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SYNTHESIS OF A PHOTOSYNTHETIC MODEL COMPOUND WITH A LONG ALKYL CHAIN AND ITS INCORPORATION INTO BOVINE SERUM ALBUMIN

Yoshiteru Sakata,* Yasuhiro Hirano, Hitoshi Tatemitsu, Soichi Misumi, Hideo Ochiai,+ and Hitoshi Shibata+

The Institute of Scientific and Industrial Research, Osaka University, Mihoga-oka, Ibaraki, Osaka 567

+Laboratory of Biochemistry, College of Agriculture, Shimane University Nishikawazu, Matsue 690

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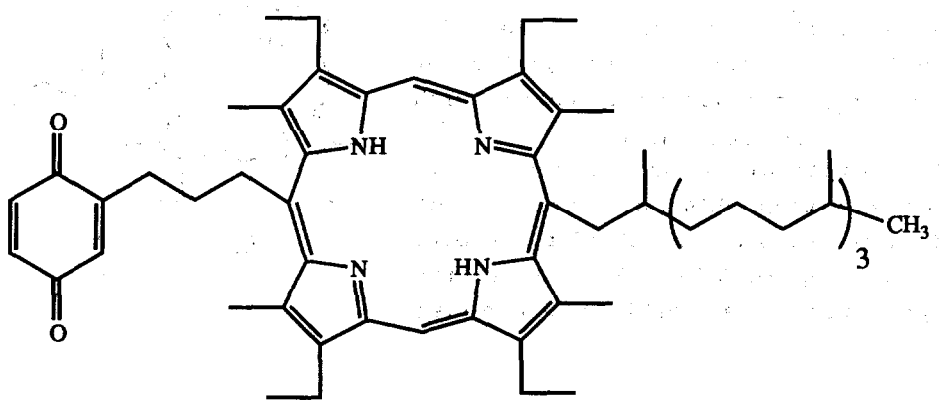
Quinone-linked porphyrin **1** having a long alkyl chain was synthesized and fixed it into bovine serum albumin (BSA) for getting the information about the effect of protein upon photosynthetic electron transfer. The complex of the reference compound **19** lacking quinone with BSA showed fluorescence, while BSA-**1** did not fluoresce at all.

In order to understand the structural factors (distance, orientation, arrangement, etc) of chromophores responsible for the photoinduced electron transfer in photosynthesis, a number of quinone-linked porphyrins have been so far prepared[1] and their photophysical properties have been investigated mainly



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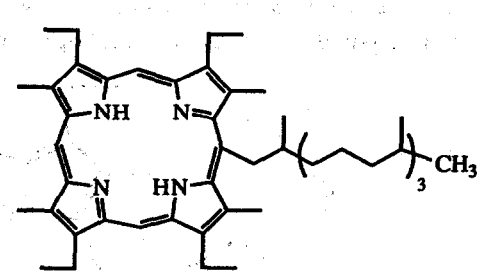
in organic solvents and in some cases in other media.[2,3] The natural pigments are, however, embedded in membrane proteins and some participation of protein upon the electron transfer is pointed out.[4] Electron transfers have been studied in protein, where the distances and orientations between redox centers are predetermined.[5-7] Reconstitution technique has also been applied to the investigation of electron transfers in protein.[8] In spite of such extensive studies, there is no direct comparison of electron transfers between in organic solvents and in protein. To understand the role of protein, electron transfers of particular donor-acceptor-linked compounds are required to be investigated in the two different media. Recently, Shibata et al[9] succeeded to prepare water soluble complexes of chlorophyll a or b with bovine serum albumin (BSA) and concluded that the porphyrin ring of chlorophyll is buried in BSA and that a long alkyl chain like phytyl group is needed for the complexation. Therefore, we designed the synthesis of quinone-linked porphyrin 1 with a long alkyl chain in the hope that the BSA complex of 1 would be prepared and hence, electron transfer rates of 1 might be measured both in organic solvents and in the protein of BSA.

Synthesis

Synthetic route of 1 is outlined in Scheme 1. Acetal 2 was prepared from acrolein via two steps in 43% yield. The Wittig reaction of phosphonium salt 3 and 2,5-dimethoxybenzaldehyde gave 4 in 88% yield. Hydrogenation and deprotection of 4 yielded 6 in 68% yield. Aldehyde 6 and pyrrole 7 were condensed in the presence of TsOH to give dipyrromethane 8 in 78% yield. In the condensation reaction a solution of 6 in benzene was added slowly into a solution of 7 in a minimum amount of benzene. Otherwise, intramolecular cyclization reaction took place to give 12 as a major product (Scheme 2). Hydrogenation of 8, followed by decarboxylation and by the Vilsmeier reaction gave 10 in a yield of 58%. The other building block of dipyrromethane 18 was prepared by hydrogenation of phytol, followed by oxidation with pyridinium chlorochromate, condensation with pyrrole 16 and by hydrolysis. The coupling reaction of the two dipyrromethanes 10 and 18 was carried out by the usual method[10] to give 19 in 24% yield. Demethylation of 19 with BBr_3, followed by oxidation with PbO_2 gave the desired compound 1.



