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Synthesis and Optical Properties of Bacteriochlorophyll-*a* Derivatives Having Various C3 Substituents on the Bacteriochlorin π-System

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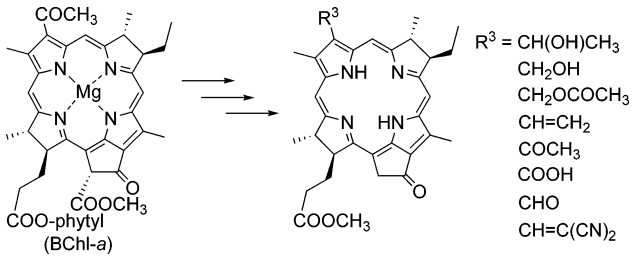
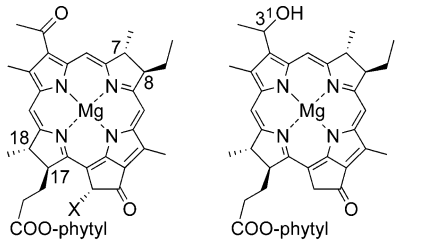


Methyl bacteriopyropheophorbide-*a* derivatives having a series of substituents at the C3 position were prepared and their optical properties were compared with the corresponding chlorin analogues. Two kinds of oxidation reaction (C3-vinyl → formyl → carboxy group) were found to be applicable with a little alteration of the free-base bacteriochlorin macrocycles. The Q_x and Q_y electronic absorption peak positions of synthetic bacteriochlorins in CH_2Cl_2 were affected by the C3 substituents and found to be more sensitive than those of the chlorins. The observed Q_x/Q_y peaks in their monomeric states were shifted to a longer wavelength in the order of 1-hydroxyethyl < hydroxymethyl < acetoxymethyl < vinyl < acetyl < carboxy < formyl < 2,2-dicyanoethynyl group. Zinc complex with the C3-hydroxymethyl group formed self-aggregates in a nonpolar organic solvent, which showed the largest red-shift of the Q_y band (2380 cm^{-1}, 726 nm in THF to 878 nm in 1% THF−cyclohexane) among those of the synthetic self-aggregative (bacterio)chlorins examined.

Introduction

Bacteriochlorophyll-*a* (BChl-*a*; left drawing in Chart 1) is the most abundant bacteriochlorin derivative in natural photosynthetic pigments, and plays significant roles in the light-harvesting, energy-migrating, and electron-transporting reactions at the initial stage of bacterial photosynthesis.[1] In the light-harvesting antennas, BChl-*a* molecules are fixed on proteins with well-ordered orientations, and the longest wavelength (Q_y) electronic absorption peaks as in B875 of LH1 and B850 of LH2 show large red-shifts compared with that of monomeric BChl-*a* (771 nm in THF).[2] To demonstrate the construction of supramolecular structures based on BChl-*a* derivatives without any proteins, we recently reported self-aggregation of synthetic 3-(1-hydroxyethyl)bacteriopyrochlorophyll-*a* (right drawing in Chart 1) in a nonpolar organic solvent, which also provided a model for main antennas of green photosynthetic bacteria.[3] The Q_y maximum of the resulting large oligomers was 860 nm with

CHART 1



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(1) (a) *Light-Harvesting Antennas in Photosynthesis*; Green, B. R., Parson, W. W., Eds.; Kluwer Academic Publishers: Dordrecht, The Netherlands, 2003. (b) Blankenship, R. E. In *Molecular Mechanisms of Photosynthesis*; Blackwell Science: London, UK, 2002.

(2) Cogdell, R. J.; Gardiner, A. T.; Roszak, A. W.; Law, C. J.; Soughall, J.; Isaacs, N. W. *Photosynth. Res.* **2004**, *81*, 207−214.

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absorbing light in a near-infrared region (<910 nm) and red-shifted by 2170 cm^{-1} from the monomeric state.

The intense absorption in the Q_y region of BChl-*a* derives from its bacteriochlorin (7,8,17,18-tetrahydroporphyrin) structure. The peak positions of the lowest energy absorption (Q_y) bands in cyclic tetrapyrroles are shifted to longer wavelengths as their π-conjugate systems are more reduced: porphyrin → chlorin (17,18-dihydroporphyrin) → bacteriochlorin. This tendency is explained by the theoretical calculation that the reduction decreases the energy gap between their HOMO and LUMO energy levels.[4] In addition to the characteristic Q_y bands, bacteriochlorins have more distinct Q_x absorption bands (500−600 nm) than those of chlorins due to one more reduction of the 7,8-double bond of the latter π-system.

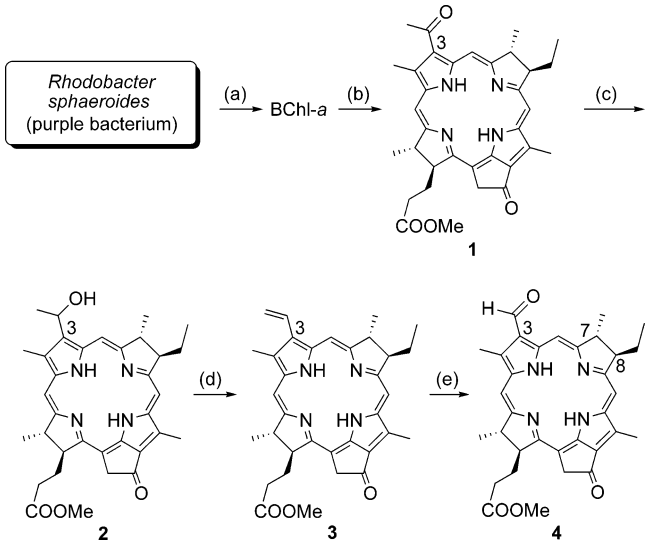
Although various studies of stable bacteriochlorins have been reported,[5,6] most of which were based on easily available synthetic porphyrins, bacteriochlorin derivatives possessing naturally occurring peripheral substituents have been quite limited,[3,5,7] probably due to the instability such as facile oxidation (7,8-dehydrogenation) from bacteriochlorin to chlorin π-conjugate systems. Thus, the determination of optical properties of bacteriochlorin derivatives would extend the knowledge in the field of cyclic tetrapyrrole chemistry, and give useful information for structural and functional elucidation of natural bacterial photosynthetic systems.

In this study, we investigated several reaction conditions including oxidation toward methyl bacteriopyropheophorbide-*a* derivatives for the systematic preparation of various bacteriochlorins, and we discuss the substituent effects on their optical properties.

