</sub>B

Similar to the synthesis of ZnC-H<sub>2</sub>B, carboxylic acid H<sub>2</sub>B-CA (4.3 mg, 7.8 µmol) was

esterified with ethylene glycol monoester ZnP-EE (4.9 mg, 7.5 µmol) by action of EDC·HCl (3.1 mg, 16 µmol) and DMAP (3.9 mg, 32 µmol) in dry dichloromethane (15 mL), and subjected to normal-phase HPLC: column, Cosmosil 5SL-II ( $10\phi \times 250$  mm); eluent, 0.15% methanol and chloroform; flow rate 2.0 mL/min. The fraction at 19.2 min was purified by recrystallization from dichloromethane and hexane to give heterodimer **ZnP-H<sub>2</sub>B** (6.5 mg, 5.5  $\mu$ mol, 73%) as a black solid: UV-Vis (THF)  $\lambda_{max}$  753 (rel., 0.25), 682 (0.03), 624 (0.12), 571 (0.04), 531 (0.12), 498 (0.03), 433 (1.00), 386 (0.33), 359 nm (0.51); <sup>1</sup>H NMR (1% pyridine-*d*<sub>5</sub>-CDCl<sub>3</sub>, 50 °C) δ 10.35 (1H, s, 5-H (ZnP)), 9.80 (1H, s, 10-H (ZnP)), 9.71 (1H, s, 20-H (ZnP)), 8.77 (1H, s, 5-H (H<sub>2</sub>B)), 8.32 (1H, s, 20-H (H<sub>2</sub>B)), 8.18 (1H, s, 10-H (H<sub>2</sub>B)), 5.48, 5.41 (each 1H, d, J = 19 Hz,  $13^{1}$ -CH<sub>2</sub> (ZnP)), 4.94, 4.75 (each 1H, d, J = 19 Hz,  $13^{1}$ -CH<sub>2</sub> (H<sub>2</sub>B)), 4.27 (4H, m,  $17^2$ -COOCH<sub>2</sub>×2), 4.18 (1H, dq, J = 2, 7 Hz, 18-H (H<sub>2</sub>B)), 3.95 (1H, dt, J = 9, 2 Hz, 17-H (H<sub>2</sub>B)), 3.90 (1H, dq, J = 4, 8 Hz, 7-H (H<sub>2</sub>B)), 3.87 (2H, q, J = 8 Hz, 8-CH<sub>2</sub> (ZnP)), 3.86 (2H, t, *J* = 8 Hz, 17-CH<sub>2</sub> (ZnP)), 3.80 (3H, s, 2-CH<sub>3</sub> (ZnP)), 3.79 (1H, dt, *J* = 8, 4 Hz, 8-H (H<sub>2</sub>B)), 3.72 (3H, s, 12-CH<sub>3</sub> (ZnP)), 3.45 (3H, s, 7-CH<sub>3</sub> (ZnP)), 3.34 (3H, s, 18-CH<sub>3</sub> (ZnP)), 3.32 (3H, s, 2-CH<sub>3</sub> (H<sub>2</sub>B)), 3.30 (6H, s, 3-COCH<sub>3</sub> (ZnP), 12-CH<sub>3</sub> (H<sub>2</sub>B)), 2.98 (3H, s, 3-COCH<sub>3</sub> (H<sub>2</sub>B)), 2.93 (2H, t, J = 8 Hz,  $17^{1}$ -CH<sub>2</sub>(ZnP)), 2.46, 2.21, 2.01 (2H+1H+1H, m, 17-CH<sub>2</sub>CH<sub>2</sub> (H<sub>2</sub>B)), 2.10, 1.70 (each 1H, m, 8-CH<sub>2</sub> (H<sub>2</sub>B)), 1.79 (3H, t, J = 8 Hz, 8<sup>1</sup>-CH<sub>3</sub> (ZnP)), 1.67 (3H, d, J = 8 Hz, 7-CH<sub>3</sub> (H<sub>2</sub>B)), 1.62 (3H, d, J = 7 Hz, 18-CH<sub>3</sub> (H<sub>2</sub>B)), 0.98 (3H, t, J = 8 Hz,  $8^{1}$ -CH<sub>3</sub> (H<sub>2</sub>B)), 0.12, -1.20 (each 1H, s, NH×2); MS (LDI) found: *m*/*z* 1188.4. Calcd. for C<sub>68</sub>H<sub>68</sub>N<sub>8</sub>O<sub>8</sub>Zn: M<sup>-</sup>, 1188.4; HRMS (APCI) found: m/z 1189.4525. Calcd. for C<sub>68</sub>H<sub>69</sub>N<sub>8</sub>O<sub>8</sub>Zn: MH<sup>+</sup>, 1189.4524.