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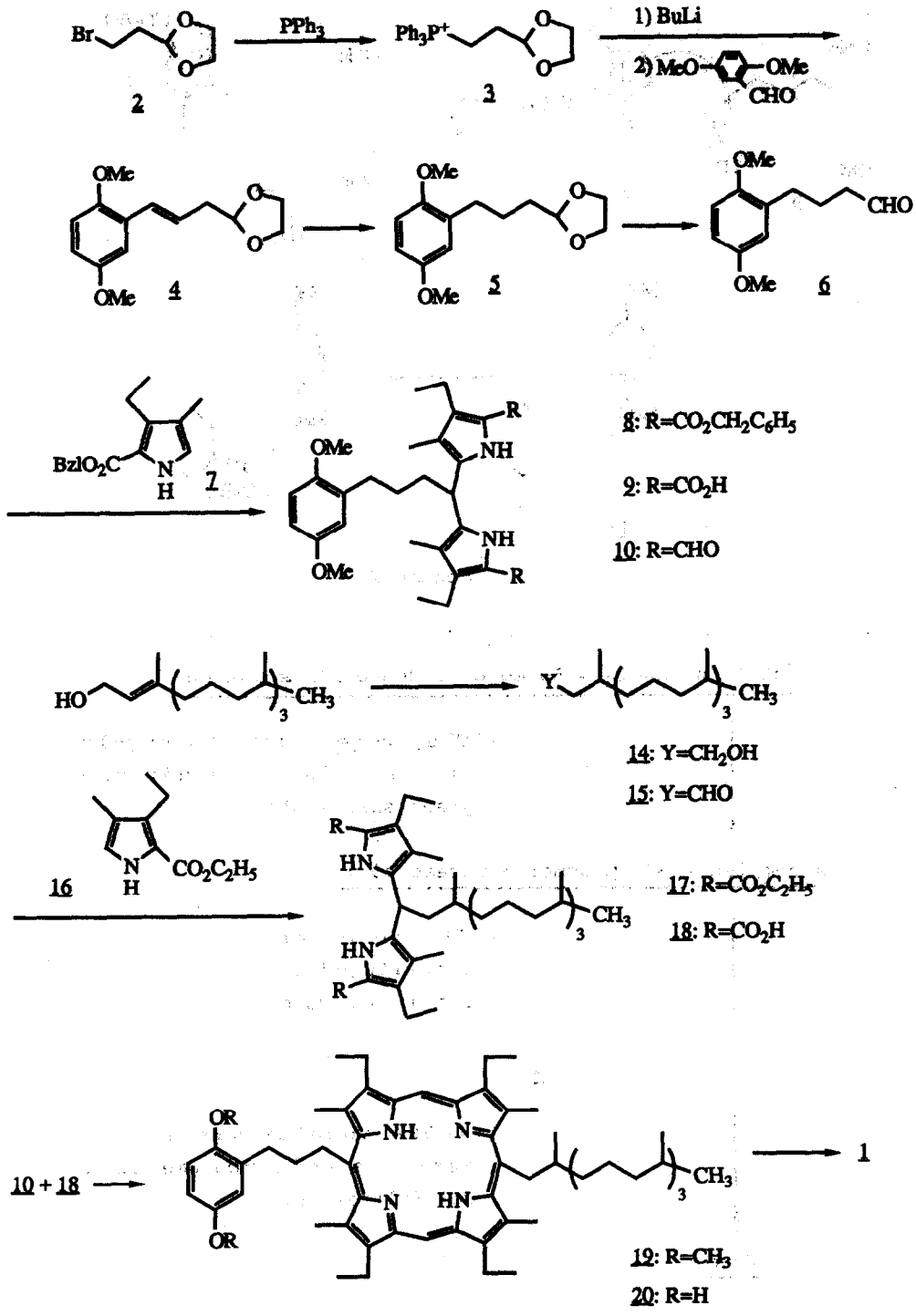
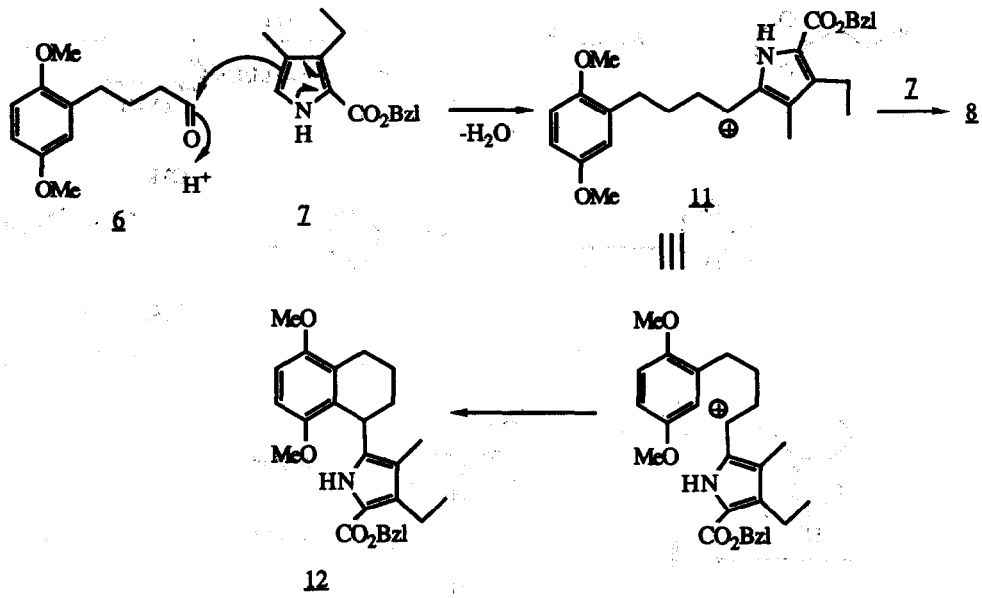
The complexation of porphyrins (1, 19, and 21) with BSA was carried out according to the similar method by Shibata et al[9] as shown in Scheme 3. Thus, the porphyrin was mixed well with a dense