Results and Discussion

Synthesis of BChl-*a* Derivatives 1−4. As shown in Scheme 1, BChl-*a* extracted from a cultured purple bacterium (*Rhodobacter sphaeroides*) was transformed to methyl bacteriopyropheophorbide-*a* (**1**) according to the reported procedures.[8] Reduction of the 3-acetyl group by $NaBH_4$ gave the 3-(1-hydroxyethyl) derivative **2** in 93% yield.[8] Although direct dehydration of the 3-(1-hydroxyethyl) group of a BChl-*a* derivative in refluxing toluene was reported,[9] mesylation of the hydroxy group was selected to convert into a better leaving group. After silica gel column chromatographic purification of the reaction mixture, 3-vinyl derivative **3** was obtained in 77% yield without isolation of the mesylated intermediate. The 3-vinyl group of **3** was then oxidatively cleaved by OsO_4 and $NaIO_4$[10] to give 3-formyl compound **4** mixed with ca. 10% of the corresponding chlorin **5** through over-oxidation (7,8-dehydrogenation), which was further purified by HPLC to give pure **4** in 62% yield. It is noteworthy that most of the bacteriochlorin macrocycle was retained under this oxidation condition. The purified sample of **4** was relatively stable even in an aerated solution.[11]

SCHEME 1. Synthesis of BChl-*a* Derivatives 1−4[a]



[a] Reagents and conditions: (a) extraction by MeOH−acetone; (b) (i) 2% aq HCl, (ii) conc H_2SO_4−MeOH, (iii) collidine, reflux; (c) $NaBH_4$, MeOH−CH_2Cl_2, 93%; (d) (i) MsCl, Et_3N, CH_2Cl_2, (ii) SiO_2, 77%; (e) OsO_4, $NaIO_4$, aq.AcOH−THF, 62%.

Comparison of Bacteriochlorin 4, Chlorin 5, and Porphyrin 6 Having an C3-Formyl Group. Figure 1 compares the electronic absorption spectra of bacteriochlorin **4** with the corresponding chlorin **5**[10] and porphyrin **6**[12] (Chart 2) in CH_2Cl_2. Bacteriochlorin **4** showed characteristic absorption maxima at the longest wavelength with strong intensity (Q_y, 766 nm), together with a distinct Q_x peak at 541 nm. On the contrary, the Soret peak of **4** (366, 390 (sh) nm) is more blue-shifted than those of chlorin **5** (387, 428 nm) or porphyrin **6** (423 nm), and the intensity of the Soret peak of **4** (molar absorption coefficient, $\epsilon = 77\,000$) is similar to that of **5** ($\epsilon = 74\,000$) but is less than half that of **6** ($\epsilon = 210\,000$).

The environment of the 3-formyl group conjugatable with a tetrapyrrole macrocycle was not affected by the degree of π-conjugation on the skeleton. When compared with the IR spectra of **4** and **5** in CH_2Cl_2, the 3-formyl carbonyl stretching

(3) Kunieda, M.; Mizoguchi, T.; Tamiaki, H. *Photochem. Photobiol.* **2004**, *79*, 55−61.

(4) Linnanto, J.; Korppi-Tommola, J. *J. Comput. Chem.* **2004**, *25*, 123−137.

(5) (a) Pandey, R. K.; Zheng, G. In *The Porphyrin Handbook*; Kadish, K. M., Smith, K. M., Guilard, R., Eds.; Academic Press: San Diego, CA, 2000; Vol. 6, pp 157−230. (b) Chen, Y.; Li, G.; Pandey, R. K. *Curr. Org. Chem.* **2004**, *8*, 1105−1134.

(6) (a) Hartwich, G.; Fiedor, L.; Simonin, I.; Cmiel, E.; Schafer, W.; Noy, D.; Scherz, A.; Scheer, H. *J. Am. Chem. Soc.* **1998**, *122*, 3675−3683. (b) Fukuzumi, S.; Ohkubo, K.; Chen, Y. H.; Pandey, R. K.; Zhan, R. Q.; Shao, J. G.; Kadish, K. M. *J. Phys. Chem. A* **2002**, *106*, 5105−5113. (c) Mironov, A. F. M.; Grin, M. A.; Tsiprovskiy, A. G.; Vadim, V. K.; Karmakova, T. A.; Plyutinskaya, A. D.; Yakubovskaya, R. I. *J. Porphyrins Phthalocyanines* **2003**, *7*, 725−730. (d) Chen, Y.; Sumlin, A.; Morgan, J.; Gryshuk, A.; Oseroff, A.; Henderson, B. W.; Dougherty, T. J.; Pandey, R. K. *J. Med. Chem.* **2004**, *47*, 4814−4817. (e) Kim, H.-J.; Lindsey, J. S. *J. Org. Chem.* **2005**, *70*, 5475−5486. (f) Brandis, A.; Mazor, O.; Neumark, E.; Rosenbach-Belkin, V.; Salomon, Y.; Scherz, A. *Photochem. Photobiol.* **2005**, *81*, 983−993.

(7) (a) Kunieda, M.; Mizoguchi, T.; Tamiaki, H. *Tetrahedron* **2004**, *60*, 11349−11357. (b) Chen, Y.; Sumlin, A.; Morgan, J.; Gryshuk, A.; Oseroff, A.; Henderson, B. W.; Dougherty, T. J.; Pandey, R. K. *J. Med. Chem.* **2004**, *47*, 4814−4817. (c) Mironov, A. F.; Grin, M. A.; Tsiprovskii, A. G.; Titeev, R. A.; Nizhnik, E. A.; Lonin, I. S. *Mendeleev Commun.* **2004**, 204−207. (d) Kunieda, M.; Tamiaki, H. *J. Org. Chem.* **2005**, *70*, 820−828.

(8) Tamiaki, H.; Kouraba, M.; Takeda, K.; Kondo, S.; Tanikaga, R. *Tetrahedron*: *Asymmetry* **1998**, *9*, 2101−2111.

(9) Struck, A.; Cmiel, E.; Katheder, I.; Schäfer, W.; Scheer, H. *Biochim. Biophys. Acta* **1992**, *1101*, 321−328.

(10) Tamiaki, H.; Amakawa, M.; Shimono, Y.; Tanikaga, R.; Holzwarth, A. R.; Schaffner, K. *Photochem. Photobiol.* **1996**, *63*, 92−93.

(11) About 0.1 mM solution of pure **4** in acetone/1,2-dichloroethane (1:9) was stored in the dark at room temperature under air, and analyzed by HPLC. Neither oxidation to chlorin **5** nor decomposition was observed for 10 days.

(12) Tamiaki, H.; Watanabe, T.; Miyatake, T. *J. Porphyrins Phthalocyanines* **1999**, *3*, 45−52.

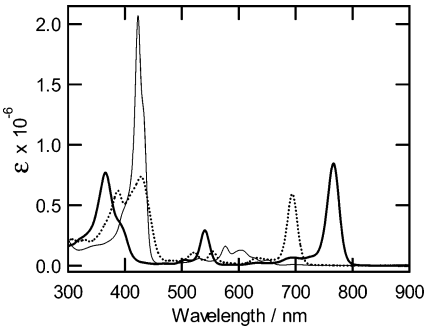
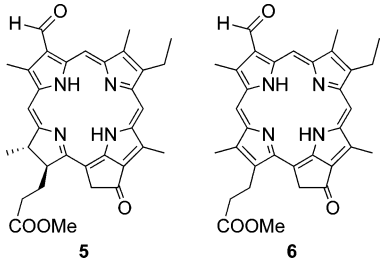


FIGURE 1. Electronic absorption spectra of bacteriochlorin **4** (solid thick line), chlorin **5** (dotted line), and porphyrin **6** (solid thin line) in CH_2Cl_2. Each spectrum was measured at 1.0×10^{-5} M.

