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SYNTHESIS OF A MODEL COMPOUND FOR THE PHOTOSYNTHETIC ELECTRON TRANSFER

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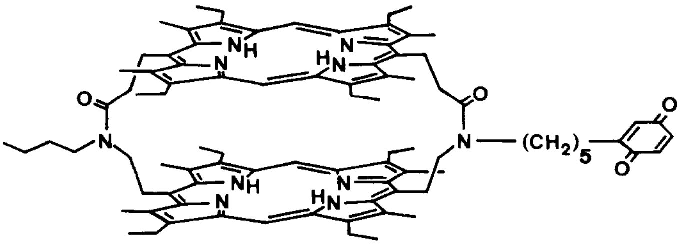
Abstract In order to elucidate the role of special pair chlorophyll in photosynthetic electron transfer, a new model compound 1, where two etioporphyrins are covalently tied in a face-to-face orientation and further linked to a quinone with a polymethylene chain, was synthesized.

The modelling of the efficient electron transfer and charge separation processes in photosynthesis has recently attracted great interest and many quinone-linked porphyrins[1] have been synthesized to investigate structural factors for the electron transfer. However, additional models of various kinds are still needed to understand the whole picture of photosynthetic electron transfer. One of the problems to be solved is the role of special pair chlorophyll. It is well known that the first critical electron donor in photosynthesis of green plants or bacteria is a special pair chlorophyll, which is considered[2] or proved[3] to



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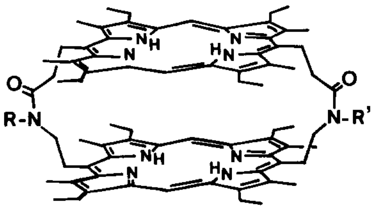
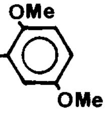
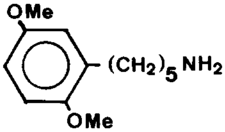


2 R = R' = Bu

3 R = Bu, R' = -$(CH_2)_5$-





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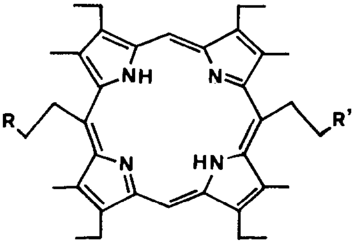
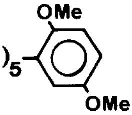


4 R = R' = CO_2Et

5 R = R' = OMes

6 R = OMes, R' = NHBu

7 R = NHBu, R' = $NH(CH_2)_5$-



8 R = R' = COCl

have a dimeric structure with face-to-face orientation. Since some electronic interaction exists between the paired chlorophyll and positive charge can delocalize over the two porphyrin rings, it is expected that the role of the dimeric porphyrins is to stabilize the photoinduced charge separated state. In order to shed light on this particular problem,[4] we designed a model **1**, where two etioporphyrins are covalently tied in a face-to-face orientation and further linked to a quinone. The model of this type is attractive, because **2**,[5] the dimeric porphyrin part in **1**, shows some characteristic features[6] of the special pair chlorophyll (P700). Thus, blue shifting of the Soret band as well as red shifting of visible bands[7] and lower redox potential[9] compared with **4** are similar to those observed for P700, although the values are somewhat smaller.[10] The chemical shift differences[11] are also closely parallel to those observed between dimeric and monomeric BChl-a.[12] Moreover, the linkage of a porphyrin and a quinone unit by single polymethylene chain has already been shown[1c,1d,13] to be effective for the study of photoinduced electron transfer problems.