Br
PPh3
Ph3P+
1) BuLi
2) MeO
OMe
CHO
2
3
OMe
4
5
6
CHO
BzlO2C
N
H
7
R
NH
8: R=CO2CH2C6H5
9: R=CO2H
10: R=CHO
HO
CH3
Y
14: Y=CH2OH
15: Y=CHO
16
CO2C2H5
17: R=CO2C2H5
18: R=CO2H
10 + 18
OR
NH
N
HN
1
19: R=CH3
20: R=H

Scheme 1



Scheme 2

1-5 mg of 1 in CH_2Cl_2 + 50 mg of a dense BSA solution

1) They were mixed thoroughly at least 20 min under dim green safe light.

1-BSA complex + BSA monomer + unreacted 1

2) The reaction mixture was centrifuged at 12,000 G for 3 min to remove unreacted 1.

1-BSA complex + BSA monomer

3) 1-BSA complex was eluted near the void volume on a gel filtration.

1-BSA complex

Scheme 3. Preparation of 1-BSA Complex

solution of BSA. After mixing, uncomplexed porphyrins were removed from the solution as precipitates by centrifugation and then, the water soluble porphyrin-BSA complexes were separated from monomeric BSA by gel filtration chromatography by using Toyopearl HW 60 which excludes proteins having molecular weight larger than $1x10^6$. The typical example of the chromatogram was shown for 21 in Fig. 1. As seen from the figure, the complex of the