CHART 2

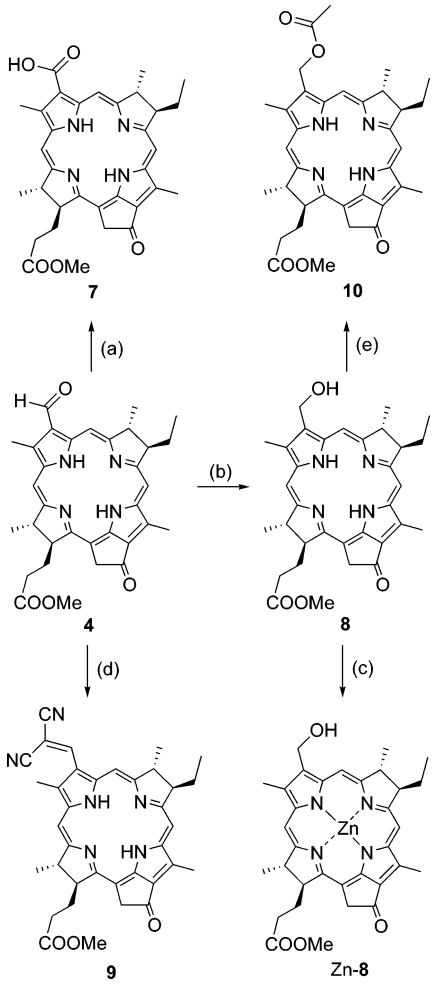


band of **4** (1674 cm^{-1}) was in almost the same position as that of **5** (1676 cm^{-1}). Moreover, it turned out that the ^{13}C NMR signal of the 3-formyl carbon atom of **4** (188.1 ppm) appeared at almost the same position as that of **5** (188.0 ppm) in $CDCl_3$. These results indicate that the 3-formyl group of bacteriochlorin **4** is expected to have a similar reactivity to that of chlorin **5**. Thus several reactions of the 3-formyl group such as oxidation, reduction, and Knoevenagel reaction, which had been successfully applied to chlorin **5**, were examined for **4** to synthesize a series of model compounds having various C3 substituents.

Synthesis of BChl-*a* Derivatives 7−10. With 3-formyl derivative **4** as a starting compound, three kinds of reactions were performed as shown in Scheme 2. Oxidation of the formyl to carboxy group was examined by the reported procedure.[13] An aqueous solution of $NaClO_2$ was added in the presence of NH_2SO_3H and 2-methyl-2-butene (radical trap) with monitoring by TLC, and about 9 equiv of $NaClO_2$ was required for the complete disappearance of **4**. After purification by silica gel and gel-permeation chromatography, a 9:1 mixture of 3-carboxybacteriochlorin **7** with the over-oxidized chlorin was obtained; this was further purified by HPLC to give pure **7** in 39% yield.[14]

Reduction of the 3-formyl group in **4** to the 3-hydroxymethyl group in **8** by *t*-$BuNH_2{\cdot}BH_3$[10] proceeded in a good yield (90%) without formation of any byproducts. The hydroxymethyl group of **8** was condensed with acetic acid to form **10** (92%), to demonstrate the possibility of further synthetic extension from

SCHEME 2. Synthesis of BChl-*a* Derivatives 7−10[a]



[a] Reagents and conditions: (a) NH_2SO_3H, $NaClO_2$, aq THF−2-methyl-2-butene, 39%; (b) *t*-$BuNH_2{\cdot}BH_3$, CH_2Cl_2, 90%; (c) $Zn(OAc)_2{\cdot}2H_2O$, CH_2Cl_2−MeOH; (d) malononitrile, Et_3N, THF, 85%; (e) AcOH, EDC·HCl, DMAP, CH_2Cl_2, 92%.

the primary alcohol. Zinc insertion to bacteriochlorin **8** required more severe conditions than that to the chlorins.[10,15] Even after refluxing in $CHCl_3$−MeOH for 12 h, 36% (crude yield after silica gel chromatography) of the desired Zn-**8** was isolated and 44% of unreacted free-base **8** was recovered. Deaerated reaction conditions and rapid purification were necessary for obtaining the pure product, because zinc complex Zn-**8** was easily oxidized to the corresponding zinc chlorin (Zn-**15**) in a solution. Knoevenagel reaction between the 3-formyl group of **4** and malononitrile[16] also cleanly proceeded to give **9** in 85% yield.

Optical Properties of BChl-*a* Derivatives 1−4, 7−10, and Their Corresponding Chlorins 5 and 11−17. Electronic absorption, fluorescence emission, and CD spectra of bacteriochlorin **10** and chlorin **17** having the same peripheral substituents including the C3-functional (acetoxymethyl) group are compared in Figure 2. The Q_y peak of **10** (725 nm) is more red-shifted than that of **17** (664 nm), while the main Soret peak of **10** (353 nm) is more blue-shifted than that of **17** (410 nm). The distinct Q_x peak (517 nm) is located between the two less intense Q_x peaks of **17** (505, 536 nm). These differences in absorption

(13) Osuka, A.; Wada, Y.; Shinoda, S. *Tetrahedron* **1996**, *52*, 4311−4326.

(14) Similar isolated yield (47%) was observed for the oxidation of chlorin **5** to **14** under the same experimental conditions, although a better yield (81%) was reported in ref 13. 2-Methyl-2-butene was used as a cosolvent to avoid chlorination at the meso positions, and oligomerized by action of excess $NaClO_2$. The resulting oligo(2-methyl-2-butene) made it difficult to purify **7** from the reaction mixture. The relatively low yield is ascribed in part to the adsorption during the repeated column chromatography.

(15) Tamiaki, H.; Yagai, S.; Miyatake, T. *Bioorg. Med. Chem.* **1998**, *6*, 2171−2178.

(16) Tamiaki, H.; Kouraba, M. *Tetrahedron* **1997**, *53*, 10677−10688.

TABLE 1. Absorption and Emission Maxima (λ_{max}/nm) of Bacteriochlorins 1−4 and 7−10 in CH_2Cl_2

	absorption: λ_{max} (I_{rel}[a]) [fwhm/cm^{-1}]			fluorescence[b]	
compd (R^3)	Soret	Q_x	Q_y	λ_{max}	Δ (cm^{-1})[c]
2 ($CH(OH)CH_3$)	353	515 (0.30) [550]	717 (0.40) [690]	727	180
8 (CH_2OH)	353	516 (0.31) [530]	721 (0.43) [660]	729	160
10 (CH_2OCOCH_3)	353	517 (0.31) [540]	725 (0.47) [620]	731	120
3 ($CH{=}CH_2$)	356	519 (0.27) [600]	726 (0.37) [750]	736	200
1 ($COCH_3$)	360	532 (0.24) [920]	754 (0.62) [630]	761	130
7 (COOH)	358	534 (0.28) [710]	756 (0.73) [450]	759	50
4 (CHO)	366	541 (0.38) [660]	766 (1.10) [430]	769	50
9 ($CH{=}C(CN)_2$)	352	554 (0.23) [1500]	790 (0.85) [760]	811	330

[a] Relative peak intensity I_{rel} was based on the Soret peak intensity. [b] Excitation wavelengths were the Q_x absorption maxima. [c] Stokes shift $\Delta = [1/\lambda_{max}(Q_y) - 1/\lambda_{max}(\text{fluorescence})] \times 10^7$.

