Pergamon

Tetrahedron, Vol. 52, No. 12, pp. 4311-4326, 1996

0040-4020/96 \$15.00 + 0.00

S0040-4020(96)00131-7

Covalently Linked Pyropheophorbide Dimers As Models of the Special Pair in the Photosynthetic Reaction Center

Atsuhiro Osuka,* Yukihisa Wada, and Satoshi Shinoda

Division of Chemistry, Graduate School of Science, Kyoto University, Sakyo-ku, Kyoto 606-01, Japan

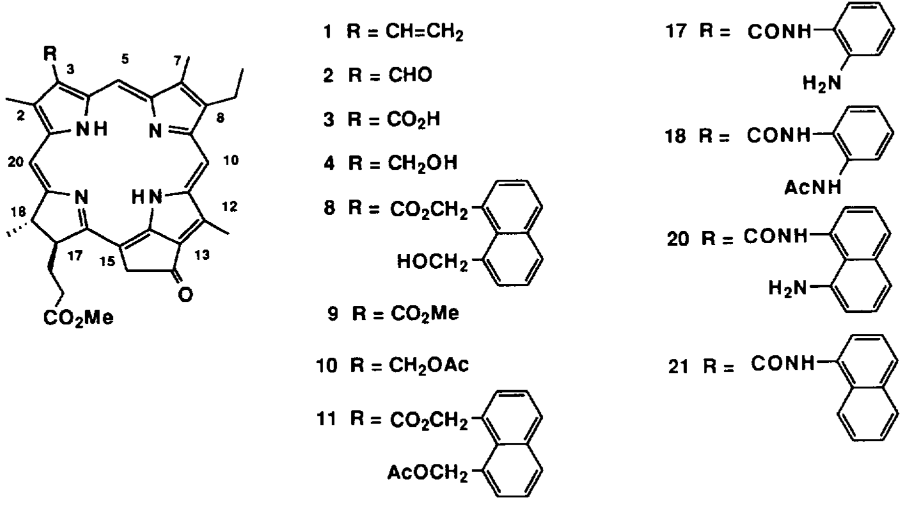
Abstract: Covalently linked pyropheophorbide dimers were prepared by the condensation reactions 3-devinyl-3-carboxylpyropheophorbide-*a*. Among these, dimers bridged by 1,8-naphthalene spacers exhibit large electronic interactions in the ^{1}H NMR and UV-visible spectra and in the redox potentials. In addition, a 1,8-naphthalene-bridged amide-linked dimer displays notable broadening and split CD effect in the Qy band as well as strong fluorescence quenching, being analogous to the special pair in the photosynthetic reaction center.

INTRODUCTION

In the photosynthetic reaction centers (RC), the cyclic tetrapyrrole pigments are held at precise distances and orientations by the protein matrix, allowing the quantitative charge separation via the efficient sequential electron-transfer reactions. With a view to better understanding the mechanism of electron and/or energy transfer in the RC, considerable effort has been directed toward the synthesis and characterization of covalently connected artificial models, mainly based on porphyrin.[1-3] Recently, increasing attention has been focused on photosynthetic models with well-defined geometries and energies, since such molecules allow to quantify the distance, orientation, energy-gap dependencies of electron-transfer reactions. In contrast to a large number of porphyrin models, there are only a limited number of models based on natural chlorin-pigments such as chlorophylls or pyropheophorbides.[4-7] These pigments stand in marked contrast to symmetric porphyrins in respects of low symmetry, considerably low S_1-energies, strong Qy absorption bands, and unique redox reactivities. Therefore, much more systematic studies on the excited-state interactions of these pigments are required for deeper understanding of molecular mechanisms in the RC.

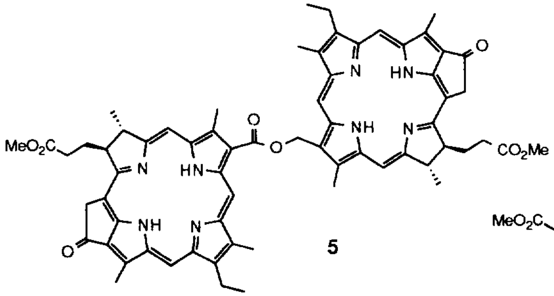
As part of our program aiming at construction of molecular mimicry of photosynthetic energy and electron transfer, we need dimeric pigment blocks that have optical and redox properties analogous to those of the special pair (SP), particularly with respect to considerably stabilized S_1-state and lower one-electron oxidation potential. These properties are essential for the vital roles of the SP as the final singlet energy sink and the initial electron donor. In the light-harvestig complexes, several hundred chlorophyll molecules participate in funnelling photonic energy to the RC, where the sequential electron-transfer relay is initiated from the lowest singlet excited state of the SP. The characteristic spectral properties of the SP are a red shift and split CD for the Qy absorption band. We sought to prepare structurally well-defined models in which such spectral changes are mainly caused by through-space interactions. Such interactions should be most effective in closely stacked face-to-face geometries as found in the natural system. The propionic acid side chain at 17-

position has been frequently used for linkages of chlorophylls and related pigments so far.[4-7] Here, we employed methyl 3-devinyl-3-carboxylpyropheophorbide-*a* (**3**) as a building block,[8] since this will lead to conformationally restricted models which may be suitable for studies on electronic interactions of the two macrocycles. In this paper, we report the concise synthesis of covalently linked pyropheophorbide dimers designed along this line.

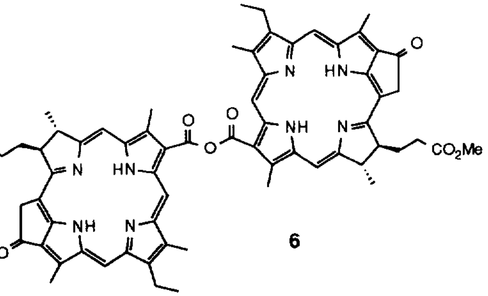


RESULTS AND DISCUSSION

Synthesis. Methyl pyropheophorbide-*a* (**1**) was obtained from *spirulina maxima* according to the usual method with some modifications.[9] Direct oxidation of **1** with $KMnO_4$ was reported to give carboxylic acid **3** in 30% yield.[10] We found that this procedure is unreliable and often gives a complex mixture consisting of a small amount of **3** (ca. 3%) and vinyl-group dihydroxylated products. Here a two-step conversion of **1** to the desired compound **3** was employed. Thus, **1** was first converted to methyl pyropheophorbide-*d* (**2**), [11] which was oxidized with $NaClO_2$ in the presence of a chlorine-atom scavenger. First we used 1,3-dimethoxybenzene as a chlorine-atom scavenger,[12] and soon found that 2-methyl-2-butene was a much superior scavenger.[13] The oxidation of **2** to **3** was achieved in ca. 80% isolated yield in a large scale. Without a scavenger, the oxidation was accompanied by concurrent chlorination at the 20-meso position. Chemoselective reduction of **2** with $NaBH_3CN$ gave alcohol **4** in 58% yield.

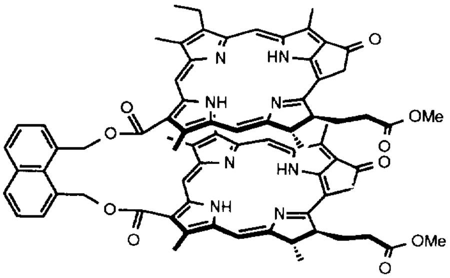


5

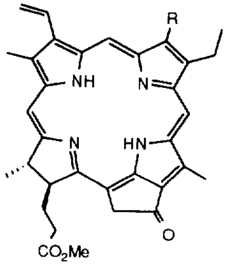


6

Ester linked dimer **5** was prepared in 80% yield by the condensation reaction of **3** and **4** with 2-chloro-1-methylpyridinium iodide (CMPI) and 4-dimethylaminopyridine (DMAP) as catalysts.12,14) We found that refluxing of a CH_2Cl_2 solution of **3** in the presence of CMPI provided anhydride dimer **6** in 62% yield.12) The anhydride dimer **6** that is often formed as a side product in condensation reactions of **3** using CMPI as a catalyst would be also of interest in view of close proximity of the two macrocycles. In order to prepare a dimer of face-to-face geometry, **3** was condensed with 1,8-bis(hydroxymethyl)naphthalene (CMPI, DMAP, benzene-CH_2Cl_2, 3.5 h) to afford dimer **7** (9%) along with monomer **8** (62%). Compounds **9**, **10**, and **11** were prepared as reference molecules. Methyl pyropheophorbide-*b* (**12**) was transformed into carboxylic acid **13** in the same manner, which was converted to anhydride dimer **14** in 50% yield.