# ZnP-H<sub>2</sub>C

Similar to the synthesis of **ZnC-H<sub>2</sub>B**, carboxylic acid **H<sub>2</sub>C-CA** (4.2 mg, 7.6  $\mu$ mol) was esterified with ethylene glycol monoester **ZnP-EE** (5.0 mg, 7.6  $\mu$ mol) by action of EDC·HCl (3.0 mg, 16  $\mu$ mol), and DMAP (3.8 mg, 31  $\mu$ mol) in dry dichloromethane (15

mL), and subjected to normal-phase HPLC: column, Cosmosil 5SL-II ( $10\phi \times 250$  mm); eluent, 0.5% methanol and chloroform; flow rate 2.0 mL/min. The fraction at 13.5 min was purified by recrystallization from dichloromethane and hexane to give heterodimer **ZnP-H<sub>2</sub>C** (6.0 mg, 5.0  $\mu$ mol, 66%) as a black solid: UV-Vis (THF)  $\lambda_{max}$  690 (rel., 0.18), 626 (0.16), 572 (0.05), 551 (0.07), 520 (0.06), 432 (1.00), 414 (sh, 0.81), 385 nm (sh, 0.55); <sup>1</sup>H NMR (1% pyridine-*d*<sub>5</sub>-CDCl<sub>3</sub>, 50 °C) δ 10.42 (1H, s, 5-H (ZnP)), 9.73 (1H, s, 10-H (ZnP)), 9.54 (1H, s, 20-H (ZnP)), 8.85 (1H, s, 5-H (H<sub>2</sub>C)), 8.68 (1H, s, 20-H (H<sub>2</sub>C)), 8.21 (1H, s, 10-H (H<sub>2</sub>C)) 5.30, 4.98 (each 1H, d, J = 19 Hz,  $13^{1}$ -CH<sub>2</sub> (H<sub>2</sub>C)), 4.56 (1H, dq, J = 2, 7 Hz, 18-H (H<sub>2</sub>C)), 4.49, 4.23 (each 1H, d, J = 19 Hz,  $13^{1}$ -CH<sub>2</sub> (ZnP)), 4.32 (4H, m, 17<sup>2</sup>-COOCH<sub>2</sub>×2), 4.20 (1H, dt, J = 9, 2, Hz, 17-H (H<sub>2</sub>C)), 3.97, 3.94 (each 1H, dq, J = 12, 8 Hz, 8-CH<sub>2</sub> (ZnP)), 3.87 (3H, s, 2-CH<sub>3</sub> (ZnP)), 3.55 (3H, s, 12-CH<sub>3</sub> (ZnP)), 3.54 (3H, s, 2-CH<sub>3</sub> (H<sub>2</sub>C)), 3.53 (3H, s, 7-CH<sub>3</sub> (ZnP)), 3.39 (3H, s, 3-COCH<sub>3</sub> (ZnP)), 3.28 (3H, s, 12-CH<sub>3</sub> (H<sub>2</sub>C)), 3.15, 3.04 (each 1H, m, 17-CH<sub>2</sub> (ZnP)), 3.07 (3H, s, 18-CH<sub>3</sub> (ZnP)), 2.94 (3H, s, 3-COCH<sub>3</sub> (H<sub>2</sub>C)), 2.74, 2.54, 2.39 (2H+3H+1H, m, 17-CCH<sub>2</sub> (ZnP), 17-CH<sub>2</sub>CH<sub>2</sub> (H<sub>2</sub>C)), 2.42 (2H, q, *J* = 8 Hz, 8-CH<sub>2</sub> (H<sub>2</sub>C)), 2.21 (3H, s, 7-CH<sub>3</sub> (H<sub>2</sub>C)), 1.89 (3H, t, J = 8 Hz, 8<sup>1</sup>-CH<sub>3</sub> (ZnP)), 1.89 (3H, d, J = 7 Hz, 18-CH<sub>3</sub> (H<sub>2</sub>C)), 1.08 (3H, t, J = 8 Hz,  $8^{1}$ -CH<sub>3</sub> (H<sub>2</sub>C)), -1.06, -2.80 (each 1H, s, NH×2); MS (LDI) found: *m*/*z* 1186.6. Calcd. for C<sub>68</sub>H<sub>66</sub>N<sub>8</sub>O<sub>8</sub>Zn: M<sup>-</sup>, 1186.4; HRMS (APCI) found: m/z 1187.4368. Calcd. for C<sub>68</sub>H<sub>67</sub>N<sub>8</sub>O<sub>8</sub>Zn: MH<sup>+</sup>, 1187.4368.