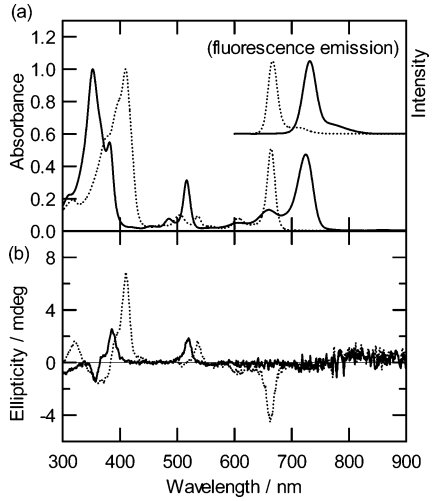
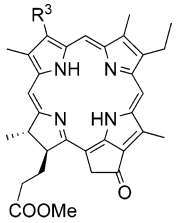


FIGURE 2. (a) Electronic absorption, fluorescence emission (excited at their Q_x peaks), and (b) CD spectra of bacteriochlorin **10** (solid line) and chlorin **17** (dotted line) in CH_2Cl_2. Absorption and emission spectra are normalized at the most intense peak. Absorption and CD spectra were measured at 1.0×10^{-5} M, while fluorescence spectra were recorded at 1.0×10^{-6} M.

CHART 3



11: $R^3 = COCH_3$
12: $R^3 = CH(OH)CH_3$
13: $R^3 = CH{=}CH_2$
14: $R^3 = COOH$
15: $R^3 = CH_2OH$
16: $R^3 = CH{=}C(CN)_2$
17: $R^3 = CH_2OCOCH_3$

maxima are similar to those in the 3-formyl derivatives **4** and **5** as shown in Figure 1, and are observed in all the (bacterio)-chlorins examined here (see the Supporting Information). When excited at the Q_x peak, both **10** and **17** showed fluorescence at their Q_y regions. The Stokes shift of **10** (120 cm^{-1}) was larger than that of **17** (50 cm^{-1}). CD signals were observed at the Soret and Q_x positions of **10** and **17**, but no signal of **10** can be seen in the Q_y region, in contrast to the negative peak of **17**. It is noteworthy that other bacteriochlorins **1**−**4**, **7**−**9**, Zn-**8**, and Mg complex (right drawing of Chart 1)[3] in their monomeric states also had no apparent CD band in their Q_y region. Spectral data of bacteriochlorins **1**−**4**, **7**−**10**, and chlorins **5** and **11**−**17** (Chart 3) are summarized in Tables 1 and 2, respectively. The peak position of the Soret band of bacteriochlorins is not greatly affected by the C3 substituent (R^3) while the Q_x and Q_y peaks are more sensitive to the nature of the functional group. Thus

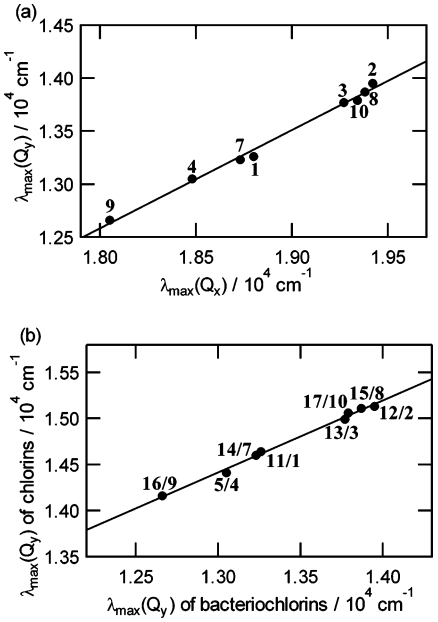


FIGURE 3. (a) Relation between Q_x and Q_y peak maxima of bacteriochlorins **1**−**4** and **7**−**10** and (b) relation between Q_y peak maxima of bacteriochlorins and chlorins.

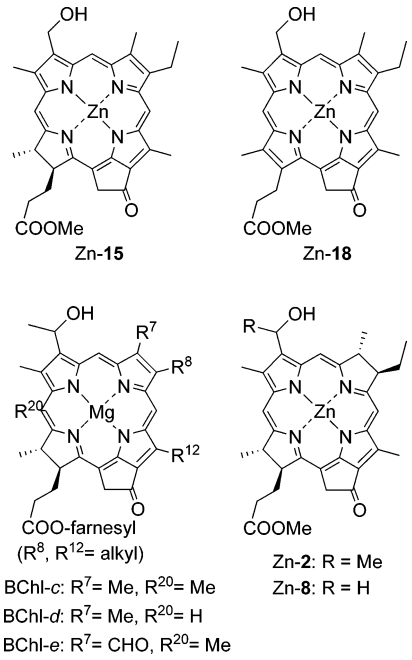
TABLE 2. Absorption Maxima (λ_{max}/nm) of Chlorins 5 and 11−17 in CH_2Cl_2

compd (R^3)	Soret	Q_x	Q_y
12 ($CH(OH)CH_3$)	410	505, 536	661
15 (CH_2OH)	410	505, 535	662
17 (CH_2OCOCH_3)	410	505, 536	664
13 ($CH{=}CH_2$)	413	509, 539	667
11 ($COCH_3$)	417	514, 547	683
14 (COOH)	418	516, 548	685
5 (CHO)	428	521, 554	694
16 ($CH{=}C(CN)_2$)	453	522, 568	706

the peak positions move to longer wavelength as the electron-withdrawing ability of the C3 substituent increases. The Q_x and Q_y peak shifts from **2** to **9** were 1370 and 1290 cm^{-1}, respectively, which were larger than those of the corresponding chlorins from **12** to **16** (640/1050 cm^{-1} for Q_x and 960 cm^{-1} for Q_y). An almost linear relationship can be seen when the energy levels of Q_x versus Q_y maxima of bacteriochlorins (correlation coefficient $r = 0.997$) or Q_y maxima of chlorins versus Q_y maxima of bacteriochlorins ($r = 0.997$) are plotted (see Figure 3).

As to the peak shape, the relationship between the nature of the substituent and the full width at half-maximum (fwhm) is not clear. However, it seems that electron-withdrawing groups

CHART 4



on the C3 position lead to a higher relative intensity of Q_y peaks. It also should be pointed out that the Stokes shifts, Δs, increase as the fwhms of Q_y bands increase.

Self-Aggregation of Zinc Methyl 3[1]-Demethyl-7,8-*trans*-dihydrobacteriopheophorbide-*d* (Zn-8). It is known that BChls-*c*/*d*/*e* (Chart 4) in chlorosomes self-aggregate to form light-harvesting antennas without any assistance from proteins.[17] The self-aggregation of these BChls is caused by the intermolecular interaction among the 3[1]-hydroxy, central metal, and 13-carbonyl moieties, together with $\pi-\pi$ interaction of the macrocycles. The macrocyclic π-systems of BChls-*c*/*d*/*e* are chlorins and not bacteriochlorins, and no self-aggregates of bacteriochlorins are observed in the chlorosomes. It is interesting to investigate the self-aggregating ability of BChl-*a* derivatives from the view of construction of artificial supramolecules as well as the development of new light-harvesting antenna models. Therefore, self-aggregation properties of zinc bacteriochlorin Zn-**8** having the 3-hydroxymethyl group were examined and compared to those of the corresponding chlorin Zn-**15** and porphyrin Zn-**18** (Chart 4).