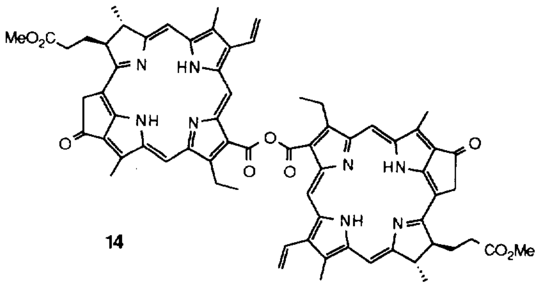
7



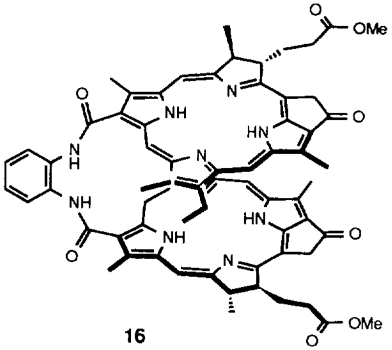
12 R = CHO

13 R = CO_2H

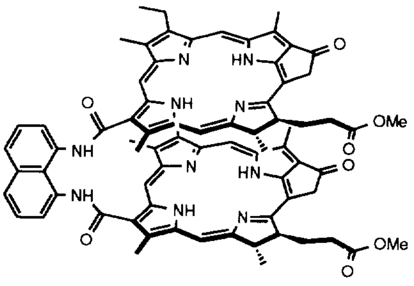
15 R = CO_2Me



14



16



19

We also examined the synthesis of amide-linked dimers starting from **3**. The carboxylic acid **3** was converted to acid chloride, which was reacted with 1,2-phenylenediamine to provide dimer **16** (45%) and monomer **17** (9%). Similar condensation with 1,8-diaminonaphthalene gave dimer **19** (5%) and monomer **20**

(41%). Compounds **18** and **21** were prepared as reference compounds. Low yield of **19** was probably due to severe steric hindrance.

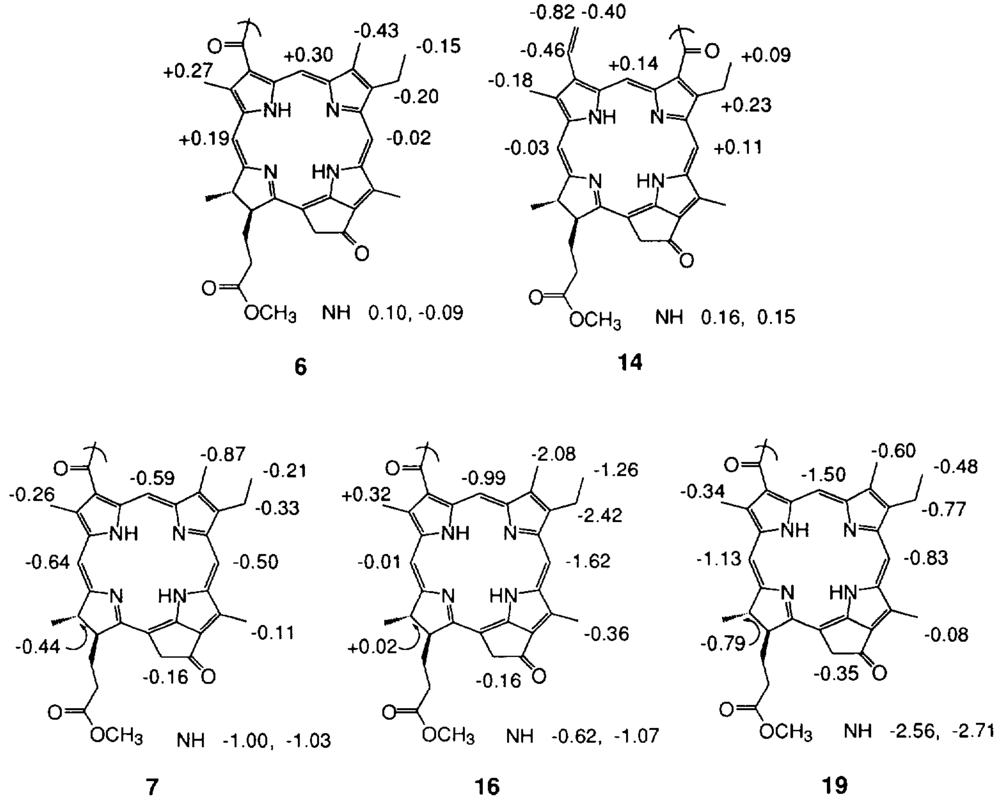


Figure 1. Chemical shift differences of the dimers **6**, **14**, **7**, **16**, and **19**. Reference monomers are **9** for **6** and **7**, **15** for **14**, **18** for **16**, and **21** for **19**, respectively. Negative values indicate upfield shift.

^{1}H NMR spectroscopy. Figure 1 shows the chemical shift changes observed for the dimers in comparison to the respective reference monomers. The ^{1}H NMR spectra of the anhydride dimers **6** and **14** in $CDCl_3$ are similar to the corresponding reference monomers except for small upfield shift of the 7-methyl and the 8-ethyl protons in **6** and of the 3-vinyl protons in **14**, respectively. The chemical shift of the 5-meso proton is sensitive to substituents at the 3-position; being downfield shifted from in the case of anhydrides and upfield shifted in the case of amides. The spectrum of **5** (see, Experimental Section) is also nearly the superposition of the respective subunits except for small upfield shifts of the 7-methyl and the 8-ethyl protons in the carboxylic acid part. In contrast, the spectrum of the 1,8-naphthalene-bridged dimer **7** displays substantial upfiled shifts for all the protons. These results imply extended conformations for **5**, **6**, and **14** in which main portion of the macrocycles are outside of the shielding region of the other and a stacked conformation for **7** in which the two macrocycles are held at proximity, probably face-to-face geometry in average. Porphyrins bearing an amide-functionality were found to aggregate extensively in $CDCl_3$, probably via hydrogen-bond network.15) Thus, comparison of the chemical shifts of the dimer with those of the monomer is not straightforward. Such aggregate formation is largely suppressed in acetone-d_6 that can act as a hydrogen-bond accepting solvent. Therefore, we compare the spectra of the amide-linked dimers **16** and **19** in acetone-d_6 with the spectra of the reference molecules **18** and **21**, respectively. In the spectrum of **16**, the protons of a half portion of the pyropheophorbide (the right side in the structure shown in Figure 1) experience large upfield shifts while the other protons appear nearly at the same chemical shifts or slightly downfield chemical shifts, indicating a partially overlapped, offset conformation (Figure 2). Offset conformations have been often observed in covalently linked porphyrin dimers and are explained in terms of their overall favorable π-π and π-σ electrostatic interactions.16) On the other hand, in the dimer **19**, all the protons experience substantial upfield shifts which are larger than those in **7**. Notably the upfield shifts of the inner NH protons reach more than 2.5 ppm. These results indicate that the two macrocycles are held at the closest face-to-face stacked conformations in average, even provided a thermal interconversion of several conformers.

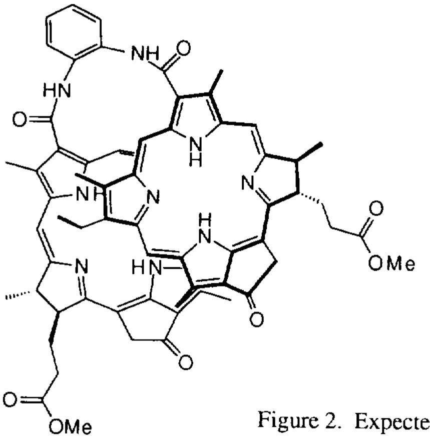


Figure 2. Expected offset geometry of the dimer **16**.

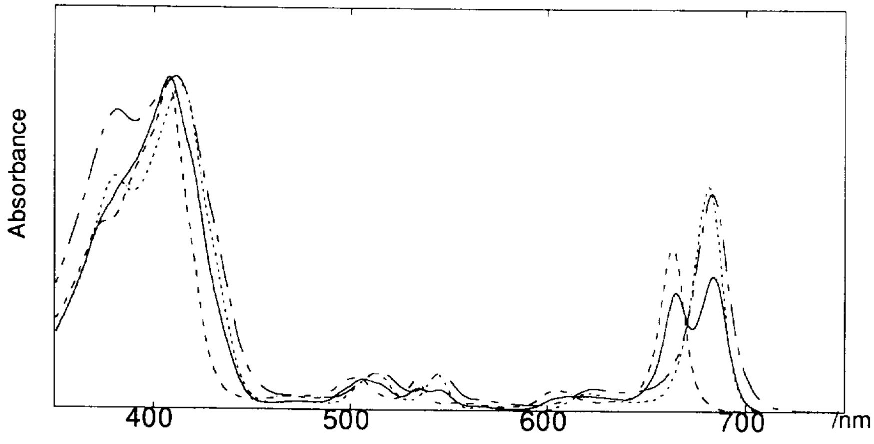


Figure 3. Absorption spectra of **5** (———), **7** (— - -), **9** (··········), and **10** (--------) in THF.