# ZnP-H<sub>2</sub>P

Similar to the synthesis of **ZnC-H<sub>2</sub>B**, carboxylic acid **H<sub>2</sub>P-CA** (4.3 mg, 7.8 µmol) was esterified with ethylene glycol monoester **ZnP-EE** (5.0 mg, 7.6 µmol) by action of EDC·HCl (3.1 mg, 16 µmol) and DMAP (3.8 mg, 31 µmol) in dry dichloromethane (15 mL), and subjected to normal-phase HPLC: column, Cosmosil 5SL-II ( $10\phi \times 250$  mm); eluent, 0.5% methanol and chloroform; flow rate 2.0 mL/min. The fraction at 13.6 min was purified by recrystallization from dichloromethane and hexane to give heterodimer

**ZnP-H<sub>2</sub>P** (4.8 mg, 4.0 µmol, 53%) as a black solid: UV-Vis (THF)  $\lambda_{max}$  627 (rel., 0.08), 577 (0.07), 534 (0.04), 409 nm (1.00); <sup>1</sup>H NMR (1% pyridine-*d*<sub>5</sub>–CDCl<sub>3</sub>, 55 °C)  $\delta$  9.96, 9.71 (each 1H, s, 5-H×2), 9.38, 9.36 (each 1H, s, 20-H×2), 8.51, 8.50 (each 1H, s, 10-H×2), 4.43, 4.20 (each 2H, br-s, 17<sup>2</sup>-COOCH<sub>2</sub>×2), 4.38 (4H, s, 13<sup>1</sup>-CH<sub>2</sub>×2), 3.89, 3.81 (each 3H, s, 2-CH<sub>3</sub>×2), 3.37, 3.34 (each 3H, s, 12-CH<sub>3</sub>×2), 3.31, 3.28 (each 3H, s, 3-COCH<sub>3</sub>×2), 3.03, 2.91 (each 3H, s, 7-CH<sub>3</sub>×2), 2.99, 2.95 (each 3H, s, 18-CH<sub>3</sub>×2), 2.98, 2.86 (each 2H, q, *J* = 8 Hz, 8-CH<sub>2</sub>×2), 2.85, 2.64 (each 2H, t, *J* = 7 Hz, 17-CH<sub>2</sub>×2), 2.74, 2.53 (each 2H, t, *J* = 7 Hz, 17-CCH<sub>2</sub>×2), 1.40, 1.39 (each 3H, t, *J* = 8 Hz, 8-CH<sub>3</sub>×2), -4.71, -5.64 (each 1H, s, NH×2); MS (LDI) found: *m*/*z* 1184.6. Calcd. for C<sub>68</sub>H<sub>64</sub>N<sub>8</sub>O<sub>8</sub>Zn: M<sup>-</sup>, 1184.4; HRMS (APCI) found: *m*/*z* 1185.4213. Calcd. for C<sub>68</sub>H<sub>65</sub>N<sub>8</sub>O<sub>8</sub>Zn: MH<sup>+</sup>, 1185.4211.

# 2. Optical data of (B)Chl-a derivatives in THF



Fig. S1 UV-Vis-NIR absorption (left) and fluorescence emission spectra (right) of  $H_2B/C/P-ME$  (upper) and ZnB/C/P-ME (lower) in THF. Fluorescence emission spectra were measured under excitation of Soret maxima.

$\Phi$ / %	$\tau$ / ns
13.5	3.2
22.6	6.8
3.6	4.4
17.7	3.5
23.5	5.0
6.2	2.3
	Φ/% 13.5 22.6 3.6 17.7 23.5 6.2

Table S1 Photophysical data of monomeric H<sub>2</sub>B/C/P-ME and ZnB/C/P-ME in THF.