The self-aggregate of Zn-**8** was prepared by diluting the monomeric solution in THF with excess cyclohexane. The formation of oligomers was confirmed by the large red-shift and broadening of the Q_y peak as represented by the spectra in Figure 4a. The observed CD signals which are much stronger than the monomeric ones also suggest the formation of well-ordered aggregates (see Figure 4b). The red-shift of the Q_y peak (2380 cm^{-1}) is larger than those of the corresponding chlorin or porphyrin analogues[18] as summarized in Table 3, and also larger than those of the magnesium analogues (right drawing of Chart 1) possessing the 3-(1-hydroxyethyl) group at the C3-position (2170 cm^{-1}).[3] The red-shift of the Q_y band of Zn-**2** is reported to be only 1150 cm^{-1} (731 nm in THF to 798 nm in 1% CH_2Cl_2−cyclohexane),[19] apparently due to the steric hindrance around the hydroxyl group of the 1-hydroxyethyl group compared to the hydroxymethyl group. Similar steric effects of the C3 substituent on the formation of self-aggregates have been reported in zinc chlorins, Zn-**12**/**15**,[10] and others.[20]

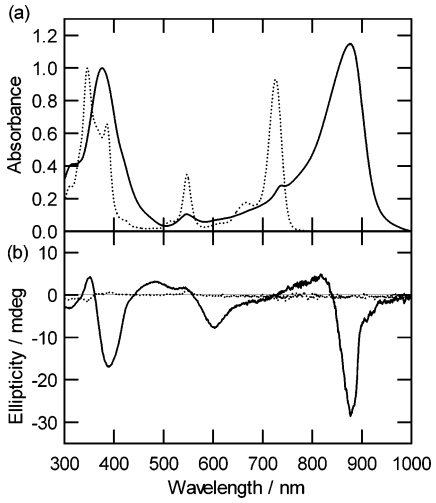


FIGURE 4. (a) Absorption and (b) CD spectra of Zn-**8** in THF (dotted line) and in 1% (v/v) THF−cyclohexane (solid line). Absorption spectra are normalized at their Soret peaks.

TABLE 3. Q_y-Band Absorption Maxima (nm) of Zinc Bacteriochlorin Zn-8, Zinc Chlorin Zn-15, and Zinc Porphyrin Zn-18 in Monomeric and Oligomeric Solutions

compd	THF	1% (v/v) THF−cyclohexane	red-shift[a]	source
Zn-**8**	726	878	2380	this work
Zn-**15**	647	741	1960	ref 18
Zn-**18**	608	644	920	ref 18

[a] Red-shift (cm^{-1}) = $[1/\lambda_{max}(\text{monomer}) - 1/\lambda_{max}(\text{aggregates})] \times 10^7$.

Conclusion

We have shown that the optical properties of synthetic BChl-*a* derivatives can be effectively tuned by the C3-functional group. Although the orientation of the C3-acetyl group on natural BChl-*a* was estimated to vary its Q_y peak maxima about 50 nm,[21] we realized much larger peak shifts by successive transformation of the C3 substituents. As an application with newly developed dyes, Zn-**8** possessing the C3-hydroxymethyl group was demonstrated to form self-aggregates in a nonpolar organic solvent, which showed the largest red-shift of the Q_y band in the synthetic (B)Chl series.

Experimental Section

General. ^1H and ^{13}C NMR spectra were recorded on a JEOL JNM-600HR spectrometer. Proton peaks were assigned by $^1H-^1H$ COSY and NOESY spectra, and carbon peaks except for quaternary

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peaks were assigned by DEPT and HMQC spectra. Methyl bacteriopyropheophorbide-*a* (**1**),[8] methyl 3-deacetyl-3-(1-hydroxyethyl)bacteriopyropheophorbide-*a* (**2**),[8] methyl pyropheophorbide-*d* (**5**),[10] and methyl protopyropheophorbide-*d* (**6**)[12] were prepared as previously reported. Methyl pyropheophorbide-*a* (**13**)[10] and its derivatives **11**,[15] **12**,[22] **14**,[13] **15**,[10] and **16**[16] were prepared according to the literature procedures. THF and CH_2Cl_2 were distilled over CaH_2 before use. Other solvents and reagents were employed as purchased without further purification. All synthetic procedures were done in the dark.

Methyl 3-Deacetyl-3-vinylbacteriopyropheophorbide-*a* (3). To a solution of **2** (347 mg, 0.61 mmol) in CH_2Cl_2 (40 mL) was added mesyl chloride (148 mg, 1.3 mmol) in CH_2Cl_2 (10 mL), the solution was stirred for 30 min, then triethylamine (146 mg, 1.4 mmol) in CH_2Cl_2 was added, and the mixture was stirred for 12 h at room temperature. The mixture was then poured into 2% aqueous HCl and extracted with CH_2Cl_2. The extract was washed with 4% aqueous $NaHCO_3$, dried over anhydrous Na_2SO_4, filtered, and concentrated. The crude product was purified by silica gel chromatography ($Et_2O-CH_2Cl_2$, 1:9) to give **3** (260 mg, 77%) as a black solid: mp 180−182 °C; VIS (CH_2Cl_2) λ_{max} 726 (ϵ, 36 000), 662 (13 000), 519 (26 000), 488 (7 100), 383 (47 000), 356 nm (98 000); ^{1}H NMR ($CDCl_3$, 600 MHz) δ 8.21 (1H, s, 10-H), 8.20 (1H, s, 5-H), 8.06 (1H, s, 20-H), 7.72 (1H, dd, J = 12, 18 Hz, 3-CH), 6.11 (1H, dd, J = 1, 18 Hz, 3^1-CH trans to 3-CH), 6.04 (1H, dd, J = 1, 12 Hz, 3^1-CH cis to 3-CH), 4.98, 4.81 (each 1H, d, J = 19 Hz, 13^1-CH_2), 4.11−4.19 (2H, m, 7-, 18-H), 4.00 (1H, dt, J = 9, 2 Hz, 17-H), 3.89 (1H, dt, J = 8, 4 Hz, 8-H), 3.63 (3H, s, $COOCH_3$), 3.36 (3H, s, 12-CH_3), 3.20 (3H, s, 2-CH_3), 2.56, 2.22 (each 1H, m, 17-CH_2), 2.50, 2.28 (each 1H, m, 17^1-CH_2), 2.30, 2.03 (each 1H, m, 8-CH_2), 1.75 (3H, d, J = 7 Hz, 7-CH_3), 1.69 (3H, d, J = 7 Hz, 18-CH_3), 1.10 (3H, t, J = 7 Hz, 8^1-CH_3), 1.38, −0.13 (each 1H, s, NH); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 195.6 (C13^1), 173.6, 170.9, 170.3, 161.3, 155.2, 147.8, 141.2, 139.5, 137.3, 133.7, 132.4, 128.8, 118.1, 108.7 (C1, 2, 3, 4, 6, 9, 11, 12, 13, 14, 15, 16, 17^3, 19), 128.8 (C3^1), 122.1 (C3^2), 99.2 (C10), 94.3 (C5), 94.1 (C20), 54.3 (C8), 51.7 (C17^5), 50.4 (C17), 49.8 (C18), 49.0 (C7), 47.4 (C13^2), 30.8 (C17^2), 30.1 (C8^1), 29.9 (C17^1), 22.6, 22.5 (C7^1, 18^1), 11.8 (C2^1), 11.3 (C12^1), 10.7 (C8^2); HRMS (FAB) m/z 551.3057 (MH^+), calcd for $C_{34}H_{39}N_4O_3$ 551.3022.