Electrochemical Properties. The oxidation and reduction potentials were measured in DMF vs ferrocene/ferrocenium ion by differential cyclic voltammetry. Selected data are summarized in Table 1. For monomers, two waves were commonly observed both in the oxidation and reduction reactions, while not well resolved or complicated results were obtained for dimers. The ester dimer **5** and the anhydride dimers **6** and **14** did not exhibit large shifts from the corresponding monomers. On the other hand, in the closely interacting dimeric models **7**, **16**, and **19**, the first oxidation potentials were shifted to lower values compared with those of the corresponding monomer; 0.13 V for **7**, 0.06 V for **16**, and 0.15 V for **19**, while the first reduction potentials did not change significantly. Here again, the largest shifts are observed in the 1,8-naphthalene-bridged dimers **7** and **19** and these shifts are larger than a cofacial cyclophane-type chlorophyll dimer reported before (0.06 V).[7] Therefore, we may conclude that the first oxidation potential is quite dependent on the relative geometry of the two macrocycles; little change in extended conformations and shifts to lower values in closely interacting stacked conformations. Finally, it may be worthy to note the observed shifts in **7** and **19** are comparable to the reported difference (0.19 V) between the oxidation potential of the SP in *Rhodobactor sphaeroides* and a monomeric bacteriochlorophyll *a*.[4]

Table 1. Redox potentials of models

compounds	*oxidation*			*reduction*	
monomer					
1	0.42	0.57		-1.32	-1.56
2	0.57	0.70		-1.25	-1.43
9	0.49	0.68		-1.36	-1.56
10	0.44	0.60		-1.48	-1.58
11	0.49	0.62		-1.35	-1.57
13	0.51	0.66		-1.44	-1.55
18	0.47	0.62		-1.34	-1.58
22	0.49	0.64		-1.32	-1.62
dimer					
5	0.44	0.58		-1.34	-1.60
6	0.48	0.65			
7	0.36	0.48	0.61	-1.34	-1.78
14	0.44	0.58	0.70		
16	0.41	0.61		-1.41	
19	0.34			-1.30	-1.70

In DMF in the presence of 0.1 M tetraethylammonium perchlorate supporting electrolyte. Reported values are vs. ferrocene/ferrocenium ion.

Absorption and Fluorescence Spectra. Table 2 and Figures 3-5 summarize the absorption and fluorescence data. First we discuss the spectral properties of the ester-linked dimers **5** and **7**. The absorption spectrum of **5** can be analyzed roughly as the sum of the respective chromophores **9** and **10**. The

Qy-bands are observed at 665.0 and 683.5 nm, which are assignable to the absorption of the pyropheophorbides in the alcohol and carboxylic acid parts, respectively; λ_{max}= 663.5 nm for **10** and λ_{max}= 681.5 nm for **9**. The fluorescence spectrum of **5** (not shown) displays an emission maximum at 685 nm with a shoulder at 666 nm, which are assigned to the emissions from the carboxylic acid and the alcohol subunits, respectively. The absorption data and the dual emission feature indicate the presence of two S_1 states with different energies that are not strongly coupled. The emission spectral shape of **5** suggests the intramolecular singlet-singlet energy transfer from the high energy alcohol subunit to the low energy carboxylic acid subunit. In this case, however, the energy difference is quite small so that the reverse energy transfer may be possible at room temperature as observed in other example.[17] In the absorption spectrum of the 1,8-naphthalene-bridged dimer **7**, the Soret band differs significantly from that of **9** but the Qy-band is almost the same. The fluorescence spectrum of **7** is virtually the same as that of **9** with exception of a 3-4 nm red shif and its intensity is ca. half relative to that of **9** or **11** in benzene and THF and is dropped to 0.15 in polar DMF.

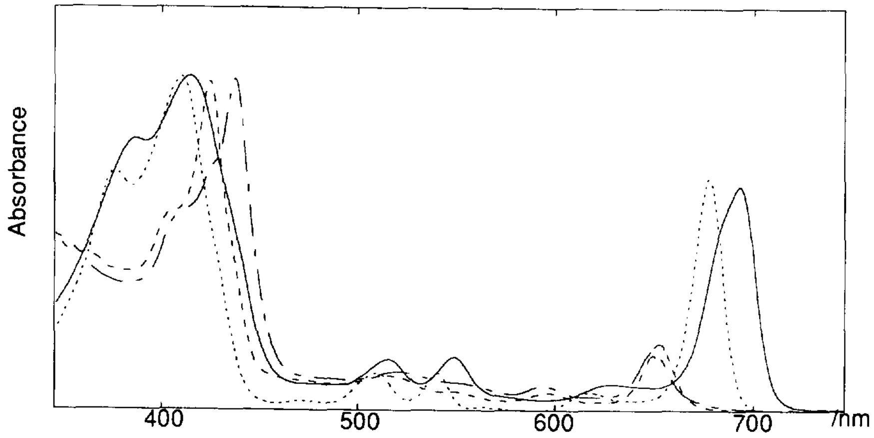


Figure 4. Absorption spectra of **6** (———), **9** (··········), **14** (— - —), and **15** (-------) in THF.

We compared the absorption spectra of the anhydride dimers **6** and **14** with those of the reference molecules **9** and **15**, respectively (Figure 4). In the case of **6**, the Soret band is broader and red-shifted by 3.5 nm and the Qy-band is red-shifted by 16.5 nm, while the Soret band becomes red-shifted by 14 nm and the Qy-band is slightly blue-shifted by ca. 3.5 nm in **14**. These different spectral changes between the anhydride dimers **6** and **14** can be understood as follows. As to the Qy-bands of chlorophylls and related chlorin pigments, the transition dipole moments are well defined to lie along a NH—NH axis.[18] Therefore, the arrangement of the Qy transition dipole moments are different between **6** and **14**, resulting in the different spectral shifts. The magnitude of exciton coupling depends on the magnitues of the oscillator strength of the transition involved as well as their relative orientation.[19,20] In this respect, larger oscillator strength of pyropheophorbide *a* compared with that of pyropheophorbide *b*[18] (in this case, **9** vs. **15**) leads to stronger exciton coupling in **6** than that in **14**.

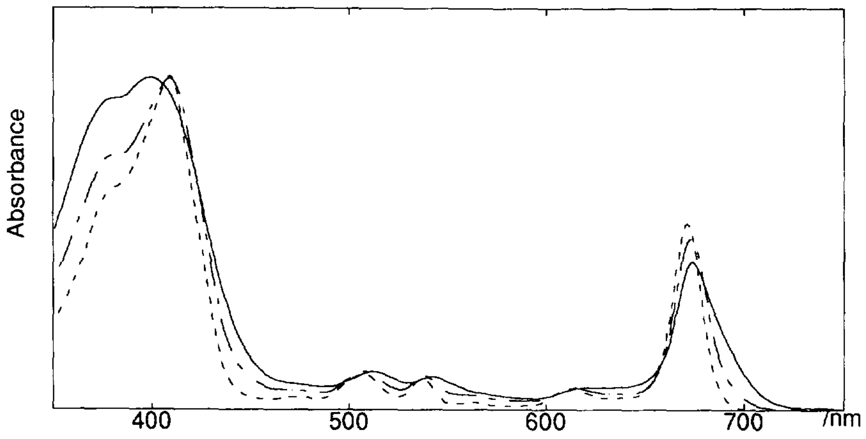


Figure 5. Absorption spectra of **16** (— - —), **18** (--------), and **19** (————) in THF.

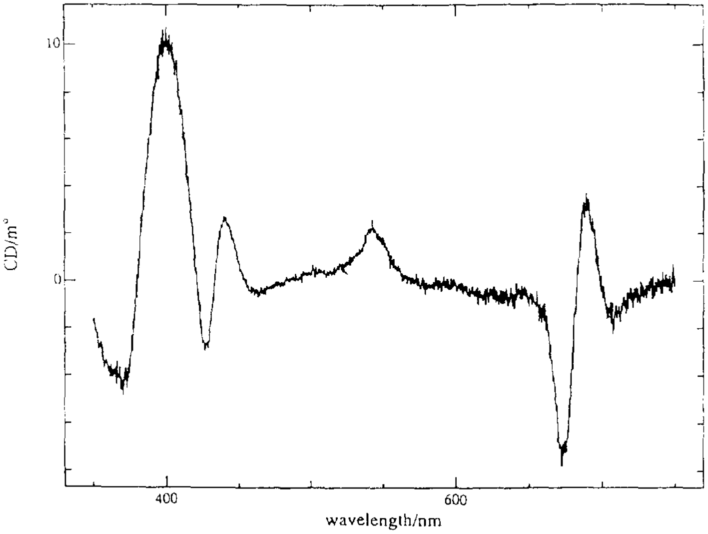


Figure 6. CD spectrum of **19** in THF.

The absorption and fluorescence spectra of the amide-linked porphyrins **16** and **19** were compared with that of the reference **18** (Figure 5; for **19**, the monomer **21** is a better reference but its spectrum is identical with that of **18** and thus is omitted). The absorption spectrum of **16** is rather similar to that of **18**. On the other hand, in the spectrum of **19** significant blue-shift and broadening at the Soret band are evident and the Qy-band also displays notable broadening with ca. 3.5 nm red-shift. These spectral changes are characteristic of face-to-face dimers of chlorophylls and related pigments.[18] The exciton couping in the Qy-band of **19** has been clearly confirmed in its split CD spectrum in THF (Figure 6). The split CD at the Qy-bamd is only detected for **19**.

Table 2 Absorption and Fluorescence Data in THF.

models	*Soret*	*Qy^a*	*λmax^b*	*$I/I^{0,c}$*
	(nm)	(nm)	(nm)	
monomer				
4	407.5	659.5	662.5	-
9	414.0	681.5	685.0	-
10	408.0	663.5	666.0	-
11	414.5	681.5	685.0	-
15	428.5	657.0	660.5	-
18	409.0	671.5	676.0	-
21	409.0	670.5	674.0	-
dimer				
5	409.0	665.0	666.0	
		683.5	685.0	-
6	417.5	698.0	702.0	0.70
14	442.5	653.0	657.5	0.77
7	411.0	683.5	688.0	0.54
16	409.0	673.0	679.0	0.64
19	396.0	674.0	682.5	0.11

[a] The peak maxima of the Qy-band. [b] The emission maxima. [c] The fluorescence intensities relative to those of the reference molecules; we used **4**, **9**, **11**, **15**, **18**, and **21** as reference for **5**, **6**, **7**, **14**, **16**, and **19**, respectively.