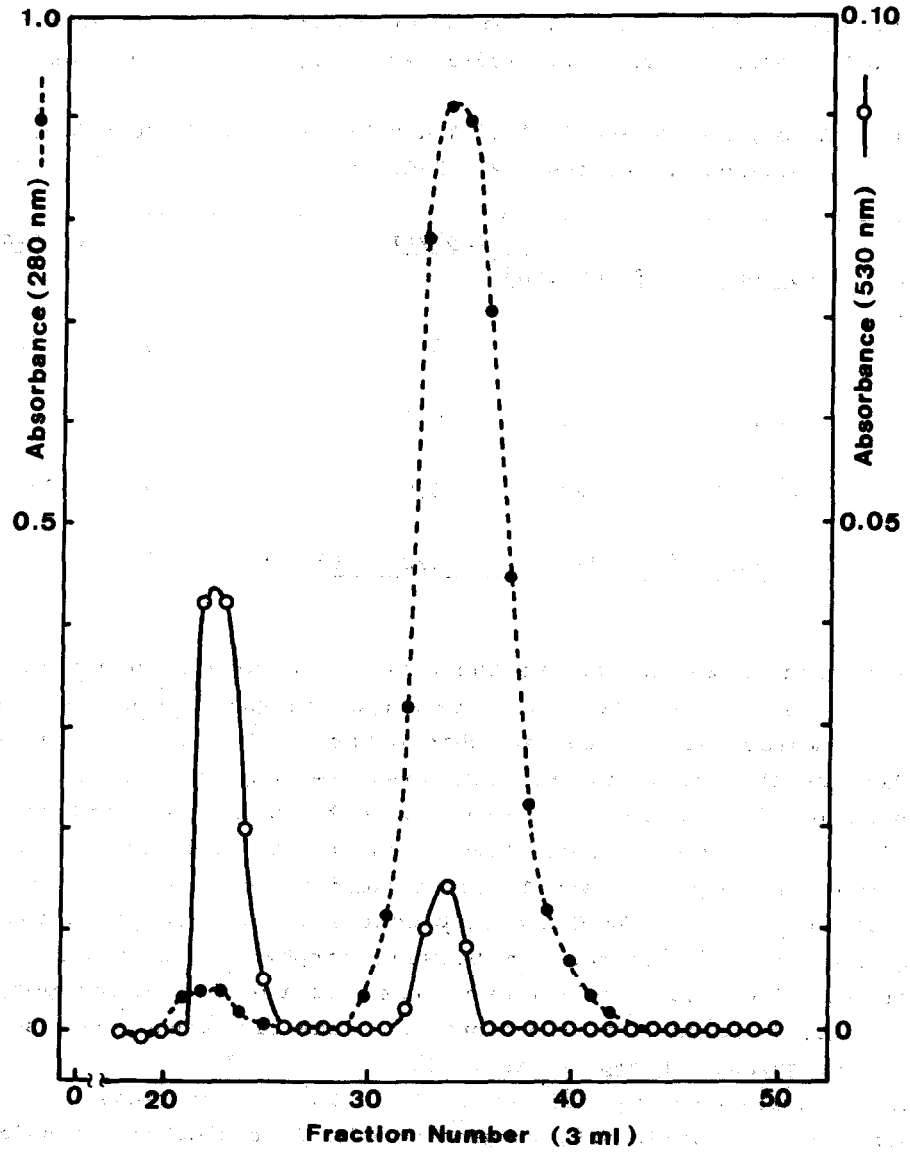


Fig. 1. Gel filtration of 21-BSA complex and BSA, monitored by 280 and 530 nm light.

porphyrin with BSA was eluted near the void volume, suggesting that the molecular weight of the complex is larger than 1×10^6 and that the long alkyl chain in **1**, **19**, and **21** plays and important role for the aggregatin of BSA as reported for Chl *a*- or Chl *b*- BSA complex.[9]

Photophysical Properties

Electronic spectra were measured for **1** and **19** in THF and for their BSA complexes in aqueous NaCl solution. Their absorption maxima are summarized in Table 1. Both spectra in the same medium are very similar with each other,

Table 1. Absorption Maxima (nm) of **1** and **19** in THF and Their BSA Complexes in Aqueous 0.2 N NaCl Solution

		Porphyrin					Quinone
Compound	Solvent	Soret band	Q Band				
1	THF	411	513	548	587	640	246
19	THF	413	513	547	585	636	
1-BSA	0.2N NaCl	420	519	555	589	642	249
19-BSA	0.2N NaCl	423	522	553	590	641	

except the region of 240 nm due to the band of quinone chromophore. This indicates that there is no plausible interaction in the ground state between the two, intramolecularly situated chromophores of **1** in the two media. However, when the spectra of the BSA complexes are compared with those of the corresponding porphyrins in THF, Soret and Q bands are shifted to longer wavelength by 9-10 and 2-9 nm, respectively and all the bands are much broader. Since the porphyrin rings of **1** and **19** are assumed to be located inside in the protein as in the case of BSA-Chl *a* or *b* complex, the spectral changes are presumably due to some interaction between porphyrin rings and residual chromophores of BSA and partly due to the interaction among porphyrin chromophores embedded closely in the protein. A similar bathochromic shift was observed for the quinone chromphore in **1**-BSA.

Relative fluorescence intensities of **1** in THF are decreased by 1/30 as compared with those of **19** in THF, suggesting efficient electron transfer from the porphyrin to the quinone ring of **1** in the solvent. On the other hand, fluorescence of BSA-**1** in aqueous 0.2N NaCl solution is completely quenched in contrast to the observable emission of BSA-**19** in the same medium. Non-

flourescent nature of BSA-1 is assumed to be due to more efficient electron transfer between the redox pair in the protein than in the organic solvent and/or to the interaction of the two chromophores of 1 with the protein in the ground state. Owing to the difficulties of the measurements of flourescence lifetime and the lifetime of the charge separated state (P^+) for BSA-1, we could not determine the real reason for the quenching.

We are now searching more adequate protein for fixing P-Q compounds.

Experimental

All melting points are uncorrected. NMR spectra were measured by JEOL PMX-60 si (60 MHz) or Brucker-WM 360 (360 MHz). IR, electronic, and fluorescence spectra were observed by Hitachi 270-30, Hitachi 330 and Hitachi MPF-24, respectively.

