

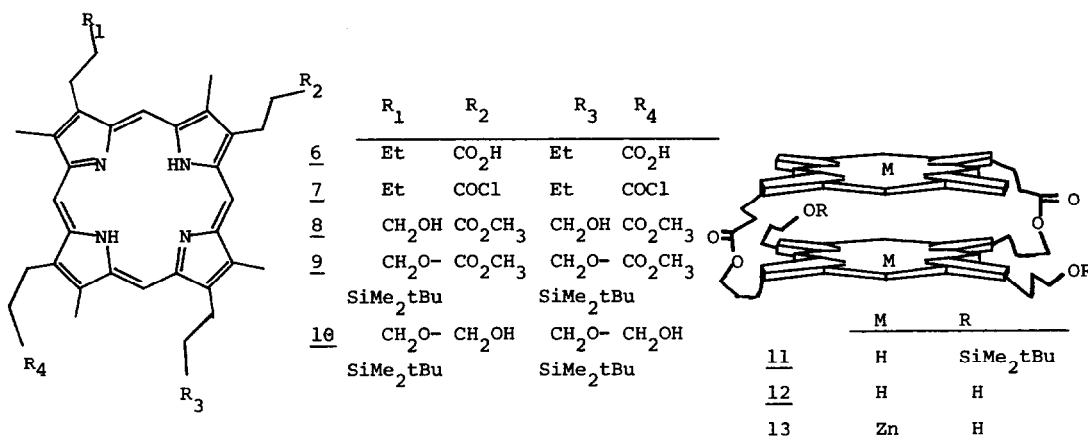
SELECTIVELY METALATED DOUBLY COFACIAL PORPHYRIN TRIMERS. NEW MODELS
FOR THE STUDY OF PHOTOINDUCED INTRAMOLECULAR ELECTRON TRANSFER.

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Summary : The preparation of a doubly cofacial porphyrin trimer consisting of a Zn mesoporphyrin - Zn mesoporphyrin - mesoporphyrin stack is described. The optical absorption and fluorescence properties of the molecule as a function of solvent are also reported.

The efficiency of photosynthetic charge separation depends critically on the orientation of the chlorophyll electron donors and chlorophyll or pheophytin electron acceptors relative to one another in the reaction center protein. In order to model photosynthetic charge separation we have been particularly interested in molecules that restrict the donor-acceptor geometry.^{2,3} Simple single donor-single acceptor molecules based on chlorophylls and porphyrins form states possessing charge transfer character a few picoseconds after photoexcitation. However, these states live only for about 1 nsec.^{3,4} Recent studies of bacterial reaction centers suggest that an intermediary bacteriochlorophyll a (BChl a) participates in the formation of the radical pair state involving the oxidized special pair donor, (BChl a)₂⁺ and the reduced bacteriopheophytin a acceptor, (BPh a⁻).⁵ This radical pair state has a 12 nsec lifetime.⁶ These results suggest a need to investigate models possessing at least two redox partners and therefore three macrocycles. In this paper we report the preparation of the first such model with a well-defined geometry.

The preparation of trimer 14 was designed to result in selective metalation of only the center and one of the outer porphyrins. The outer two porphyrins of 14 are mesoporphyrin II derivatives. Mesoporphyrin II, 6 was synthesized from 2-carboxy-3,5-dimethyl-4-ethylpyrrole, 1⁷ and 2-carboxy-4-(2'-carbethoxyethyl)-5-formyl-3-methylpyrrole, 2^{7,8} using the modified pyrromethene synthesis of Chang.⁹ The central selectively functionalized porphyrin, 8 was prepared from pyrrole 2 and 2-carboxy-3,5-dimethyl-4-(3'-hydroxypropyl)pyrrole, 5. Pyrrole 5 was prepared in near quantitative yield by the reduction of benzyl 2-carboxy-4-(2'-carbethoxyethyl)-3,5-dimethylpyrrole, 3⁸ with BH₃/THF