The fluorescence emission maxima are shifted to longer wavelength by 3 nm in **16** and by 8.5 nm in **19**. In THF the relative fluorescence intensity of **16** to **18** is 0.64 and that of **19** to **21** is only 0.11. The relative fluorescence intensities decrease in polar DMF; 0.44 and 0.07 in **16** and **19**, respectively. These results, which are quite similar to **7** and the reported ethene-bridged magnesium pyropheophorbide dimer,[11] seem to indicate that the electronic interactions of the two S_1-states result in a new lower lying excited state with charge-transfer character that might be stabilized in polar environments. Therefore, the S_1-states of **7**, **16**, and **19** have additional nonradiative decaying pathway to the ground state via the interactions with these lower lying excited states. These decays may be accerelated in polar environments. Detail ultrafast excited-state behaviors of these dimers will be revealed by picosecond time-resolved techniques such as the fluorescence lifetime measurement and the transient absorption spectroscopy that are now in progress.

In summary, the carboxylic acid **3** has been shown to be an useful building block for preparation of a variety of pyropheophorbide dimers. In the stacked dimers **7**, **16**, and **19**, the electronic interactions are strong enough to induce significant changes in the key properties of the S_1 state and the one-electron oxidation potentials. These dimeric pyropheophorbides will provide a new oppotunity for study on the electronic interactions between spatially proximate photosynthetic pigments.

EXPERIMENTAL

All solvents and reagents were purified by standard methods before use. The instruments were previously reported.12) The ^{1}H-NMR spectra were recorded on a 500 MHz JEOL α-500 spectrometer. The mass spectra were recorded on a JEOL HX-110 spectrometer using positive FAB ionization method (accelerating voltage 1 kV, Xe atom as the primary ion source, and a mixture of *m*-nitrobenzyl alcohol and $CHCl_3$ as the FAB matrix).

Isolation of methyl pheophorbide-*a* and methyl pyropheophorbide-*a* from *spirulina maxima*. *Spirulina* (Nippon INK, 2 kg) suspended in acetone (3 L) was stirred by a mechanical stirrer for 30 min and was filtered. This operation was repeated several times until the color of filtrate became pale. The filtrates are combined and concentrated to ca. 1/5 volume. The resulting solution was poured into water and extracted with CH_2Cl_2. The organic layer was separated and thoroughly washed with water. When emulsion is formed, brine was added so as to induce phase separation. The organic layer was separated and dried over anhydrous Na_2SO_4. Evaporation of the solvent left dark brown oil, which was dissolved to methanol (500 mL). To this solution, concentrated H_2SO_4 (10 mL) was carefully added and the resulting solution was stirred overnight at room temperature in the dark. The mixture was poured into water (1 L) and extracted with CH_2Cl_2 until the organic extract became colorless. Combined organic layers were neutralized with saturated $NaHCO_3$ solution and dried over anhydrous Na_2SO_4 and the organic solvent was evaporated. This mixture was separated over a silica gel gravity column. Elution with hexane separated yellow bands of carotenoids, and elution with a 1:1 mixture of hexane and ethyl acetate first separated red bands which were followed by a deep green band. This green fraction was separated and the organic solvent was evaporated. Recrystallization from a mixture of CH_2Cl_2 and methanol gave methyl pheophorbide-*a* (ca. 10 g) as blue-green solid. This substance was found to be almost pure by ^{1}H NMR examination.

Methyl pheophorbide (3 g) thus obtained was dissolved to 2,4,6-collidine (50 mL) and the resulting mixture was refluxed for 3 h under N_2 (oil bath temperature was kept at 160° C). After the mixture was cooled, collidine was removed under reduced pressure. Larger vessel is recommended for removal of collidine. Remaining collidine was removed by heating under reduced pressure. Recrystallization from a mixture of CH_2Cl_2 and methanol gave methyl pyropheophorbide-*a* (ca. 2.3 g). Final purification was carried out over a flash silica gel column using a 1:1 mixture of hexane-ethyl acetate as eluent.

Methyl 3-devinyl-3-carboxypyropheophorbide-*a* (3). A mixture of **2** (330 mg, 0.60 mmol), NH_2SO_3H (351 mg, 3.6 mmol), 2-methyl-2-butene in THF (15 mL) and H_2O (1.5 mL) was stirred at room temperature for 10 min under a nitrogen atmosphere. Sodium chlorite (163 mg, 1.80 mmol) dissolved in H_2O (0.75 mL) was added dropwise to the mixture in 15 min and the solution was stirred at room temperature for 45 min. The reaction mixture was poured into H_2O (300 mL) and extracted with $CHCl_3$. The extract was washed three times with water and dried over anhydrous Na_2SO_4. After removal of the solvent, the residue was separated by a flash silica gel column eluting with a mixture of MeOH and CH_2Cl_2 (4:96) to give **3**. Yield 275 mg (81%). ^{1}H-NMR($CDCl_3$); -2.28 (s, 1H, NH), 1.63 (t, 3H, J = 8.0 Hz, 8^2-CH_3), 1.87 (d, 3H, J = 7.5 Hz, 18-CH_3), 2.28-2.37, 2.55-2.62, 2.71-2.77 (m, 2H+1H+1H, 17-CH_2CH_2), 3.17 (s, 3H, 7-CH_3), 3.55 (m, 2H, 8^1-CH_2), 3.57 (s, 3H, 12-CH_3), 3.63 (s, 3H, CO_2CH_3), 3.73 (s, 3H, 2-CH_3), 4.35 (m, 1H, 17-H), 4.55 (m, 1H, 18-H), 5.14, 5.34 (d, 1H+1H, *J* = 20.0 Hz, 13^2-H_2), 8.80 (s, 1H, 20-H), 9.35 (s, 1H, 10-H), 10.31 (s, 1H, 5-H). IR(KBr) ν_{max} 1734 (CO_2CH_3), 1701 (CO_2H), 1685 (C=O) cm^{-1}. MS(FAB): Found: m/z 567. calcd for $\text{C}_{33}\text{H}_{34}\text{N}_4\text{O}_5$: M^++1, 567.

Methyl 3-devinyl-3-hydroxymethylpyropheophorbide *a* (4). A mixture of **2** (55 mg, 0.10 mmol), sodium cyanoborohydride (63 mg, 1.0 mmol) in CH_2Cl_2 (3 mL) and MeOH (7 mL) was stirred for 10 h under an argon atmosphere. The reaction mixture was poured into H_2O (200 mL) and extracted with CH_2Cl_2. The extract was washed three times with water and dried over anhydrous Na_2SO_4. After removal of the solvent, the residue was separated by a flash silica gel column eluting with a mixture of MeOH and CH_2Cl_2 (0.5:99.5) to give **4** (32 mg, 58%). ^{1}H-NMR(CDCl_3); -2.07, 0.14 (s, 1H+1H, NH), 1.61 (t, 3H, *J* = 7.5 Hz, 8^2-CH_3), 1.69 (d, 3H, *J* = 7.5 Hz, 18-CH_3), 2.00-2.07, 2.24-2.35, 2.47-2.60 (m, 1H+1H+2H, $17\text{-CH}_2\text{CH}_2$), 3.16 (s, 3H, 7-CH_3), 3.34 (s, 3H, 2-CH_3), 3.42 (s, 3H, 12-CH_3), 3.54 (m, 2H, 8^1-CH_2), 3.65 (s, 3H, CO_2CH_3), 4.05 (m, 1H, 17-H), 4.35 (m, 1H, 18-H), 4.91, 5.02 (d, 1H+1H, *J* = 19.5 Hz, 13^2-H_2), 5.70 (s, 2H, 3-CH_2), 8.44 (s, 1H, 20-H), 9.14 (s, 1H, 5-H), 9.27 (s, 1H, 10-H). IR(KBr) ν_{max} 1732 (CO_2CH_3), 1692 (C=O) cm^{-1}. MS(FAB): Found: m/z 553. calcd for $\text{C}_{33}\text{H}_{36}\text{N}_4\text{O}_4$: M^++1, 553.