4-(2,5-Dimethyoxyphenyl)-3-butenal ethylene acetal (4). A solution of 2[11] (13.1 g, 71.5 mmol) and triphenyl phosphine (22.4 g, 85.2 mmol) in acetonitrile (20 ml) was refluxed for 2.5 days. After reaction was over, dry ether was added to the reaction mixture and the starting material in the ethereal solution was removed by decantation. This procedure was repeated for three times and then, yielded phosphonium salt was dried under reduced pressure to give 3 in a quantitative yield. Without further purification 3 was used for the following reaction. To a stirred suspension of 3 in dry tetrahydrofuran (600 ml) was added dropwisely BuLi (44.7 ml of 1.6 M hexane solution, 71.5 mmol) at room temperature under N_2. After additional stirring for 1.5 h, a solution of 2.5-dimethoxybenzaldehyde (10.8 g, 65 mmol) in dry tetrahydrofuran was added to the mixture. Stirring was continued for 8 h. An aqueous solution saturated with NaCl was added to the mixture and yielded triphenyl phosphine oxide was filtered off. Water phase was extracted with ether and then, organic phase was washed twice with saturated aqueous NaCl and dried ($MgSO_4$). After removal of the solvent, the crude product was purified by column chromatography on silica gel with hexane-ethyl acetate (7:3) to give 14.3 g (88% yield) of 4 as yellow oil. ^1H NMR ($CDCl_3$, 60 MHz) δ 2.4-2.7(m,2,CH_2), 3.7(s,6,OCH_3), 3.8(m,4,OCH_2CH_2O), 4.9(q,J=5 Hz,1,CH), 5.5-6.4(m,2,CH=CH), 6.6-6.9 ppm(m,3,ArH).

4-(2,5-Dimethoxyphenyl)butanal ethylene acetal (5). A mixture of 4 (2.91 g, 11.6 mmol) and 5% Pd/C (0.3 g) in tetrahydrofuran (150 ml) was stirred under hydrogen atmosphere for 12 h. The catalyst was filtered off and the solvent was removed to give 2.76 g (95% yield) of 5 as colorless oil. ^1H NMR ($CDCl_3$, 60 MHz) δ 1.5-1.8(m,4,CH_2), 2.4-2.7(m,2,$ArCH_2$), 3.6(s,6,OCH_3), 3.8(m,4,OCH_2CH_2O), 4.8(q,J=5 Hz,1,CH), 6.6(br.s,3,ArH).

4-(2,5-Dimethoxyphenyl)butanal (6). A solution of 5 (3.0 g, 11.9 mmol) and 2N HCl (18 ml) in tetrahydrofuran (35 ml) was stirred at room temperature for 3 days under N_2. After reaction was over, the reaction mixture was powered onto

water and it was extracted with ether. Combined organic phase was washed with saturated aqueous solutions of $NaHCO_3$, followed with that of NaCl, and dried ($MgSO_4$). The product was a mixture of **5** and **6**, whose ratio was determined by gpc and crude **6** was used for the following reaction without further purification. **6**: 72% yield, pale yellow oil. ^{1}H NMR ($CDCl_3$, 60 MHz) δ 1.6-2.1(m,2,CH_2), 2.2-2.8(m,4,$ArCH_2$ and CH_2CHO), 3.7(s,6,OCH_3), 6.7(s,3,ArH), 9.7 ppm(s,1,CHO); IR (neat) 1722 cm^{-1}.

1,1-Bis(5-benzyloxycarbonyl-4-ethyl-3-methylpyrrol-2-yl)-4-(2,5-dimethoxyphenyl)-butane (8). To a refluxed solution of **7**[10] (5.80 g, 23.9 mmol) and p-toluenesulfonic acid (600 mg) in dry benzene (3 ml) was dropwisely added under N_2 a solution of **6** (1.74 g, 8.37 mmol) in dry benzene (8 ml) in a period of 2.5 h. After additional heating with reflux for 2 h, the organic phase was washed successively with saturated aqueous solution of $NaHCO_3$ and that of NaCl, and dried ($MgSO_4$). The solvent was removed and the crude product was purified by column chromatography on silica gel with hexane-ethyl acetate (95:5), followed by recrystallization from ethanol to give **8** in 78% yield. **8**: colorless microcrystals, mp 118-119 °C. ^{1}H NMR ($CDCl_3$, 360 MHz) δ 1.05(t,J=7.53 Hz,6,$CH_2\underline{CH_3}$), 1.49-1.60(m,2,$ArCH_2\underline{CH_2}$), 1.90(s,6,CH_3), 1.94-2.02(m,2,$ArCH_2CH_2\underline{CH_2}$), 2.57(t,J=7.53 Hz,2,$ArCH_2$), 2.69(q,J=7.53 Hz,4,$\underline{CH_2}CH_3$), 3.66(s,3,$OCH_3$), 3.69(s,3,$OCH_3$), 4.13(t,J=7.93 Hz,1,CH), 6.61-6.73(m,3,ArH), 7.23-7.36(m,10,Ph-H), 9.00 ppm(br.s,2,NH); IR (nujol mull) 3372, 1704, 1680, 1640 cm^{-1}; Mass m/e 677(M^+). Anal. Calcd for $C_{42}H_{48}N_2O_6$: C, 74.53; H, 7.15; N, 4.14%. Found: C, 74.65; H, 7.21; N, 4.21%.