Methyl 3-Deacetyl-3-formylbacteriopyropheophorbide-*a* (4). According to the reported procedure,[10] 3-vinylbacteriochlorin **3** (140 mg, 0.25 mmol) was oxidized by OsO_4 (ca. 50 mg), $NaIO_4$ (535 mg, 2.5 mmol), and AcOH (0.5 mL) in water (6 mL) and THF (30 mL). The product was purified by silica gel chromatography ($Et_2O-CH_2Cl_2$, 1:9) to afford a mixture of **4** (major) and chlorin **5** (ca. 10%). Further purification was performed by HPLC (Cosmosil 5SL-II, 10 mm ϕ × 250 mm, acetone/1,2-dichloroethane 1:9; 2.0 mL min^{-1}; **4**, t_R 12 min; **5**, t_R 10 min) to give **4** (85 mg, 62%) as a black solid; mp 264−266 °C; VIS (CH_2Cl_2) λ_{max} 766 (ϵ, 85 000), 694 (6 800), 541 (29 000), 505 (4 900), 366 nm (77 000); ^{1}H NMR ($CDCl_3$, 600 MHz) δ 11.33 (1H, s, CHO), 9.38 (1H, s, 5-H), 8.55 (1H, s, 20-H), 8.54 (1H, s, 10-H), 5.16, 4.99 (each 1H, d, J = 19 Hz, 13^1-CH_2), 4.32−4.38 (2H, m, 7-, 18-H), 4.18 (1H, dt, J = 9, 2 Hz, 17-H), 4.08 (1H, dt, J = 9, 4 Hz, 8-H), 3.64 (3H, s, $COOCH_3$), 3.62 (3H, s, 2-CH_3), 3.48 (3H, s, 12-CH_3), 2.62, 2.23 (each 1H, m, 17-CH_2), 2.56, 2.29 (each 1H, m, 17^1-CH_2), 2.39, 2.08 (each 1H, m, 8-CH_2), 1.84 (3H, d, J = 8 Hz, 7-CH_3), 1.76 (3H, d, J = 7 Hz, 18-CH_3), 1.11 (3H, t, J = 7 Hz, 8^1-CH_3), 0.08, −1.22 (each 1H, s, NH); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 195.7 (C13^1), 188.1 (C3^1), 173.4, 170.4, 167.7, 164.9, 158.4, 146.9, 140.2, 140.0, 136.3, 136.1, 130.9, 126.7, 122.4, 109.2 (C1, 2, 3, 4, 6, 9, 11, 12, 13, 14, 15, 16, 17^3, 19), 99.0 (C10), 96.9 (C20), 96.7 (C5), 55.4 (C8), 51.7 (C17^5), 51.6 (C17), 49.0, 48.3 (C7, 18), 47.8 (C13^2), 30.8 (C17^2), 30.1 (C8^1), 29.8 (C17^1), 23.2 (C7^1, 18^1), 11.6 (C12^1), 11.0 (C2^1), 10.7 (C8^2); HRMS (FAB) m/z 553.2822 (MH^+), calcd for $C_{33}H_{37}N_4O_4$ 553.2815.

Methyl 3-Deacetyl-3-carboxybacteriopyropheophorbide-*a* (7). According to the reported procedure,[13] 3-formylbacteriochlorin **4** (20 mg, 0.036 mmol) was oxidized by NH_2SO_3H (35 mg, 0.36 mmol) and $NaClO_2$ (30 mg, 0.33 mmol) in water (0.6 mL), 2-methyl-2-butene (2 mL), and THF (5 mL). The product was purified by silica gel chromatography ($MeOH-CH_2Cl_2$, 1:9) followed by GPC column (polystyrene packed column; Jaigel, $CHCl_3$) and HPLC (Cosmosil 5SL-II, 10 mm ϕ × 250 mm, 2-PrOH/1,2-dichloroethane 1:19, 2.0 mL/min, t_R 18 min) to give **7** (8.0 mg, 39%) as a dark brown solid: mp >300 °C; VIS (CH_2Cl_2) λ_{max} 756 (relative intensity, 73%), 687 (12), 534 (28), 500 (6), 387 (61), 358 nm (100); ^{1}H NMR ($CDCl_3$, 600 MHz) δ 9.61 (1H, s, 5-H), 8.57 (1H, s, 20-H), 8.52 (1H, s, 10-H), 5.17, 5.01 (each 1H, d, J = 19 Hz, 13^1-CH_2), 4.42 (1H, dq, J = 2, 7 Hz, 7-H), 4.36 (1H, br-q, J = 7 Hz, 18-H), 4.18 (1H, br-d, J = 10 Hz, 17-H), 4.09 (1H, br-m, 8-H), 3.70 (3H, s, 2-CH_3), 3.64 (3H, s, $COOCH_3$), 3.46 (3H, s, 12-CH_3), 2.64, 2.26 (each 1H, m, 17-CH_2), 2.57, 2.31 (each 1H, m, 17^1-CH_2), 2.41, 2.12 (each 1H, m, 8-CH_2), 1.89 (3H, d, J = 7 Hz, 7-CH_3), 1.77 (3H, d, J = 7 Hz, 18-CH_3), 1.16 (3H, t, J = 7 Hz, 8^1-CH_3), 0.28, −1.06 (each 1H, s, NH); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 195.9 (C13^1), 173.5, 170.6, 170.4, 168.1, 164.4, 157.9, 147.2, 141.3, 139.7, 137.1, 136.8, 130.5, 121.7, 121.1, 109.0 (C1, 2, 3, 3^1, 4, 6, 9, 11, 12, 13, 14, 15, 16, 17^3, 19), 99.1 (C10), 97.3 (C5), 96.6 (C20), 55.3 (C8), 51.7 (C17^5), 51.4 (C17), 49.3 (C18), 48.7 (C7), 47.8 (C13^2), 30.8 (C17^2), 30.2 (C8^1), 29.9 (C17^1), 23.3 (C7^1), 23.1 (C18^1), 13.6 (C2^1), 11.6 (C12^1), 10.8 (C8^2); HRMS (FAB) m/z 569.2774 (MH^+), calcd for $C_{33}H_{37}N_4O_5$ 569.2764.