Ester-linked Dimer 5. A mixture of **3** (17 mg, 0.03 mmol), **4** (14 mg, 0.025 mmol), 2-chloro-1-methyl-pyridinium iodide (CMPI) (20 mg, 0.08 mmol), and 4-dimethylaminopyridine (DMAP) (12 mg, 0.10 mmol) in a mixture of CH_2Cl_2 (3 mL) and benzene (7 mL) was refluxed for 2.5 h under an argon atmosphere. The reaction mixture was poured into H_2O (200 mL) and extracted with CH_2Cl_2. The extract was washed three times with water and dried over anhydrous Na_2SO_4. After removal of the solvent, the residue was separated by a flash silica gel column (eluting with a mixture of MeOH and CH_2Cl_2 (0.3:99.7) to give **5** (22 mg, 80%). ^{1}H-NMR(CDCl_3);-2.21, -0.20 (s, 1H+1H, NH), -1.70 , 0.28 (s, 1H+1H, $\text{NH}^{3\text{-CH}_2}$), 1.45 (t , 3H, *J* = 7.5 Hz, 8^2-CH_3), 1.58 (t, 3H, *J* = 7.5 Hz, $8^2\text{-CH}_3{}^{3\text{-CH}_2}$), 1.68 (d, 3H *J* =7.5 Hz, $18\text{-CH}_3{}^{3\text{-CH}_2}$), 1.80 (d, 3H, *J* =7.5 Hz, 18-CH_3), 2.15-2.38, 2.45-2.72 (m, 4H+4H, $17\text{-CH}_2\text{CH}_2$), 2.54 (s, 3H, 7-CH_3), 3.19 (s, 3H, $7\text{-CH}_3{}^{3\text{-CH}_2}$), 3.40 (q, 2H, *J* = 7.5 Hz, $8^1\text{-CH}_2{}^{3\text{-CH}_2}$), 3.50, 3.55 (each s, 3H, $\text{CO}_2\text{CH}_3{}^{3\text{-CH}_2}$, CO_2CH_3), 3.60 (s, 3H, $12\text{-CH}_3{}^{3\text{-CH}_2}$), 3.61 (q, 2H, *J* = 7.5 Hz, $8^1\text{-CH}_2{}^{3\text{-CH}_2}$), 3.62 (s, 3H, 2-CH_3), 3.63 (s, 3H, 12-CH_3), 3.67 (s, 3H, $2\text{-CH}_3{}^{3\text{-CH}_2}$), 4.24 (m, 1H, $17\text{H}^{3\text{-CH}_2}$), 4.29 (m, 1H, 17-H), 4.40 (m, 1H, $18\text{H}^{3\text{-CH}_2}$), 4.50 (m, 1H, 18-H), 5.05, 5.09, 5.20, 5.23 (each d, 1H+1H, *J* = 19.5 Hz, $13^2\text{-H}_2{}^{3\text{-CH}_2}$, 13^2-H_2), 7.02 (q, 2H, *J* = 6.0 Hz, $3\text{-C}\underline{\text{H}}_2\text{CO}_2$), 8.67 (s, 1H, 20-H), 8.70 (s, 1H, $20\text{-H}^{3\text{-CH}_2}$), 9.45 (s, 1H, 10-H), 9.51 (s, 1H, $10\text{-H}^{3\text{-CH}_2}$), 9.79 (s, 1H, $5\text{-H}^{3\text{-CH}_2}$), 10.43 (s, 1H, 5-H). IR(KBr) ν_{max} 1734 (CO_2CH_3), 1693 (C=O) cm^{-1} . MS(FAB): Found: m/z 1101. calcd for $\text{C}_{66}\text{H}_{68}\text{O}_8\text{N}_8$: M^++2, 1101.

Methyl pyropheophorbide-*a* anhydride dimer 6. A mixture of **3** (29 mg 0.05 mmol), CMPI (38 mg, 0.15 mmol) and DMAP (24 mg, 0.2 mmol) in CH_2Cl_2 (10 mL) was refluxed for 2 h under an argon atmosphere. The reaction mixture was poured into H_2O (200 mL) and extracted with CH_2Cl_2. The extract was washed three times with water and dried over anhydrous Na_2SO_4. After removal of the solvent, the residue was separated by a flash silica gel column eluting with a mixture of MeOH and CH_2Cl_2 (0.6:99.4) to give **6** (18 mg, 62%). ^{1}H-NMR(CDCl_3); -1.97, -0.17 (s, 2H+2H, NH), 1.55 (t, 6H, *J* = 8.0 Hz, 8^2-CH_3), 1.88 (d, 3H, *J* = 7.5 Hz, 18-CH_3), 2.30-2.43, 2.57-2.66, 2.71-2.77 (m, 4H+2H+2H, $17\text{-CH}_2\text{CH}_2$), 2.87 (s, 6H, 7-CH_3), 3.53 (q, 4H, *J* = 7.5 Hz, 8-CH_2), 3.64 (s, 6H, 12-CH_3), 3.72 (s, 6H, CO_2CH_3), 3.98 (s, 6H, 2-CH_3), 4.42 (m, 2H, 17-H), 4.62 (m, 2H, 18-H), 5.21, 5.41 (d, 2H+2H, *J* = 20.0 Hz, 13^2-H_2), 8.99 (s, 2H, 20-H), 9.57 (s, 2H, 10-H), 10.73 (s, 2H, 5-H). IR(KBr) ν_{max} 1735 (CO_2CH_3), 1701 (C=O), 1685 (C=O) cm^{-1}. MS(FAB): Found: m/z 1115. calcd for $C_{66}H_{66}N_8O_9$: M^++2, 1115.

1,8-Naphthalene-bridged ester-linked dimer 7. A mixture of **3** (29 mg, 0.05 mmol), CMPI (38 mg, 0.15 mmol), DMAP (12 mg, 0.10 mmol), and 1,8-bis(hydroxymethyl)naphthalene (4.7 mg, 0.025 mmol) in dry CH_2Cl_2 (3 mL) and dry benzene (7 mL) was refluxed for 3.5 h under an argon atmosphere. After the usual workup, the products were separated by a flash silica gel column eluting with a mixture of MeOH and CH_2Cl_2 (0.5:99.5). The first fraction was **8** (23 mg, 62%) and the second fraction was **7** (3 mg, 9%). **7**: ^{1}H-NMR($CDCl_3$); -3.21, -1.10 (s, 2H+2H, NH), 1.49 (t, 6H, *J* = 8.0 Hz, 8^2-CH_3), 1.61 (d, 6H, *J* = 7.5 Hz, 18-CH_3), 1.98-2.03, 2.10-2.15, 2.18-2.22, 2.24-2.28 (m, 2H+2H+2H+2H, 17-CH_2CH_2), 2.43 (s, 6H, 7-CH_3), 3.40 (m, 4H, 8^1-CH_2), 3.45 (s, 6H, 2-CH_3), 3.60 (s, 6H, 12-CH_3), 3.63 (s, 6H, CO_2CH_3), 4.04 (m, 2H, 17-H), 4.09 (m, 2H, 18-H), 4.98, 5.15 (d, 2H+2H, *J* = 19.5 Hz, 13^2-H_2), 6.55, 6.59 (q, 4H, *J* = 6.5 Hz, Ar-$\underline{CH_2}$), 7.77 (t, 2H, *J* = 7.5 Hz, Ar-H), 8.14 (d, 2H, *J* = 7.0 Hz, Ar-H), 8.16 (s, 2H, 20-H), 8.42 (d, 2H, *J* = 8.5 Hz, Ar-H), 9.09 (s, 2H, 10-H), 9.84 (s, 2H, 5-H). IR(KBr) ν_{max} 1736 (CO_2CH_3), 1701 (C=O), 1685 (C=O) cm^{-1}. MS(FAB): Found: m/z 1285. calcd for $C_{78}H_{76}O_{10}N_8$: M^++2, 1285. **8**: H^1-NMR($CDCl_3$); -2.19, -0.21 (s, 1H+1H, NH), 1.58 (t, 3H, *J* = 8.0 Hz, 8^2-CH_3), 1.80 (d, 3H, *J* = 7.5 Hz, 18-CH_3), 2.05 (s, 1H, OH), 2.25-2.35, 2.54-2.58, 2.63-2.68 (m, 2H+1H+1H, 17-CH_2CH_2), 2.60 (s, 3H, 7-CH_3), 3.55 (s, 3H, 2-CH_3), 3.60 (q, 2H, *J* = 7.5 Hz, 8^1-CH_2), 3.64 (each s, 3H, 12-CH_3, CO_2CH_3), 4.30 (m, 1H, 17-H), 4.50 (m, 1H, 18-H), 5.11, 5.19 (d, 1H+1H, *J* = 19.5 Hz, 13^2-H_2), 5.40 (s, 2H, $\underline{CH_2}$OH), 6.53 (s, 2H, 3-$CO_2\underline{CH_2}$), 7.53 (t, 2H, *J* = 7.0 Hz, Ar-H), 7.62 (t, 1H, *J* = 7.0 Hz, Ar-H), 8.01 (d, 1H, *J* = 7.0 Hz, Ar-H), 8.05 (d, 2H, *J* = 7.0 Hz, Ar-H), 8.75 (s, 1H, 20-H), 9.47 (s, 1H, 10-H), 10.17 (s, 1H, 5-H). IR(KBr) ν_{max} 3438 (OH), 1734 (CO_2CH_3), 1695 (C=O) cm^{-1}. MS(FAB): Found: m/z 737. calcd for $C_{45}H_{44}N_4O_6$: M^++1, 737.