to benzyl 2-carboxy-4-(3'-hydroxypropyl)-3,5-dimethylpyrrole, 4 followed by hydrogenolysis. The modified pyrromethen synthesis was used to give a 12% yield of trans dimethyl ester trans diol porphyrin 8. The alcohol functions of 8 were protected with the *t*-Bu(CH₃)₂Si group to yield 9. Disilyl compound 9 was reduced in 82% yield to trans diol 10 with LiAlH₄ in THF at 20°. Dimer 11 was prepared in 69% yield from diacid chloride 7 and diol 10 using high dilution techniques in refluxing CH₂Cl₂ containing 4-dimethylamino-pyridine as an acylation catalyst. The silyl groups of 11 were removed with 1% aqueous HCl in THF. The resulting dimer diol 12 was refluxed in CHCl₃ containing Zn(OAc)₂ to yield the double Zn substituted dimer diol 13. Once again high dilution reaction of 13 with an equimolar amount of 7 gave a 65% yield of the desired triple decker sandwich 14, (mass spec: *m/e* M⁺ = 1785 by field desorption).

Trimer 14 actually consists of a mixture of three isomers. These isomers are the three possible combinations of the asymmetric porphyrin monomers that result from two different face-to-face couplings for each of two coupling reactions. While these isomers are separable with some difficulty by HPLC,¹⁰ the properties of the individual isomers measured thus far are identical and accordingly will be reported for the mixture.

The optical absorption spectrum of 14 in solvents that ligate both Zn atoms, such as toluene/1% pyridine and DMF, can be represented to a first approximation as the superposition of the spectra of two Zn mesoporphyrins and one mesoporphyrin. Fluorescence emission from 14 occurs almost exclusively from mesoporphyrin at 627 nm and does not depend strongly on the excitation wavelength. This implies that energy transfer is rapid between the Zn porphyrins and the metal free porphyrin.

Fajer et al.¹¹ have shown that Cl⁻ coordination to a Zn porphyrin results in a change in the optical absorption spectrum of the Zn porphyrin and makes the Zn porphyrin easier to oxidize by as much as 200 mV. We have used this effect to differentiate between the outer and central Zn porphyrins of trimer 14. Figure 1 shows the optical absorption spectrum of 14 both in the presence and absence of Cl⁻. The spectrum indicates that only one of the Zn porphyrins coordinates Cl⁻. Similarly, AC voltammetric measurements¹²

of the redox potentials of 14, Table 1, in the presence of Cl^- show two distinct one electron Zn porphyrin oxidation waves, whereas only a single such wave is present in the absence of Cl^- . Increasing $[\text{Cl}^-] / [\text{14}]$ to about 10^6 results in only about 60% Cl^- ligated Zn porphyrin. Since the bulky tetraalkylammonium ion probably forms a reasonably tight ion pair with the Cl^- ion in CH_2Cl_2 , the entire salt cannot fit well between the macrocyclic planes. Thus, only the outer Zn porphyrin with one unblocked face is ligated.

The data in Table 2 show that the fluorescence of 14 is quenched as the dielectric constant of the solvent increases. Yet, the fluorescence is most strongly quenched in CH_2Cl_2 containing Cl^- ion. Moreover, the measured fluorescence lifetime of 14 is roughly proportional to the degree of quenching. This implies that the quenching is due principally to non-radiative depletion of the S_1 population of 14 rather than a large change in the radiative rate. The relative quantum yields of triplet formation for 14 remain roughly constant. Thus, the enhanced degree of quenching of 14 in the presence of Cl^- may be due to an increase in the non-radiative rate for the return of excited 14 directly to the ground state or may reflect the presence of another competing state. We hypothesize the involvement of a charge transfer state of 14 based on spectroscopic studies of monometalated porphyrin dimers.⁴

