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Covalently Linked Porphyrin Ubiquinones(0) as Model Compounds for Photosynthetic Reaction Center.

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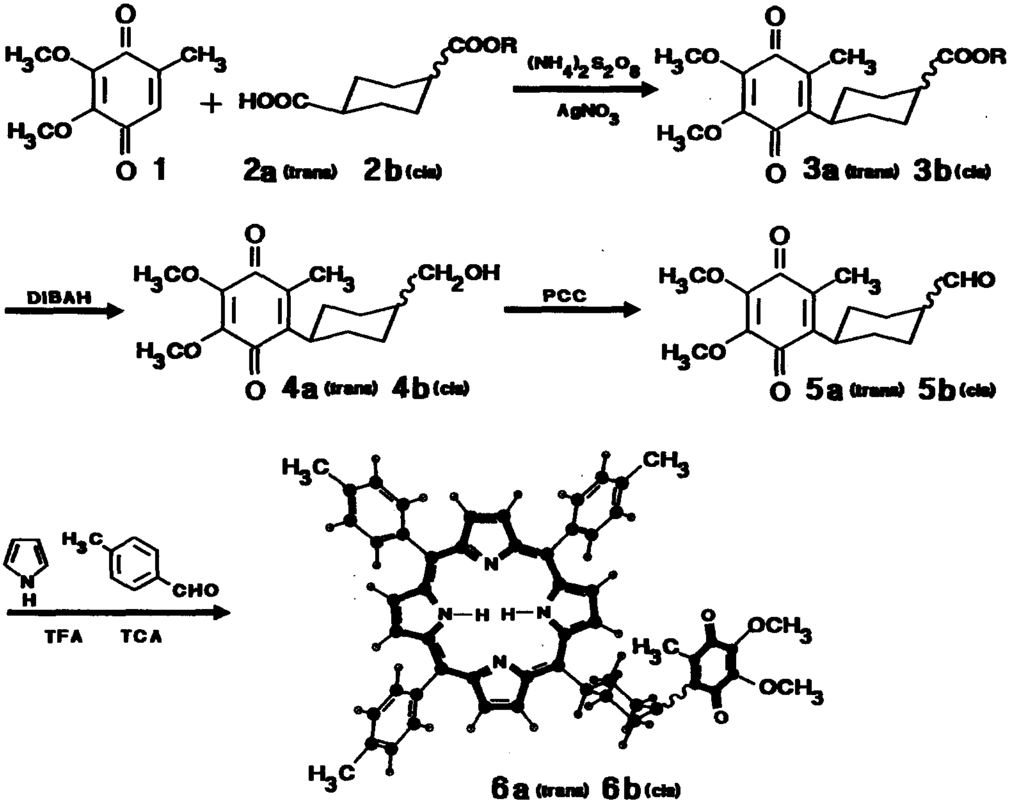
Abstract: *trans-* and *cis-* cyclohexylene linked porphyrin ubiquinones(0) have been synthesized and characterized by NMR and optical spectroscopy. ENDOR spectra of the corresponding porphyrin semiquinone radical anions are discussed.

The donor and acceptor pigments of the photosynthetic reaction centers are fixed in precise distances and relative orientations by the protein matrix. For studies of photoinduced electron transfer (ET) reactions between these primary reactants, porphyrin quinones (P-Q) have been widely used as biomimetic model compounds.[1] Rigidly linked derivatives are particularly suited, since they allow detailed insight into the dependence of the ET properties on structural and electronic parameters. By time-resolved fluorescence spectroscopy,[2] we have previously shown that model compounds with a porphyrin donor and a quinone acceptor linked via a cyclohexylene bridge, exhibit at ambient temperature fast singlet ET on the picosecond scale. On cooling, singlet triplet intersystem crossing becomes competitive and triplet ET (from the excited porphyrin to the quinone moiety) can be observed by time-resolved EPR spectroscopy allowing unambiguous detection of the charge separated biradical intermediate in triplet state.[3] Since one of the factors which governs effective ET in these systems is the redox potential of donor and acceptor (and thereby the driving force ΔG), we have synthesized similar model compounds with methoxy and methyl substituents at the quinone fragment. In the present paper, we describe the synthetic route to these compounds and in addition some preliminary static optical and EPR results.