Methyl 3-devinyl-3-carbomethoxypyropheophorbide-*a* (9). A mixture of **3** (29 mg, 0.05 mmol), CMPI (38 mg, 0.15 mmol), and DMAP (24 mg, 0.20 mmol) in CH_2Cl_2 (10 mL) and MeOH (1 mL) was refluxed for 1 h under an argon atmosphere. After the usual workup, the products were separated by a flash silica gel column eluting with a mixture of MeOH and CH_2Cl_2 (0.2:99.8) to give **9** (25 mg, 86%). ^{1}H-NMR($CDCl_3$); -2.07, -0.08 (s, 1H+1H, NH), 1.69 (t, 3H, *J* = 8.0 Hz, 8^2-CH_3), 1.81 (d, 3H, *J* = 7.5 Hz, 18-CH_3), 2.25-2.32, 2.54-2.59, 2.68-2.74 (m, 2H+1H+1H, 17-CH_2CH_2), 3.30 (s,3H, 7-CH_3), 3.59 (s, 3H, 2-CH_3), 3.69 (each s, 3H, 2-CH_3, CO_2CH_3), 3.73 (q, 2H, *J* = 7.5 Hz, 8^1-CH_2), 4.34 (m, 1H, 17-H), 4.36 (s, 3H, 3-CO_2CH_3), 4.53 (m, 1H, 18-H), 5.14, 5.33 (d, 1H+1H, *J* = 20.0 Hz, 13^2-H_2), 8.80 (s, 1H, 20-H), 9.59 (s, 1H, 10-H), 10.43 (s, 1H, 5-H). IR(KBr) ν_{max} 1736 (CO_2CH_3), 1701 (C=O), 1685 (C=O) cm^{-1}. MS(FAB): Found: m/z 581. calcd for $C_{34}H_{36}N_4O_5$: M^++1, 581.

Methyl 3-devinyl-3-acetoxymethylpyropheophorbide-*a* (10). A mixture of **4** (18 mg, 0.035 mmol) and dry pyridine (40 mL, 0.49 mmol) in dry CH_2Cl_2 (5 mL) was stirred at room temperature for 5 min under an argon atmosphere. Acetyl chloride (25 mL, 0.35 mmol) was added to the solution and the mixture was stirred at room temperature for 3 h. Then, MeOH (3 mL) was added and the resulting reaction mixture was stirred further for 15 min. After the usual workup, the products were separated by a flash silica gel column eluting with a mixture of MeOH and CH_2Cl_2 (0.5:99.5) to give **10** (11 mg, 53%). ^{1}H-NMR($CDCl_3$); -1.84, 0.24 (s, 1H+1H, NH), 1.70 (t, 6H, *J* = 8.0 Hz, 8^2-CH_3), 1.82 (d, 6H, *J* = 7.5 Hz, 18-CH_3), 2.19 (s, 3H, 3-CO_2CH_3), 2.26-2.33, 2.53-2.59 (m, 2H+2H, 17-CH_2CH_2), 3.25 (s, 3H, 7-CH_3), 3.44 (s, 3H, 2-CH_3), 3.62 (s, 3H, 12-CH_3), 3.65 (s, 3H, CO_2CH_3), 3.69 (q, 2H, *J* = 7.5 Hz, 8^1-CH_2), 4.30 (m, 1H, 17-H), 4.49 (m, 1H, 18-H), 5.10, 5.25 (d, 1H+1H, *J* = 19.5 Hz, 13^2-H_2), 6.35 (s, 2H, 3-CH_2), 8.60 (s, 1H, 20-H), 9.39(s, 1H, 5-H), 9.48(s, 1H, 10-H). IR(KBr) ν_{max} 1780 (CO_2CH_3), 1734 (CO_2CH_3), 1690 (C=O) cm^{-1}. MS(FAB): Found: m/z 595. calcd for $C_{35}H_{38}N_4O_5$: M^++1, 595.

Methyl 3-devinyl-3-(8-acetoxymethyl-naphth-1-yl)methoxycarbonylpyropheophorbide-*a* (11). A mixture of 3 (29 mg 0.05 mmol), CMPI (38 mg, 0.15 mmol), DMAP (24 mg, 0.2 mmol), and 1-acetoxymethyl-8-hydroxymethylnapthalene (15 mg, 0.1 mmol) in CH_2Cl_2 (10 mL) was refluxed for 2 h under an argon atmosphere. After the usual workup, the products were separated by a flash silica gel column eluting with a mixture of MeOH and CH_2Cl_2 (0.2:99.8) to give **11** (8 mg, 21%). ^{1}H-NMR($CDCl_3$); -2.11 (s, 1H, NH), -0.13 (s, 1H, NH), 1.66 (t, 3H, *J* = 8.0 Hz, 8^2-CH_3), 1.83 (d, 3H, *J* = 7.5 Hz, 18-CH_3), 2.10 (s, 3H, $CO\underline{CH_3}$), 2.27-2.35, 2.55-2.63, 2.70-2.77 (m, 2H+1H+1H, 17-CH_2CH_2), 2.60 (s, 3H, 7-CH_3), 3.60 (s, 3H, CO_2CH_3), 3.62 (q, 2H, *J* = 7.5 Hz, 8^1-CH_2), 3.67 (s, 3H, 12-CH_3), 3.71 (s, 3H, 2-CH_3), 4.36 (m, 1H, 17-H), 4.55 (m, 1H, 18-H), 5.15, 5.32 (d, 1H+1H, *J* = 20.0 Hz, 13^2-H_2), 5.91 (s, 2H, $\underline{CH_2}COCH_3$), 6.41 (s, 2H, 3-$\underline{CH_2}CO$), 7.26 (m, 2H, Ar-H), 7.67 (m, 1H, Ar-H), 7.78 (m, 1H, Ar-H), 7.95 (m, 1H, Ar-H), 8.81 (s, 1H, 20-H), 9.58 (s, 1H, 10-H), 10.22 (s, 1H, 5-H). IR(KBr) ν_{max} 1734 (CO_2CH_3), 1695 (C=O) cm^{-1}. MS(FAB): Found: m/z 779. calcd for $C_{47}H_{46}N_4O_7$: M^++1, 779.

7-Deformyl-7-carboxypyropheophorbide-*b* methyl ester (13). ^{1}H-NMR($CDCl_3$); -1.79 (s, 1H, NH), -0.23 (s, 1H, NH), 1.70 (t, 3H, *J* = 8.0 Hz, 8^2-CH_3), 1.85 (d, 3H, *J* = 7.5 Hz, 18-CH_3), 2.25-2.40, 2.54-2.59, 2.61-2.65 (m, 2H+1H+1H, 17-CH_2CH_2), 3.36 (s, 3H, 2-CH_3), 3.53 (s, 3H, 12-CH_3), 3.61 (s, 3H, CO_2CH_3), 3.79 (q, 2H, *J* = 7.5 Hz, 8^1-CH_2), 4.25 (m, 1H, 17-H), 4.47 (dt, 1H, 18-H), 5.03, 5.23 (d, 1H+1H, *J* = 20.0 Hz, 13^2-H_2), 6.18 (dd, 1H, *J* = 1.5, 11.5 Hz, 3-CH=$\underline{CH_2}$), 6.32 (dd, 1H, *J* = 1.5, 18.0 Hz, 3-CH=$\underline{CH_2}$), 7.91 (dd, 1H, *J* = 12.0, 17.5 Hz, 3-$\underline{CH}$=CH_2), 8.80 (s, 1H, 20-H), 9.35 (s, 1H, 10-H), 10.31 (s, 1H, 5-H). IR(KBr) ν_{max} 1738 (C=O), 1732 (C=O), 1693 (C=O) cm^{-1}. MS(FAB): Found: m/z 579. calcd for $C_{34}H_{34}N_4O_5$: M^++1, 579.

Pyropheophorbide-*b* anhydride dimer 14. A mixture of **13** (12 mg 0.02 mmol), CMPI (15 mg, 0.06 mmol), and DMAP (9 mg, 0.08 mmol) in CH_2Cl_2 (10 mL) was refluxed for 2 h under an argon atmosphere. After the usual workup, the separation over a flash silica gel column eluting with a mixture of MeOH and CH_2Cl_2 (0.5:99.5) gave **14** (5.7 mg, 50%). ^{1}H-NMR($CDCl_3$); -1.42, 0.59 (s, 2H+2H, NH), 1.80 (d, 6H, *J* = 7.5 Hz, 18-CH_3), 1.86 (t, 6H, *J* = 8.0 Hz, 8^2-CH_3), 2.25-2.36, 2.54-2.62, 2.69-2.75 (m, 4H+2H+2H, 17-CH_2CH_2), 3.19 (s, 6H, 2-CH_3), 3.62 (s, 6H, CO_2CH_3), 3.70 (s, 6H, 12-CH_3), 4.28 (m, 2H, 17-H), 4.32 (q, 4H, *J* = 7.5 Hz, 8-CH_2), 4.47 (m, 2H, 18-H), 5.08, 5.23 (d, 2H+2H, *J* = 20.0 Hz, 13^2-H_2), 5.36 (dd, 2H, *J* = 1.5, 12.0 Hz, 3-CH=$\underline{CH_2}$), 5.94 (d, 2H, *J* = 1.5, 12.0 Hz, 3-CH=$\underline{CH_2}$), 7.52 (dd, 2H, *J* = 11.5, 17.5 Hz, 3-$\underline{CH}$=CH_2), 8.48 (s, 2H, 20-H), 9.80 (s, 2H, 10-H), 10.66 (s, 2H, 5-H). IR(KBr) ν_{max} 1735 (CO_2CH_3), 1701 (C=O), 1685 (C=O) cm^{-1}. MS(FAB): Found: m/z 1139. calcd for $C_{68}H_{66}N_8O_9$: M^++2, 1139.