1,1-Bis(5-carboxy-4-ethyl-3-methylpyrrol-2-yl)-4-(2,5-dimethoxyphenyl)butane (9). To a solution of **8** (2.5 g, 3.7 mmol) in tetrahydrofuran (200 ml) was added three drops of triethylamine and 0.3 g of 5% Pd/C and the mixture was stirred for 12 h under hydrogen atmosphere. The catalyst was filtered off and the solution was concentrated to dryness. Crude **9** was recrystallized from chloroform-hexane to give 1.75 g (95% yield) of **9**. **9**: colorless microcrystals, mp 163-164 °C with decomp. ^{1}H NMR ($CDCl_3$, 360 MHz) δ 1.09(t,J=7.53 Hz,6,$CH_2\underline{CH_3}$), 1.48-1.52(m,2,$ArCH_2\underline{CH_2}$), 2.05(s,6,CH_3), 2.09-2.13(m,2,$ArCH_2CH_2\underline{CH_2}$), 2.53-2.57(m,2,$ArCH_2$), 2.70-2.73(m,4,$\underline{CH_2}CH_3$), 3.65(s,3,$OCH_3$), 3.67(s,3,$OCH_3$), 4,22(t,J=7.93 Hz,1,CH), 6.59-6.68(m,3,ArH), 11.00 ppm(br.S,4,NH and COOH); IR (nujol mull) 3308, 1660 cm^{-1}. Anal. Calcd for $C_{28}H_{36}N_2O_6$: C, 67.72; H, 7.31; N, 5.64%. Found: C, 67.57; H, 7.06; N, 5.68%.

1,1-Bis(5-formyl-4-ethyl-3-methylpyrrol-2-yl)-4-(2,5-dimethoxyphenyl)butane (10). Compound **9** (0.75 g, 1.51 mmol) was dissolved in freshly distilled N,N-dimethylformamide (5 ml) and it was heated with reflux at a bath-temperature of 160 °C under N_2. After reaction was over, the reaction mixture was cooled with ice-salt bath. To the stirred mixture 0.72 ml (6.16 mmol) of benzoyl chloride was added slowly with a syringe. After stirring for 15 min, a solution of

Na_2CO_3 (0.64 g) in water-ethanol (24 ml, 1:1) was added to the mixture and it was heated at 80-90 °C for 15 min. The reaction mixture was extracted with chloroform. The extract was washed with aqueous NaCl and dried ($MgSO_4$). The solvent was removed and the residue was recrystallized from ethanol to give 430 mg (61% yield) of **10**. **10**: colorless fine needles, mp 167-168 °C. ^{1}H NMR ($CDCl_3$, 360 MHz) δ 1,20(t,J=7.53 Hz,6,$CH_2\underline{CH_3}$), 1.50-1.57(m,2,$ArCH_2\underline{CH_2}$), 2.05(s,6,CH_3), 2.15-2.21(m,2,$ArCH_2CH_2\underline{CH_2}$), 2.56-2.61(m,2,$ArCH_2$), 2.71(q,J=7.53 Hz,4,$\underline{CH_2}CH_3$), 3.69(s,6,$OCH_3$), 4.24(t,J=7.93 Hz,1,CH), 6.60-6.71(m,3,ArH), 9.56(s,2,CHO), 11.25 ppm(br.s,2,NH); IR (nujol mull) 3272, 1644, 1612 cm^{-1}. Anal. Calcd for $C_{28}H_{30}N_2O_4$: C, 72.39; H, 7.81; N, 6.03%. Found: C, 72.28; H, 7.92; N, 6.26%.

3,7,11,15-Tetramethylhexadecanol (14). A suspension of phythol (10.0 g, 33.7 mmol) and 5% Pd/C (1.0 g) in tetrahydrofuran (200 ml) was stirred at room temperature for 12 h under H_2. The catalyst was filtered off and the solvent was evaporated to give 9.1 g (91% yield) of **14** as pale yellow oil. ^{1}H NMR ($CDCl_3$, 60 MHz) δ 0.85(d,15,CH_3), 1.0-1.7(m,20,CH_2), 2.0-2.5(m,4,CH), 3.6(t,J=7 Hz,2,CH_2OH), 5.2 ppm(br.s,1,OH). Anal. Calcd for $C_{20}H_{42}O$: C,80.46; H,14.18%. Found: C,80.65; H,14.33%.