Methyl 3-Deacetyl-3-hydroxymethylbacteriopyropheophorbide-*a* (8). According to the reported procedure,[10] 3-formylbacteriochlorin **4** (55 mg, 0.10 mmol) was reduced by *t*-$BuNH_2 \cdot BH_3$ (30 mg, 0.34 mmol) in CH_2Cl_2. The product was purified by silica gel chromatography ($MeOH-CH_2Cl_2$, 1:99) to give **8** (50 mg, 90%) as a black solid: mp 213−215 °C; VIS (CH_2Cl_2) λ_{max} 721 (ϵ, 50 000), 657 (16 000), 516 (36 000), 485 (9 100), 382 (63 000), 353 nm (120 000); ^{1}H NMR ($CDCl_3$, 600 MHz) δ 8.33 (1H, s, 5-H), 8.18 (1H, s, 10-H), 8.02 (1H, s, 20-H), 5.65 (2H, s, 3-CH_2), 4.92, 4.74 (each 1H, d, J = 19 Hz, 13^1-CH_2), 4.06−4.13 (2H, m, 7-, 18-H), 3.88 (1H, dt, J = 9, 2 Hz, 17-H), 3.86 (1H, dt, J = 9, 4 Hz, 8-H), 3.61 (3H, s, $COOCH_3$), 3.33 (3H, s, 12-CH_3), 3.19 (3H, s, 2-CH_3), 2.80 (1H, br-s, OH), 2.47, 2.08 (each 1H, m, 17-CH_2), 2.40, 2.18 (each 1H, m, 17^1-CH_2), 2.25, 1.96 (each 1H, m, 8-CH_2), 1.75 (3H, d, J = 7 Hz, 7-CH_3), 1.60 (3H, d, J = 7 Hz, 18-CH_3), 1.05 (3H, t, J = 7 Hz, 8^1-CH_3), 1.30, −0.15 (each 1H, s, NH); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 195.8 (C13^1), 173.5, 171.0, 170.3, 161.4, 155.2, 147.7, 140.9, 139.5, 137.3, 134.6, 134.5, 128.7, 118.1, 108.6 (C1, 2, 3, 4, 6, 9, 11, 12, 13, 14, 15, 16, 17^3, 19), 99.1 (C10), 94.2 (C20), 94.1 (C5), 55.8 (C3^1), 54.2 (C17), 51.6 (C17^5), 50.3 (C8), 49.7, 48.9 (C7, 18), 47.3 (C13^2), 30.7 (C17^2), 30.0 (C8^1), 29.7 (C17^1), 22.5 (C7^1), 22.3 (C18^1), 11.2 (C12^1), 10.8 (C2^1), 10.7 (C8^2); HRMS (FAB) m/z 555.2964 (MH^+), calcd for $C_{33}H_{39}N_4O_4$ 555.2971.

Zinc Methyl 3-Deacetyl-3-hydroxymethylbacteriopyropheophorbide-*a* (Zn-8). To a solution of **8** (50 mg, 0.090 mmol) in $CHCl_3$ (20 mL) was added a solution of $Zn(OAc)_2 \cdot 2H_2O$ (500 mg, 2.3 mmol) in MeOH (10 mL), and the mixture was refluxed for 12 h. The mixture was poured into 4% aqueous $NaHCO_3$, extracted with CH_2Cl_2, and concentrated. The crude product was purified by silica gel chromatography to recover unreacted **8** (22 mg, 44%) as the first eluent ($Et_2O-CH_2Cl_2$, 2:8) and to give the zinc complex Zn-**8** (20 mg, 36%) as the second eluent (2% $MeOH-CH_2Cl_2$). Further purification by HPLC (Cosmosil 5SL-II, 10 mm ϕ × 250 mm, acetone/1,2-dichloroethane 1:4, 3.0 mL min^{-1}, t_R 14 min) gave an analytical sample: mp >300 °C; VIS (THF) λ_{max} 726 (rel, 93%), 666 (18), 547 (35), 386 (66), 346 nm (100); ^{1}H NMR (1% pyridine-d_5/$CDCl_3$, 600 MHz) δ 8.15 (1H, s, 10-H), 8.10 (1H, s, 5-H), 7.86 (1H, s, 20-H), 5.55, 5.54 (each 1H, d, J = 13 Hz, 3-CH_2), 4.86,

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4.72 (each 1H, d, J = 19 Hz, 13^1-CH_2), 4.03 (1H, br, 18-H), 4.00 (1H, br, 7-H), 3.88 (1H, br, 17-H), 3.83 (1H, br, 8-H), 3.52 (3H, s, $COOCH_3$), 3.34 (3H, s, 12-CH_3), 3.08 (3H, s, 2-CH_3), 2.38, 2.13 (each 1H, m, 17-CH_2), 2.26, 1.93 (each 1H, m, 17^1-CH_2), 2.16, 1.90 (each 1H, m, 8-CH_2), 1.60 (3H, d, J = 7 Hz, 7-CH_3), 1.57 (3H, d, J = 7 Hz, 18-CH_3), 0.88 (3H, t, J = 7 Hz, 8^1-CH_3); HRMS (FAB) m/z 617.2124 (MH^+), calcd for $C_{33}H_{37}N_4O_4{}^{64}Zn$ 617.2106.

Methyl 3-Deacetyl-3-(2,2-dicyanoethenyl)bacteriopyropheophorbide-*a* (9). According to the reported procedure,[16] Knoevenagel reaction of 3-formylbacteriochlorin **4** (11.1 mg, 0.020 mmol) was performed with malononitrile (86 mg, 1.3 mmol) and Et_3N (30 mg, 0.30 mmol) in THF (30 mL). The crude product was purified by silica gel chromatography ($Et_2O-CH_2Cl_2$, 1:19) to give **9** (10.2 mg, 85%) as a purple solid: mp 244−246 °C; VIS (CH_2Cl_2) λ_{max} 790 (ϵ, 82 000), 554 (22 000), 352 nm (93 000); ^{1}H NMR ($CDCl_3$, 600 MHz) δ 9.24 (1H, s, 3-CH), 8.59 (1H, s, 10-H), 8.57 (1H, s, 20-H), 8.37 (1H, s, 5-H), 5.17, 5.20 (each 1H, d, J = 19 Hz, 13^1-CH_2), 4.33−4.38 (2H, m, 7-, 18-H), 4.19 (1H, dt, J = 9, 2 Hz, 17-H), 4.14 (1H, dt, J = 8, 4 Hz, 8-H), 3.63 (3H, s, $COOCH_3$), 3.49 (3H, s, 12-CH_3), 3.47 (3H, s, 2-CH_3), 2.63, 2.22 (each 1H, m, 17-CH_2), 2.55, 2.28 (each 1H, m, 17^1-CH_2), 2.40, 2.12 (each 1H, m, 8-CH_2), 1.87 (3H, d, J = 7 Hz, 7-CH_3), 1.76 (3H, d, J = 7 Hz, 18-CH_3), 1.10 (3H, t, J = 7 Hz, 8^1-CH_3), −0.04, −1.20 (each 1H, s, NH); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 195.7 ($C13^1$), 173.4, 169.1, 167.8, 165.6, 159.2, 147.0, 140.8, 136.9, 135.2, 135.0, 131.4, 124.6, 123.4, 114.2, 113.3, 109.5, 86.9 (C1, 2, 3, 3^2, 3^3 × 2, 4, 6, 9, 11, 12, 13, 14, 15, 16, 17^3, 19), 154.7 ($C3^1$), 99.3 (C10), 97.4 (C20), 94.7 (C5), 55.6 (C8), 51.8 (C17), 51.7 ($C17^5$), 49.0, 48.2 (C7, 18), 47.9 ($C13^2$), 30.7 ($C17^2$), 30.0 ($C8^1$), 29.8 ($C17^1$), 23.3 ($C7^1$, 18^1), 14.5 ($C2^1$), 11.7 ($C12^1$), 10.7 ($C8^1$); HRMS (FAB) m/z 601.2918 (MH^+), calcd for $C_{36}H_{37}N_6O_3$ 601.2927.