Syntheses: Radical alkylation of **1** (see Scheme) was performed by oxidative decarboxylation of a mixture of **2a** and **2b**[4] with $(NH_4)_2S_2O_8$ and $AgNO_3$ as the catalyst[5] yielding **3a** and **3b** in a ratio of 2:3 [chromatography (SiO_2, CH_2Cl_2: ether = 20:1), total yield 35%]. Reduction of the mixture of **3a** and **3b** with DIBAH[6] in diethylether yielded **4a** and **4b** in a ratio of 1:2 [chromatography (SiO_2, CH_2Cl_2: acetone = 10:1; total yield 62%]. Oxidation of this mixture using pyridinium chlorochromate (PCC)[7] yielded the desired aldehydes **5a** and **5b** in a ratio of 1:1.2 [chromatography (SiO_2, CH_2Cl_2: ether = 20:1; total yield 75%]. Condensation of the mixture of **5a** and **5b** with 4-methylbenzaldehyde and pyrrole in a ratio of 1:3:4 in CH_2Cl_2[8] using trifluoroacetic acid as a catalyst, followed by repetitive chromatography

(CH_2Cl_2: 2-propanol = 99:1) yielded the target compounds **6a** and **6b** in a ratio of 3:1 (total yield 3.2%). Separation of the diastereoisomers was achieved by HPLC (Nucleosil 50, CH_2Cl_2:H_2O = 99.2:0.8).[9]



Cyclic voltammetry: For an understanding of ET properties of these systems knowledge of the energetics, i. e. energy differences between ground and excited states of the porphyrin moiety and those of the charge separated states is of greatest importance. In this respect, valuable information can be obtained by cyclic voltammetry which yields the redox potentials of one-electron transitions,[10] e. g. those of P-Q/$P^{\cdot+}$-Q and P-Q/P-$Q^{\cdot-}$. We have determined the redox potentials at a Pt electrode vs. SCE of **6a** ($E_{1/2}^{+}$ = 965 mV; $E_{1/2}^{-}$ = -692 mV) and **6b** ($E_{1/2}^{+}$ = 957 mV; $E_{1/2}^{-}$= -696 mV) in CH_2Cl_2 using tetrabutylammonium perchlorate as the supporting electrolyte and for comparison, suitable fragments such as 5-cyclohexyl-10,15,20-triphenylporphyrin ($E_{1/2}^{+}$ = 1020 mV), and cyclohexyl-Q(0) ($E_{1/2}^{-}$ = -784 mV). It turned out that the potentials of the donor and quinone moieties of the P-Q's cannot be regarded as localized fragments. This finding is of importance for theoretical interpretations of ET processes of these systems.

Optical spectra: Absorption and steady-state fluorescence spectra were measured with a Perkin-Elmer PE 330 and a Perkin-Elmer PE 555 spectrometer respectively, in CH_2Cl_2 (concentrations for fluorescence measurements $<5 \cdot 10^{-6}$ m). Whereas the absorption spectra of the porphyrins are slightly perturbed by the appended quinone, the fluorescence spectra correspond to the well-known spectra of tetraphenylporphyrin (TPP). However, due to singlet ET between the porphyrin and the quinone moiety, the fluorescence intensities (the quantum yields of the P-Q's) are significantly reduced as compared with that of TPP. Assuming the quenching to be solely caused by ET and taking the fluorescence lifetime of TPP (τ_F = 7.6 ns, unpublished) as standard, the rate constants can be estimated to be $2.8 \cdot 10^9$ sec^{-1} and $2.2 \cdot 10^9$ sec^{-1} for **6a** and **6b**, respectively.