3,7,11,15-Tetramethylhexadecanal (15). To a stirred suspension of pyridinium chlorochromate (11.0 g, 51.0 mmol) in dry CH_2Cl_2 (4 ml) and the stirring was continued for 1.5 h. The reaction mixture was triturated well with hexane and the organic phase was separated by decantation. The procedure was repeated for three times. Combined organic layer was filtered over Celite and the solvent was evaporated. The residue was passed through a short column of Florisil with hexane-ethyl acetate (4:1) to give 9.4 g(95% yield) of **15** as colorless oil. ^{1}H NMR ($CDCl_3$, 60 MHz) δ 0.85(d,15,CH_3), 1.0-1.7(m,20,CH_2), 2.0-2.5(m,4,CH), 2.2(m,2,CH_2CHO), 9.7 ppm(br.s,1,CHO); IR (neat) 1730 cm^{-1}.

1,1-Bis(5-ethoxycarbonyl-4-ethyl-3-methylpyrrol-2-yl)-3,7,11,15-tetramethylhexadecane (17). A solution of **15** (4.7 g, 15.9 mmol), **16** (5.2 g, 28.7 mmol), and p-toluenesulfonic acid (0.5 g) in dry benzene (80 ml) was refluxed for 3 h under N_2 in a flask fitted with a Dean-Stark apparatus. Organic phase was washed successively with saturated aqueous solution of $NaHCO_3$ and with that of NaCl and dried ($MgSO_4$). The solvent was evaporated and the residue was chromatographed on silica gel with hexane-ethyl acetate (95:5) to give 7.5 g (81% yield) of **17** as pale yellow viscous oil. ^{1}H NMR ($CDCl_3$, 360 MHz) δ 0.80-0.90(m,15,CH_3), 1.04-1.48(m,20,CH_2), 1.09(t,J=7.53 Hz,6,$ArCH_2\underline{CH_3}$), 1.32(t,J=7.13 Hz,6,$OCH_2\underline{CH_3}$), 1.76-2.22(m,4,CH), 1.93(s,6,$ArCH_3$), 2.71(q,J=7.53 Hz,4,$Ar\underline{CH_2}CH_3$), 4.22(t,J=7.53 Hz,1,CH), 4.27(q,J=7.13 Hz,4,OCH_2), 8.72-8.75 ppm(br.s,2,NH); IR (nujol mull) 3364, 1692, 1348 cm^{-1}. Anal. Calcd for $C_{48}H_{68}N_2O_4$: C,74.95; H,10.69; N,4.37%. Found: C,74.84; H,10.09; N,4.18%.

1,1-Bis(5-carboxy-4-ethyl-3-methylpyrrol-2-yl)-3,7,11,15-tetramethylhexadecane (18). To a solution of **17** (1.28 g, 1.95 mmol) in ethanol (28 ml) was added

aqueous solution (2 ml) of sodium hydroxide(0.73 g, 18.3 mmol). The mixture was refluxed for 12 h under N_2 and then, the solvent was removed under reduced pressure. To the residue was added 30 ml of water and then, 1.2 g (2.0 mmol) of acetic acid was added. The mixture was extracted with ether. The extract was washed with saturated aqueous NaCl and dried ($MgSO_4$). Evaporation of the solvent gave 1.1 g (94% yield) of **18**, which was used for the following reaction without further purification. ^{1}H NMR ($CDCl_3$,360 MHz) δ 0.71-0.87(m,15,CH_3), 1.00-1.43(m,26,CH_2+Ar$CH_2\underline{CH}_3$), 1.76-2.22(m,4,CH), 2.06(s,6,ArCH_3), 2.71(br.s,4,Ar$\underline{CH}_2CH_3$), 4.30(t,1,CH), 10.9(br.s,2,COOH or NH), 11.0 ppm(br.s,2,COOH or NH). IR (nujol mull) 3320, 1650 cm^{-1}.