Synthesis of **1** was carried out as follows. Dimesylate **5**[8] was treated with a large excess[14] of butylamine in DMF at 70 ℃ for 9h. Reaction products were separated by column chromatography on silica gel with $CHCl_3$-MeOH-NEt_3(20:1:0.05) to obtain **6** in 38% yield. Similar reaction of **6** with amine **9** was carried out in DMF at 70 ℃ for 7 days. Purification of the crude product by column chromatography on silica gel with $CHCl_3$-MeOH-NEt_3 (35:1:0.05) gave **7** in 67% yield. Coupling reaction of **7** and **8**[8] was done in a manner similar to Collman et al.[8] Crude product was passed through a short column of silica gel with $CHCl_3$-MeOH-NEt_3(30:1:0.05) and then, purified by preparative t.l.c. with $CHCl_3$-MeOH-NEt_3(98.5:1:0.5) to give **3** in 42% yield. Demethylation of **3** was carried out in CH_2Cl_2 with BBr_3 at -78 ℃ for 5h and then at 0 ℃ for 2h, followed by oxidation with DDQ to give the desired compound **1**[15] in 28% yield, which was purified by careful preparative t.l.c. with $CHCl_3$-MeOH-Et_3N (20:1:0.3) and by following recrystallization from CH_2Cl_2-pentane [^{1}H NMR ($CDCl_3$, 100 MHz) δ -2.51(br.s,4H,NH), 1.3-1.6(m,24H,$CH_2\underline{CH_3}$), 3.29(s,12H,CH_3), 3.32(s,12H,CH_3), 3.5-4.0(m,16H,$\underline{CH_2}CH_3$), 4.7-

5.3(m,8H,CH_2), 6.71-6.73(m,1H,quinone-H), 6.80-6.81(m,2H,quinone-H), 9.32(s,2H,meso-H), 9.41(s,2H,meso-H); FD MS m/e 1384(M^+); λ_{max} (THF) 404 nm(log ε 5.43), 516(4.30), 552(3.93), 592(3.90), 644(3.10)].

In ^1H NMR spectra, the chemical shifts of quinone protons of **1** are not affected by the large magnetic anisotropy of the porphyrin rings (chemical shift differences from the corresponding protons of toluquinone are less than 0.1 ppm). This implies that the quinone ring neither locates over the porphyrin plane nor inserts between the two porphyrin rings: it may take mainly an extended conformation in the solvent. The electronic spectra of **1** in the region of 350-700 nm are very similar to that of **2**, indicating that there is no appreciable interaction in the ground state between the dimeric porphyrin and the quinone groups. However, the relative fluorescence yields of **1** in several solvents such as tetrahydrofuran, dioxane, aceton, and benzene are ca. 10% ~ several % of **2**. This suggests that an efficient photoinduced electron transfer takes place from the porphyrin dimer unit to the quinone ring. An additional evidence supporting the electron transfer quenching mechanism was given by the fluorescence lifetime measurements. The results obtained by photon counting system with a combination of picosecond dye laser are summarized in Table 1. The decay curves of **1** in various solvents are composed of three components, which are presumably due to different conformers, and their weights seem to be affected to some extent by the nature of the solvent. The shortest lifetime component has the largest weight in general.

Table 1. Fluorescence lifetimes[a]

	$\mathbf{1}^b$			**2**
Solvent	τ_1	τ_2	τ_3	τ
Benzene	140 ps(100)	1.04 ns(22)	6.76 ns(11)	
Tetrahydrofuran	130 (100)	1.21 (10)	8.10 (8)	10.1 ns
Acetonitrile	60 (100)	1.10 (30)	5.12 (4)	

[a] Measured by the method of time correlated single photon counting on a Photochemical Research Associates picosecond lifetime fluorometer.

[b] Values in parentheses are relative weight.

Above results clearly indicate that **1** is a suitable model compound for studying the role of special pair chlorophyll in photosynthetic electron transfer. Detailed picosecond time-resolved transient spectra of **1** will be reported elsewhere.

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4. Although linear or loosely stacked dimers of porphyrins containing a covalently linked acceptor have been prepared,[1b,1f] interaction between two porphyrin rings in these models appears to be minimal.
5. Compound **2**[15] was prepared in a manner similar to the synthesis of **3**.
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7. λ_{max} in $CHCl_3$-Et_3N(99.5:0.5),**2**:408, 515, 554, 586, 638 nm; **4**[8]:410, 510, 545, 578, 627 nm.
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9. $E^{ox}_{1/2}$ in CH_2Cl_2 vs S. C. E., **2**: 550 mV; **4**: 660 mV.
10. It is reported[6] that the longest wavelength in the absorption spectra of P700 shifts to the longer wavelength by 30-40 nm and oxidation potential is lower by 440 mV as compared with monomeric Chl-a.
11. ^1H NMR ($CDCl_3$) in the aromatic region, δ **2**: 9.31, 9.41; **4**: 9.89 ppm.
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14. After several examinations, 200 eq. of butylamine and 0.14 mmol of **5** in 14 ml of DMF gave the highest yield.
15. Satisfactory elemental analyses (C, H, N) were obtained.

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