EPR/ENDOR experiments: In a recent ENDOR study of semiquinones, we have observed different conformations of cyclohexyl substituted ubiquinones,[11] which may also occur in the P-Q's. Therefore, and in order to determine the spin density distributions of the radical state of the quinone moieties, we have studied the radical anions of **6a** and **6b** (2-propanol, reductant benzoin, base benzyltrimethylammonium hydroxide, argon protection) by ENDOR. Figure 1 shows the EPR, ENDOR, and ENDOR-induced EPR (EIE)[12] spectra of the zinc complex of the *cis*-semiquinone **6b**$^-$. The EIE experiments clearly revealed two different paramagnetic species with different hyperfine coupling constants to be present in the sample under study. Similar results were obtained for Zn-**6a**$^-$. It may be assumed that these different conformations are caused by different sterically hindered geometrical arrangements of the cyclohexylene bridge.

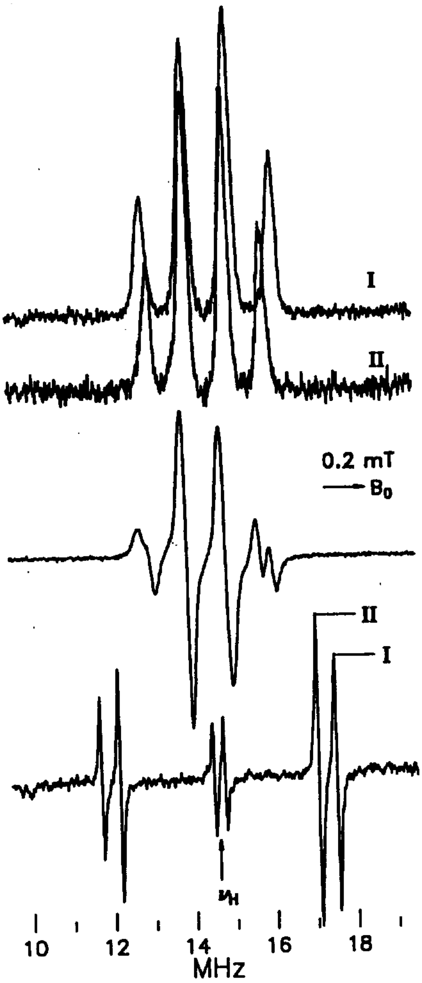


Figure 1. EPR (center), ENDOR (bottom), and EIE (top) spectra of the radical anion of Zn-6b (Bruker ER200D, Bruker cavity ER200ENB, laboratory-built NMR facilities decribed elsewhere[12]). I and II in the ENDOR spectrum denote the rf pumping frequencies for the EIE spectra I and II.

Time-resolved optical and EPR measurements of the new P-Q's in isotropic and in liquid-crystalline solution are in progress.

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9. ^{1}H-NMR data of P-Q's ($CDCl_3$). **6a**: -2.65 (s, 2H, N-H); 2.13 (m, $2H_e$); 2.35 (s, 3H, CH_3-Q(0)); 2.69 (s, 3H, CH_3-tolyl); 2.75 (m, 8H: $2CH_3$-tolyl and $2H_a$); 2.88 (m, $2H_e$); 3.25 (m, $2H_a$); 3.45 (t,t, $1H_a$); 4.08 (s, 3H, CH_3O-Q(0)); 4.15 (s, 3H, CH_3O-Q(0)); 5.4 (t,t, $1H_a$); 7.55 (m, 6H, phenyl-H); 8.08 (m, 6H, phenyl-H); 8.80 (m, 4H, porphyrin-H); 8.93 (m, 2H, porphyrin-H); 9.66 (m, 2H, porphyrin-H). **6b**: -2.64 (s, 2H, N-H); 2.12 (m, 2H: 2H-cyclohexylene); 2.34 (s, 3H, CH_3-Q(0)); 2.68 (s, 3H, CH_3-tolyl); 2.72 (m, 10H, $2CH_3$-tolyl and 4H-cyclohexylene); 3.50 (m, 2H-cyclohexylene); 3.60 (m, 1H-cyclohexylene); 4.08 (s, 3H, CH_3O-Q(0)); 4.14 (s, 3H, CH_3O- Q(0)); 5,48 (m, 1H-cyclohexylene); 7.56 (m, 6H, phenyl-H); 8.08 (m, 6H, phenyl-H); 8.80 (m, 4H, porphyrin-H); 8.92 (m, 2H, porphyrin-H); 9.62 (m, 2H, porphyrin-H).
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