**Fig. S2** UV-Vis-NIR absorption (a–d), fluorescence emission (e–h), and excitation spectra (i–l) of heterodimers in THF. Fluorescence emission spectra were measured under excitation of Soret maxima of each zinc and free-base chlorophyll species. Fluorescence excitation spectra were recorded at emission peaks of each zinc and free-base chlorophyll species. In parts (i–l), the UV-Vis-NIR absorption spectra of heterodimers are shown as dashed lines. Asterisks in parts (i–l) show the secondary diffraction of the emission.



#### 3. Optical data of co-assemblies of chlorosomal J-aggregates with heterodimers

Fig. S3 UV-Vis-NIR absorption (a–d), fluorescence emission (e–h), and excitation spectra (i) of Model-C with 1%(mol/mol) heterodimers in 1%(v/v) THF–hexane: [Model-C]/[heterodimer] = 10/0.1  $\mu$ M. Fluorescence emission spectra were measured under the excitation of Soret maxima of Model-C J-aggregates ( $\lambda_{ex}$  = 450 nm). Fluorescence excitation spectra of Model-C with ZnP-H<sub>2</sub>B were recorded at 820 nm. In parts (e–h) and (i), fluorescence emission and Vis-NIR absorption spectra of sole Model-C J-aggregates in 1%(v/v) THF–hexane are shown as dotted and dashed lines, respectively.



Fig. S4 UV-Vis-NIR absorption (a–d), fluorescence emission (e–h), and excitation spectra (i–k) of Model-P with 1%(mol/mol) heterodimers in 1%(v/v) THF–hexane: [Model-P]/[heterodimer] = 10/0.1  $\mu$ M. Fluorescence emission spectra were measured under the excitation of Soret maxima of Model-P J-aggregates ( $\lambda_{ex}$  = 470 nm). Fluorescence excitation spectra of Model-P with ZnC-H<sub>2</sub>C, ZnP-H<sub>2</sub>B, and ZnP-H<sub>2</sub>C were recorded at 730, 760, and 720 nm, respectively. In a part (j), excitation spectrum of Model-P with ZnP-H<sub>2</sub>B at 790 nm is shown as a dotted line. In parts (e–h) and (i–k), fluorescence emission and Vis absorption spectra of sole Model-P J-aggregates in 1%(v/v) THF–hexane are shown as dotted and dashed lines, respectively.

# 4. References

- S1. H. Tamiaki, M. Kouraba, K. Takeda, S. Kondo and R. Tanikaga, Asymmetric synthesis of methyl bacteriopheophorbide-*d* and analogues by stereoselective reduction of the 3-acetyl to the 3-(1-hydroxyethyl) group, *Tetrahedron: Asymmetry*, 1998, 9, 2101–2111.
- S2. A. Osuka, S. Marumo, Y. Wada, I. Yamazaki, T. Yamazaki, Y. Shirakawa and Y. Nishimura, Synthesis of 1,3-dioxane-bridged pyropheophorbide-diimide and pyropheophorbide dimer and their intramolecular electron and energy transfer, *Bull. Chem. Soc. Jpn.*, 1995, **68** 2909–2915.
- S3. S. Fukuzumi, K. Ohkubo, X. Zheng, Y. Chen, R. K. Pandey, R. Zhan and K. M. Kadish, Metal bacteriochlorins which act as dual singlet oxygen and superoxide generators, *J. Phys. Chem. B*, 2008, **112**, 2738–2746.
- S4. H. H. Inhoffen, P. Jäger, R. Mählhop and C.-D. Mengler, Chlorophyll and hemin. XII. Electrochemical reductions of porphyrins and chlorins, *Justus Liebigs Ann. Chem.*, 1967, **704**, 188–207.
- S5. H. Tamiaki, S. Yagai and T. Miyatake, Synthetic zinc tetrapyrroles complexing with pyridine as a single axial ligand, *Bioorg. Med. Chem.*, 1998, **6**, 2171–2178.
- S6. H. Tamiaki, K. Fukai, H. Shimazu and S. Shoji, Synthesis of zinc chlorophyll homo/hetero-dyads and their folded conformers with porphyrin, chlorin, and bacteriochlorin  $\pi$ -systems, *Photochem. Photobiol.*, 2014, **90**, 121–128.