7-Deformyl-7-carbomethoxypyropheophorbide-*b* methyl ester (15). ^{1}H-NMR($CDCl_3$); -1.57 (s, 1H, NH), 0.43 (s, 1H, NH), 1.77 (t, 3H, *J* = 8.0 Hz, 8^2-CH_3), 1.79 (d, 3H, *J* = 7.5 Hz, 18-CH_3), 2.25-2.32, 2.50-2.61, 2.65-2.70 (m, 2H+1H+1H, 17-CH_2CH_2), 3.37 (s, 3H, 2-CH_3), 3.60 (s, 3H, 12-CH_3), 3.67 (s, 3H, CO_2CH_3), 4.09 (q, 2H, *J* = 7.5 Hz, 8^1-CH_2), 4.26 (m, 1H, 17-H), 4.28 (s, 3H, 3-CO_2CH_3), 4.46 (m, 1H, 18-H), 4.28 (s, 3H, 3- CO_2CH_3), 5.06, 5.25 (d, 1H+1H, *J* = 20.0 Hz, 13^2-H_2), 6.18 (dd, 1H, *J* = 1.5, 11.5 Hz, 3-CH=$\underline{CH_2}$), 6.34 (dd, 1H, *J* = 1.5, 18.0 Hz, 3-CH=$\underline{CH_2}$), 7.98 (dd, 1H, *J* = 11.0 , 18.0

Hz, 3-<u>CH</u>=CH_2), 8.51 (s, 1H, 20-H), 9.69 (s, 1H, 10-H), 10.52 (s, 1H, 5-H). MS(FAB): Found: m/z 593. calcd for $C_{35}H_{36}N_4O_5$: M^++1, 593.

1,2-Phenylene-bridged amide-linked dimer (16). A solution of **3** (57 mg, 0.10 mmol) in dry pyridine (60 μL, 0.74 mmol) and dry benzene (5 mL) was stirred at room temperature under an argon atmosphere for 5 min. Thionyl chloride (25 μL, 0.34 mmol) was added and the mixture was stirred for 30 min. After solvent was evaporated under reduced pressure, 1,2-phenylenediamine (5.4 mg 0.05 mmol) and dry pyridine (60 μL, 0.74 mmol) in dry benzene (5 mL) were added, and the resulting mixture was stirred at room temperature overnight. After the usual workup, the products were separated over a flash silica gel column eluting with a mixture of MeOH and CH_2Cl_2 (0.5:99.5). The first fraction was **17** (6 mg, 9%) and the second fraction was **16** (27 mg, 45%). **16**: ^{1}H-NMR(acetone-d_6); -2.63, -1.02 (s, 2H+2H, NH), 0.43 (t, 6H, J = 8.0 Hz, 8^2-CH_3, 1.18 (s, 6H, 7-CH_3), 1.33, 1.45 (m, 2H+2H, 8^1-CH_2) 1.88 (d, 6H, J = 7.5 Hz, 18-CH_3), 2.25-2.33, 2.36-2.44, 2.56-2.62 (m, 2H+4H+2H, 17-CH_2CH_2), 3.32 (s, 6H, 2-CH_3), 3.63 (s, 6H, CO_2CH_3), 3.85 (s, 6H, 12-CH_3), 4.53 (m, 2H, 17-H), 4.75 (m, 2H, 18-H), 5.00, 5.21 (d, 2H+2H, J = 19.5 Hz, 13^2-H_2), 7.68 (d, 2H, J = 5.5 Hz, Ar-H), 7.88 (s, 2H, 10-H), 8.40 (m, 2H, Ar-H), 8.88 (s, 2H, 5-H), 9.07 (s, 2H, 20-H), 10.36 (s, 2H, amide-H). IR(KBr) ν_{max} 1734 (CO_2CH_3), 1685 (C=O) cm^{-1}. MS(FAB): Found: m/z 1205. calcd for $C_{72}H_{72}O_8N_{10}$: M^++2, 1205. **17**: ^{1}H-NMR(acetone-d_6); -2.01, 0.05 (s, 1H+1H, NH), 1.67 (t, 3H, J = 8.0 Hz, 8^2-CH_3), 1.85 (d, 3H, J = 7.5 Hz, 18-CH_3), 2.20 (s, 3H, $COCH_3$), 2.28-2.35, 2.41-2.48, 2.62-2.68 (m, 1H+1H+2H, 17-CH_2CH_2), 3.26 (s, 3H, 7-CH_3), 3.53 (s, 3H, CO_2CH_3), 3.69 (s, 3H, 12-CH_3), 3.73 (s, 3H, 2-CH_3), 3.77 (q, 2H, J = 7.5 Hz, 8^1-CH_2), 4.49 (m, 1H, 17-H), 4.73 (m, 1H, 18-H), 5.16, 5.30 (d, 1H+1H, J = 19.5 Hz, 13^2-H_2), 6.87 (t, 1H, J = 7.5 Hz, Ar-H), 7.08 (d, 1H, J = 8.0 Hz, Ar-H), 7.15 (t, 1H, J = 8.5 Hz, Ar-H), 7.72 (d, 1H, J = 7.5 Hz, Ar-H), 9.06 (s, 1H, 20-H), 9.91 (s, 1H, 10-H), 9.94 (s, 1H, 5-H). IR(KBr) ν_{max} 1732 (CO_2CH_3), 1693 (C=O), 1682 (C=O) cm^{-1}. MS(FAB): Found: m/z 657. calcd for $C_{39}H_{40}N_6O_4$: M^++1, 657.

Methyl 3-devinyl-3-(2-aminophenyl)carbamoylpyropheophorbide-*a* (18). A mixture of **3** (29 mg 0.05 mmol), CMPI (38 mg, 0.15 mmol), 2-acetylaminoaniline (15 mg, 0.1 mmol), and DMAP (24 mg, 0.2 mmol) in CH_2Cl_2 (10 mL) was refluxed for 2 h under an argon atmosphere. After the usual workup, the separation over a flash silica gel column gave **18** (26 mg, 74%). ^{1}H-NMR(acetone-d_6); -2.01, 0.05 (s, 1H+1H, NH), 1.69 (t, 3H, J = 8.0 Hz, 8^2-CH_3), 1.86 (d, 3H, J = 7.5 Hz, 18-CH_3), 2.10 (s, 3H, $COCH_3$), 2.28-2.35, 2.41-2.48 (m, 2H+2H, 17-CH_2CH_2), 3.26 (s, 3H, 7-CH_3), 3.53 (s, 3H, CO_2CH_3), 3.69 (s, 3H, 12-CH_3), 3.73 (s, 3H, 2-CH_3), 3.77 (q, 2H, J = 7.5 Hz, 8^1-CH_2), 4.49 (m, 1H, 17-H), 4.73 (m, 1H, 18-H), 5.16, 5.34 (d, 1H+1H, J = 19.5 Hz, 13^2-H_2), 7.34 (m, 1H, Ar-H), 7.47 (t, 1H, Ar-H), 7.55 (d, 1H, J = 7.0 Hz, Ar-H), 8.39 (d, 1H, J = 7.0 Hz, Ar-H), 9.08 (s, 1H, 20-H), 9.50 (s, 1H, amide-H), 9.87 (s, 1H, 10-H), 9.94 (s, 1H, 5-H), 10.18 (s, 1H, amide-H). IR(KBr) ν_{max} 3405 (NH), 1736 (CO_2CH_3), 1699 (C=O), 1685 (C=O) cm^{-1}. MS(FAB): Found: m/z 699. calcd for $C_{41}H_{42}N_6O_5$: M^++1, 699.