Methyl 3-Deacetyl-3-acetoxymethylbacteriopyropheophorbide-*a* (10). To a solution of **8** (22 mg, 0.040 mmol) in CH_2Cl_2 was added AcOH (12 mg, 0.20 mmol), EDC·HCl (38 mg, 0.20 mmol), and DMAP (49 mg, 0.40 mmol), and the mixture was stirred for 2 h at room temperature. The mixture was poured into 3% aqueous HCl, extracted with CH_2Cl_2, washed with 4% aqueous $NaHCO_3$, and concentrated. The product was purified by silica gel chromatography ($Et_2O-CH_2Cl_2$, 1:9) followed by recrystallization from CH_2Cl_2−hexane to give **10** (22 mg, 92%) as black plates: mp 145−147 °C; VIS (CH_2Cl_2) λ_{max} 725 (ϵ, 50 000), 660 (14 000), 517 (33 000), 468 (8 100), 382 (58 000), 353 nm (110 000); ^{1}H NMR ($CDCl_3$, 600 MHz) δ 8.30 (1H, s, 10-H), 8.27 (1H, s, 5-H), 8.15 (1H, s, 20-H), 6.16, 6.09 (each 1H, d, J = 13 Hz, 3-CH_2), 5.02, 4.85 (each 1H, d, J = 19 Hz, 13^1-CH_2), 4.19−4.22 (2H, m, 7-, 18-H), 4.05 (1H, dt, J = 9, 2 Hz, 17-H), 3.94 (1H, dt, J = 9, 4 Hz, 8-H), 3.63 (3H, s, $COOCH_3$), 3.39 (3H, s, 12-CH_3), 3.26 (3H, s, 2-CH_3), 2.58, 2.22 (each 1H, m, 17-CH_2), 2.51, 2.27 (each 1H, m, 17^1-CH_2), 2.34, 2.06 (each 1H, m, 8-CH_2), 2.19 (3H, s, $COCH_3$), 1.79 (3H, d, J = 7 Hz, 7-CH_3), 1.70 (3H, d, J = 7 Hz, 18-CH_3), 1.13 (3H, t, J = 7 Hz, 8^1-CH_3), 1.08, −0.36 (each 1H, s, NH); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 195.6 ($C13^1$), 173.5, 171.0, 170.6, 170.0, 161.8, 155.4, 147.6, 140.2, 139.0, 137.6, 136.2, 129.7, 129.1, 118.6, 108.9 (C1, 2, 3, 3^3, 4, 6, 9, 11, 12, 13, 14, 15, 16, 17^3, 19), 99.2 (C10), 94.7 (C20), 94.0 (C5), 56.9 ($C3^1$), 54.4 (C8), 51.6 ($C17^5$), 50.5 (C17), 49.8, 48.9 (C7, 18), 47.4 ($C13^2$), 30.8 ($C17^2$), 30.2 ($C8^1$), 29.8 ($C17^1$), 22.6 ($C7^1$, 18^1), 21.0 ($C3^4$), 11.3 ($C12^1$), 11.0 ($C2^1$), 10.8 ($C8^1$); HRMS (FAB) m/z 597.3081 (MH^+), calcd for $C_{35}H_{41}N_4O_5$ 597.3077.

Methyl 3-Devinyl-3-acetoxymethylpyropheophorbide-*a* (17). Condensation reaction of 3-hydroxymethylchlorin **15** (28 mg, 0.050 mmol) with AcOH (15 mg, 0.25 mmol) using EDC·HCl (48 mg, 0.25 mmol) and DMAP (61 mg, 0.50 mmol) in CH_2Cl_2 (10 mL) was carried out as described for the preparation of **10**. The product was purified by silica gel chromatography ($Et_2O-CH_2Cl_2$, 1:19) followed by recrystallization from CH_2Cl_2−hexane to give **17** (29 mg, 98%) as dark green needles: mp 265−267 °C; VIS (CH_2Cl_2) λ_{max} 664 (ϵ, 57 000), 607 (8 800), 536 (11 000), 505 (11 000), 410 nm (110 000); ^{1}H NMR ($CDCl_3$, 600 MHz) δ 9.40 (1H, s, 10-H), 9.32 (1H, s, 5-H), 8.59 (1H, s, 20-H), 6.29 (2H, s, 3-CH_2), 5.27, 5.12 (each 1H, d, J = 19 Hz, 13^1-CH_2), 4.49 (1H, dq, J = 2, 7 Hz, 18-H), 4.30 (1H, br-d, J = 8 Hz, 17-H), 3.64 (3H, s, $COOCH_3$), 3.62 (2H, q, J = 8 Hz, 8-CH_2), 3.61 (3H, s, 12-CH_3), 3.42 (3H, s, 2-CH_3), 3.22 (3H, s, 7-CH_3), 2.69, 2.28 (each 1H, m, 17-CH_2), 2.57, 2.28 (each 1H, m, 17^1-CH_2), 2.20 (3H, s, $COCH_3$), 1.83 (3H, d, J = 7 Hz, 18-CH_3), 1.67 (3H, t, J = 8 Hz, 8^1-CH_3), 1.30, −0.15 (each 1H, s, NH); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 196.1 ($C13^1$), 173.4, 171.2, 171.1, 160.3, 154.9, 150.9, 148.7, 144.9, 140.7, 137.9, 136.2, 135.9, 135.1, 131.9, 130.6, 128.5, 106.2 (C1, 2, 3, 3^3, 4, 6, 7, 8, 9, 11, 12, 13, 14, 15, 16, 17^3, 19), 103.9 (C10), 96.8 (C5), 93.3 (C20), 57.0 ($C3^1$), 51.7 (C17, 17^5), 49.9 (C18), 48.0 ($C13^2$), 30.9 ($C17^2$), 29.8 ($C17^1$), 23.1 ($C18^1$), 21.1 ($C3^4$), 19.4 ($C8^1$), 17.4 ($C8^2$), 12.0 ($C12^1$), 11.2 ($C2^1$, 7^1); HRMS (FAB) m/z 595.2923 (MH^+), calcd for $C_{35}H_{39}N_4O_5$ 595.2920.

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Supporting Information Available: ^{1}H and ^{13}C NMR spectra of **3**, **4**, **7**−**10**, and **17** in $CDCl_3$, and ^{1}H NMR spectrum of Zn-**8** in 1% pyridine-d_5/$CDCl_3$ (Figures S1−S15); absorption spectra of bacteriochlorins **1**−**3**, **7**−**10**, and their corresponding chlorins **11**−**17** in CH_2Cl_2 (Figures S16−S22). This material is available free of charge via the Internet at http://pubs.acs.org.

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