2,8,12,18-Tetraethyl-3,7,13,17-tetramethyl-5-(2,6,10,14-tetramethylpentadecyl)-15-(3-(2,5-dimethoxyphenyl)propyl)porphyrin (19). To a solution of **18** (170 mg, 0.291 mmol) in dry CH_2Cl_2 (300 ml) was added a solution of trichloroacetic acid (3.4 M) in dry CH_2Cl_2 (2 ml) with a syringe under N_2. To the stirred mixture was added at once **10** (131 mg, 0.282 mmol) and the mixture was refluxed for 24 h. After addition of p-benzoquinone (200 mg), the mixture was continued heating for 2 h. The organic phase was washed successively with saturated aqueous solutions of $NaHCO_3$ and of NaCl and dried (K_2CO_3). The solvent was evaporated and the crude product was purified by preparative TLC of silica gel with benzene-ethyl acetate (96:4) to give 62.7 mg (24.1% yield) of reddish purple solid. ^{1}H NMR ($CDCl_3$, 360 MHz) δ -1.59(br.s,2,NH), 0.21-0.58(m,3,CH_3), 0.59-0.93(m,12,CH_3), 0.93-1.71(m,18,CH_2), 1.79-2.09(m,3,CH), 1.73-1.82(m,12,Ar$CH_2\underline{CH}_3$), 2.09-2.87(m,2,Ar$CH_2\underline{CH}_2$), 2.91-3.28(m,2,ArCH_2), 3.49(s,3,ArCH_3), 3.54(s,3,ArCH_3), 3.55(s,3,ArCH_3), 3.57(s,3,ArCH_3), 3.72(s,3,OCH_3), 3.81(br.s,3,OCH_3), 3.91-4.17(m,8,Ar$\underline{CH}_2CH_3$), 4.63-4.99(m,2,CH), 4.99-5.19(m,2,Ar$CH_2CH_2\underline{CH}_2$), 6.68-6.98(m,3,ArH), 9.98 ppm(br.s,2,meso-H); Mass m/e 923 (M^+).

Synthesis of 1. A solution of **19** (98.3 mg, 0.106 mmol) in dry CH_2Cl_2 (30 ml) was cooled with ice-salt bath. To the stirred solution was added a solution of boron tribromide (1.4 ml, 15.1 mmol) in dry CH_2Cl_2 (4 ml) under N_2. The stirring was continued at the temperature for 4 h and then, at room temperature for 4 h. To the reaction mixture was added carefully ice and then, water and the mixture was extracted with CH_2Cl_2. The organic phase was washed with water and dried (Na_2SO_4). The solvent was evaporated and the crude product was passed through a short column of Florisil with hexane-ethyl acetate (4:1) to give **20**, which was dissolved in 25 ml of dry CH_2Cl_2. To the solution was added lead dioxide (0.65 g) and the mixture was stirred for 30 min. After reaction was over, insoluble material was filtered off and the solvent was removed from the filtrate. Crude product was purified by preparative TLC (silica gel) with benzene-ethyl acetate (96:4) to give **1** (36.1 mg, 53.4% yield based on **19**) as dark violet solid. ^{1}H NMR ($CDCl_3$, 360 MHz) δ -1.56(br.s,2,NH), 0.19-0.57(m,3,CH_3), 0.57-0.92(m,12,CH_3), 0.92-1.68(m,18,CH_2), 1.68-2.03(m,4,CH),

1.76-1.80(m,12,$ArCH_2\underline{CH_3}$), 2.06-2.79(m,2,$ArCH_2\underline{CH_2}$), 2.35-3.07(m,2,$ArCH_2$), 3.54(s,3,$ArCH_3$), 3.55(s,3,$ArCH_3$), 3.566(s,3,$ArCH_3$), 3.57(s,3,$ArCH_3$), 3.88-4.20(m,8,$Ar\underline{CH_2}CH_3$), 4.61-5.03(m,2,CH), 5.00-5.22(m,2,$ArCH_2CH_2\underline{CH_2}$), 5.97-6.78(m,3,ArH), 9.97 ppm(br.s,2,meso-H); Mass m/e 893 (M^+), 894, 895, 896.

2,8,12,18-Tetraethyl-3,7,13,17-tetramethyl-5-(2,6,10,14-tetramethylpentadecyl) porphyrin (21). The coupling reaction of **18** and 4,4'-diethyl-3,3'-dimethyl-5,5'-diformyl-2,2'-dipyrrlmethane was carried out by the similar method described for the synthesis of **19**. **21**: 29.8% yield, reddish purple solid. ^1H NMR ($CDCl_3$, 360 MHz) δ -1.59(br.s,2,NH), 0.08-0.37(m,3,CH_3), 0.55-0.85(m,12,CH_3), 0.87-1.58(m,18,CH_2), 1.76-2.20(m,4,CH), 1.73-1.87(m,12,$ArCH_2CH_3$), 3.54(s,3,$ArCH_3$), 3.55(s,3,$ArCH_3$), 3.58(s,3,$ArCH_3$), 3.61(s,3,$ArCH_3$), 3.91-4.17(m,8,$Ar\underline{CH_2}CH_3$), 4.56-5.32(m,2,CH_2), 9.82(br.s,1,meso-H), 10.00 ppm(br.s,2,meso-H). Anal Calcd for $C_{51}H_{76}N_4$: C,82.20; H,10.28; N,7.52%. Found: C,81.60; H,10.56; N,7.71%.

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