1,8-Naphthalene-bridged amide-linked dimer 19. A solution of **3** (57 mg, 0.10 mmol) in dry pyridine (60 μL, 0.74 mmol) and dry benzene (5 mL) was stirred at room temperature under an argon atmosphere for 5 min. Thionyl chloride (25 μL, 0.34 mmol) was added and the mixture was stirred for 30 min. After the solvent was evaporated under reduced pressure, 1,8-diaminonaphthalene (7.9 mg, 0.05 mmol) and dry pyridine (60 μL, 0.74 mmol) in dry benzene (5 mL) were added, and the resulting mixture was stirred at room temperature overnight. After the usual workup, the products were separated over a flash silica gel column eluting with a mixture of MeOH and $CHCl_3$ (0.3:99.7). The first fraction was **20** (29 mg, 41%) and the second fraction was **19** (3 mg, 5%). **19**: H^1-NMR(acetone-d_6): -4.57, -2.67 (s, 2H+2H, NH), 1.20 (t, 6H, J = 8.0 Hz, 8^2-CH_3), 1.42 (d, 6H, J = 7.5 Hz, 18-CH_3), 2.51-2.59, 2.62-2.68, 2.72-2.79 (m, 2H+4H+2H, 17-CH_2CH_2), 2.64 (s, 6H, 7-CH_3), 3.02 (m, 4H, 8^1-CH_2), 3.39 (s, 6H, 2-CH_3), 3.43 (s, 6H, 12-CH_3), 3.71 (s, 6H, CO_2CH_3), 3.78 (m, 2H, 17-H), 3.92 (d, 2H, 18-H), 4.80, 5.03 (d, 2H+2H, J = 19.5 Hz, 13^2-H_2), 7.78 (t, 2H, J = 8.0 Hz, Ar-H), 7.91 (s, 2H, 5-H), 8.12 (d, 2H, J = 8.5 Hz, Ar-H), 8.30 (d, 2H, J = 7.0 Hz, Ar-H), 8.42 (s, 2H, 20-H), 9.02 (s, 2H, 10-H), 10.56 (s, 2H, amide-H). IR(KBr) ν_{max} 1734 (CO_2CH_3), 1685 (C=O) cm^{-1}. MS(FAB): Found: m/z 1255. calcd for $C_{76}H_{74}O_8N_{10}$: M$^+$+2, 1255. **20**: ^{1}H-NMR(acetone-d_6); -2.01, 0.08 (s, 1H+1H, NH), 1.67 (t, 3H, J = 8.0 Hz, 8^2-CH_3), 1.86 (d, 3H, J = 7.5 Hz, 18-CH_3), 2.28-2.36, 2.40-2.48 (m, 2H+2H, 17-CH_2CH_2), 3.23 (s, 3H, 7-CH_3), 3.54 (s, 3H, CO_2CH_3), 3.66 (each s, 3H, 12-CH_3, 2-CH_3), 3.75 (q, 2H, J = 7.5 Hz, 8^1-CH_2), 4.48 (m, 1H, 17-H), 4.71 (m, 1H, 18-H), 5.15, 5.31 (d, 1H+1H, J = 20.0 Hz, 13^2-H), 6.66 (d, 1H, J = 6.5 Hz, Ar-H), 7.04 (d, 1H, J = 7.0 Hz, Ar-H), 7.23 (m, 2H, Ar-H), 7.28 (d, 1H, J = 8.5 Hz, Ar-H), 7.36 (t, 1H, J = 7.5 Hz, Ar-H), 9.05 (s, 1H, 20-H), 9.86 (s, 1H, 10-H), 10.03 (s, 1H, 5-H). IR(KBr) ν_{max} 1736 (CO_2CH_3), 1701 (C=O), 1686 (C=O) cm^{-1}. MS(FAB): Found: m/z 707. calcd for $C_{43}H_{42}N_6O_4$: M$^+$+1, 691, 707.

Methyl 3-devinyl-3-(naphth-1-yl)carbamoylpyropheophorbide-*a* (21). A mixture of **3** (29 mg, 0.05 mmol), CMPI (38 mg, 0.15 mmol), 1-aminonaphthalene (14 mg, 0.10 mmol), DMAP (24 mg, 0.20 mmol) in CH_2Cl_2 (3 mL) and benzene (7 mL) was refluxed for 2 h under an argon atmosphere. After the usual workup, the separation over a flash silica gel column eluting with a mixture of MeOH and CH_2Cl_2 (0.5:99.5) gave **21** (13 mg, 36%). ^{1}H-NMR(acetone-d_6); -2.00, 0.04 (s, 1H+1H, NH), 1.69 (t, 3H, J = 8.0 Hz, 8^2-CH_3), 1.86 (d, 3H, J = 7.5 Hz, 18-CH_3), 2.28-2.36, 2.40-2.48 (m, 2H+2H, 17-CH_2CH_2), 3.23 (s, 3H, 7-CH_3), 3.54 (s, 3H, CO_2CH_3), 3.66 (s, 3H, 12-CH_3), 3.67 (s, 3H, 2-CH_3), 3.77 (m, 2H, J = 7.5 Hz, 8^1-CH_2), 4.48 (m, 1H, 17-H), 4.71 (m, 1H, 18-H), 5.15, 5.32 (d, 1H+1H, J = 20.0 Hz, 13^2-H), 7.65 (m, 2H, Ar-H) , 7.76 (m, 1H, Ar-H), 7.97 (m, 1H, Ar-H), 8.08 (m, 1H, Ar-H), 8.46 (m, 1H, Ar-H), 8.59 (m, 1H, Ar-H), 9.08 (s, 1H, 20-H), 9.85 (s, 1H, 10-H), 9.92 (s, 1H, 5-H), 10.22 (s, 1H, amide-H). IR(KBr) ν_{max} 1736 (CO_2CH_3), 1699 (C=O), 1685 (C=O) cm^{-1} .MS(FAB): Found: m/z 691. calcd for $C_{43}H_{40}N_5O_4$: M$^+$+1, 691.

Acknowledgment: This work was partly supported by Grant-in-Aids from the Ministry of Education, Science, Sports, and Culture of Japan (No. 07228232 (Priority-Area-Research on "Photoreaction Dynamics" and No. 07454249 to A.O.) and by Izumi Science Foundation. The authors thank Dr. M. Mimuro of National Institute for Basic Biology and Prof. H. Nozawa of Tohoku University for the measurement of CD spectra.

REFERENCES AND NOTES

1. Wasielewski, M. R. *Chem. Rev.* **1992**, *92*, 435-461.
2. Gust, D.; Moore T. A.; Moore, A. L. *Acc. Chem. Res.* **1993**, *26*, 198-205.
3. Maruyama, K.; Osuka, A.; Mataga, N. *Pure Appl. Chem.* **1994**, *66.*, 867-872.
4. Sakata, Y. *J. Synth. Org. Chem. Jpn.* **1981**, 39, 909-917. Boxer, S. G. *Biochim. Biophys. Acta* **1983**, *726*, 265-292. Wasielewski, M. R. in *Chlorophylls*, Scheer, H. Ed.; CRC press: New York, 1991; pp. 269-286.

5. Boxer, S. G.; Closs, G. L. *J. Am. Chem. Soc.* **1976**, *98*, 5406-5408. Boxer, S. G.; Bucks, R. R. *J. Am. Chem. Soc.* **1982**, *101*, 1883-1885. Bucks, R. R.; Boxer, S. G. *J. Am. Chem. Soc.* **1982**,*104*, 340-343. Bucks, R. R.; Netzel, T. L.; Fujita, I.; Boxer, S. G. *J. Phys. Chem.* **1982**, *86*, 1947-1955.
6. Wasielewski, M. R.; Studier, M. H.; Katz, J. J. *Proc. Natl. Acad. USA* **1976**, 73, 4282-4286. Yuen, M. J.; Closs, G. L.; Katz, J. J.; Roper, J. A.; Wasielewski, M. R.; Hindman, J. C. *Proc. Natl. Acad. USA* **1980**, *77*, 5598-5601. Wasielewski, M. R.; Svec, W. A. *J. Org. Chem.* **1980**, *45*, 1969-1974. Wasielewski, M. R.; Johnson, D. G.; Svec, W. A. in *Supramolecular Chemistry*, NATO ASI Series C214, Balzani, V. Ed.; Reidel Publishing Company: Dordrecht, 1987; pp. 256-266.
7. Wasielewski, M. R.; Smith, U. H.; Cope, B. T.; Katz, J. J. *J. Am. Chem. Soc.* **1977**, *99*, 4172-4173. Wasielewski, M. R.; Svec, W. A.; Cope, B. T. *J. Am. Chem. Soc.* **1978**, *100*, 1962-1974.
8. Similar strategy was used in pyropheophorbide-quinone models. Liddell, P.A.; Bareett, D.; Makings, L. R.; Pessiki, P. J.; Gust, D.; Moore, T. A. *J. Am. Chem. Soc.* **1986**, *108*, 535-5352.
9. Smith, K. M.; Goff, D. A.; Simpson, D. J. *J. Am. Chem. Soc.* **1985**, *107*, 4946-4954.
10. Gust, D.; Moore, T. A.; Moore, A. L., Liddell, P. A. *Methods in Enzymology* **1992**, *213*, 87-100.
11. Johnson, D. G.; Svec, W. A.; Wasielewski, M. R. *Israel J. Chem.* **1988**, *28*, 193-203.
12. Osuka, A.; Shinoda, S.; Marumo, S.; Yamada, H.; Katoh, T.; Yamazaki, I.; Nishimura, Y.; Tanaka, Y.; Taniguchi, S.; Okada, T.; Nozaki, K.; Ohno, T. *Bull. Chem. Soc. Jpn.* **1995**, *68*, 3255-3268.
13. Shinoda, S.; Osuka, A.; Nishimura, Y.; Yamazaki, I. *Chem. Lett.* **1995**, 1139-1140.
14. Mukaiyama, T.; Usui ; Saigo, K. *Chem. Lett.* **1975**, 1163-1166.
15. These phenomena are interesting in view of supramolecular structure of the bacteriochlorophylls-*c* found in chlorosomes and the details will be reported elsewhere.
16. Hunter, C. A.; Sanders, J. K. M. *J. Am. Chem. Soc.* **1990**, *112*, 5525-5534.
17. Osuka, A.; Marumo, S.; Wada, Y.; Yamazaki, I.; Yamazaki, T.; Shirakawa, Y.; Nishimura, Y. *Bull. Chem. Soc. Jpn.* **1995**, *68*, 2909-2915.
18. Hoff, A. J.; Amesz, J. P. in *Chlorophylls*, Scheer, H. Ed.; CRC press: New York, 1991; pp. 723-738.
19. Kasha, M. *Radiat. Res.* **1963**, *20*, 55-71. Fulton, R. L.; Gouterman, M. *J. Chem. Phys.* **1961**, *35*, 1059-1071.
20. Osuka, A.; Maruyama, K. *J. Am. Chem. Soc.* **1988**, *110*, 3354-3356.

(*Received in Japan* 21 *December* 1995; *accepted* 24 *January* 1996)