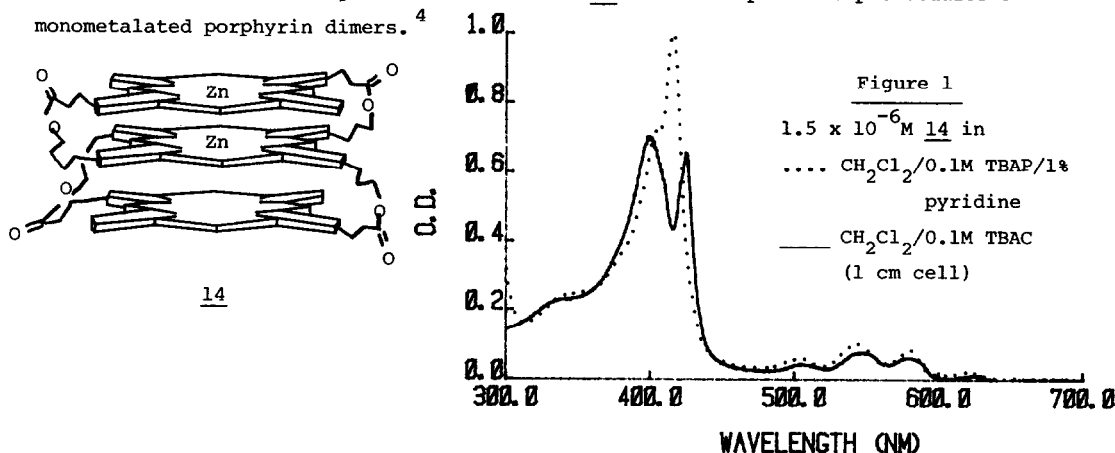


Figure 1

$1.5 \times 10^{-6} \text{ M } \text{14}$ in
 $\text{CH}_2\text{Cl}_2/0.1\text{M TBAP}/1\%$
 pyridine
 — $\text{CH}_2\text{Cl}_2/0.1\text{M TBAC}$
 (1 cm cell)

Table 1. Redox Potentials (Volts vs SCE)

Solvent	$E_{1/2}^+$	$E_{1/2}^-$
DMF/0.1M TBAP ^a	0.62, 0.85	-1.31, -1.60
$\text{CH}_2\text{Cl}_2/0.1\text{M TBAP}^a$	0.61, 0.85	-1.30, -1.60
$\text{CH}_2\text{Cl}_2/0.1\text{M TBAC}^b$	0.52, 0.85	-1.31, -1.62
	0.62	^c

^a tetra-n-butylammonium perchlorate

^b tetra-n-butylammonium chloride

^c not observed due to solvent and electrolyte background.

Table 2. Fluorescence Data

Solvent	quantum yield	fluorescence lifetime (ns)
toluene/ 1% pyridine	0.046	15.2
$\text{CH}_2\text{Cl}_2/0.1\text{M TBAP}/$ 1% pyridine	0.024	12.5
$\text{CH}_2\text{Cl}_2/0.1\text{M TBAC}$	0.014	8.2
DMF	0.018	11.0

The energies of the possible charge transfer states of 14 in $\text{CH}_2\text{Cl}_2/0.1 \text{ M TBAC}$ can be estimated from the sum of the oxidation and reduction potentials of the molecule. These states are 1.83, 1.92, and 2.12 eV, respectively, for $\text{ZnP}_{\text{out}}^+ \text{ZnP}_{\text{in}}^- \text{P}^-$, $\text{ZnP}_{\text{out}}^- \text{ZnP}_{\text{in}}^+ \text{P}^-$, and $\text{ZnP}_{\text{out}}^+ \text{ZnP}_{\text{in}}^- \text{P}$. Since the outer Zn porphyrin is easier to oxidize than the inner Zn porphyrin, photoinduced charge separation should lead to cationic character on the outer Zn porphyrin and anionic character on the metal free porphyrin. The outer Zn porphyrin and metal free porphyrin of 14 have an average distance of 8-10 Å. Thus, the presence of the intermediary Zn porphyrin should insure a rapid forward rate⁴ for charge transfer while at the same time permit the final oxidized donor and reduced acceptor to maintain a distance sufficient to impede rapid collapse of the resulting radical pair. We are currently examining the excited state behaviour of 14 more closely to determine whether the hypothetical charge transfer states participate significantly in the photochemistry of 14.

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