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Three homologous cofacial diporphyrins that have interplanar distances ranging from 6.4Å to 4.2Å have been synthesized. Their absorption and emission spectra revealed strong exciton coupling in the diporphyrin. Magnesium complexes of diporphyrins were studied and their application as a model for P700 photoactive center was discussed.

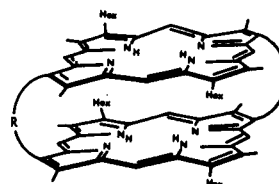
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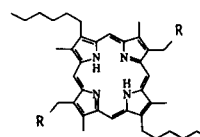
Considerable effort has gone into the chemical and physical characterization of the photosystem I reaction center (PSI). It is believed that this primary electron donor unit in photosynthesis consists of a special pair of chlorophyll a (P700) molecules bridged by two water ligands (2-7). Current emphasis has been concerned with the *in vitro* preparation and characterization of the reaction center chlorophyll (5-7). It has been reasoned that chlorophyll and porphyrin dimers covalently linked together may serve as biomimetic P700 models (6-9) and several syntheses of cofacial porphyrin dimers with an interplanar separation in the neighborhood of 6.4Å have recently been reported (10-13). Since the utility of the dimeric porphyrin arises from the parallel interaction of the two porphyrin rings, clearly the distance between the two would have predominant effect on the properties of diporphyrin. A systematic study of the properties of diporphyrin as a function of the ring separation, therefore, is essential to our complete understanding of these compounds. We report here the synthesis and interesting properties of three homologous cofacial diporphyrins 1-3, that have interplanar distances ranging from 6.4Å to 4.2Å.

Synthetically the preparation of a diporphyrin with very short ring separation would be difficult, if not impossible, with tetraarylporphyrin derivatives for steric reasons. β -Alkyl porphyrins, therefore, have to be used despite the fact that the resulting diporphyrins may contain more than one stereoisomers. We have recently reported an efficient total synthesis of alkyl substituted porphyrins with proper symmetry as well as a high-yield coupling procedure to prepare stacked macrocyclic ligands (14,10). Therefore, type II porphyrin dipropionic acid 4 and diacetic acid 5 were synthesized and the carboxyl groups transformed into the corresponding acid chlorides and amines (6-9) as previously described (10). The coupling of 6 and 7 gave 1, 7 and 8 gave 2, and 8 and 9 yielded 3. All couplings were carried out under high dilution conditions using the syringe pump technique described earlier (14,10). The resulting diporphyrins were purified by triple chromatography on thick layer silica gel plates. Typical yields from a 0.2 mmole batch

were around 50-65% for 1 and 2 and 40% for 3, based upon the monomers. These compounds have been characterized by pmr, cmr, mass spectral and elemental analyses. They have excellent solubility in almost any polar or nonpolar solvents (15) and are very stable toward acids or bases. It was noticed that their amide linkages



- 1 Diporphyrin-7, R = -CH₂CH₂CON(n-Bu)CH₂CH₂CH₂-
- 2 Diporphyrin-6, R = -CH₂CON(n-Bu)CH₂CH₂CH₂-
- 3 Diporphyrin-5, R = -CH₂CON(n-Bu)CH₂CH₂-



- 4 R = CH₂CO₂H
- 5 R = CO₂H
- 6 R = CH₂COCl
- 7 R = CH₂CH₂NH-Bu
- 8 R = COCl
- 9 R = CH₂NH-Bu

cannot be cleaved over a 30 minute period in refluxing aqueous formic acid-hydrochloric acid mixtures.

The interplanar distance of the diporphyrins has been determined by studying the dipolar interaction of two Cu²⁺ paramagnetic centers. The epr spectrum of the di-Cu complex of 3 (16) is shown in Figure 1. The appearance of the seven-line parallel hyperfine pattern as well as the intense signals observed in the half-field region ($\Delta M_s = \pm 2$) clearly documents the dipolar interaction

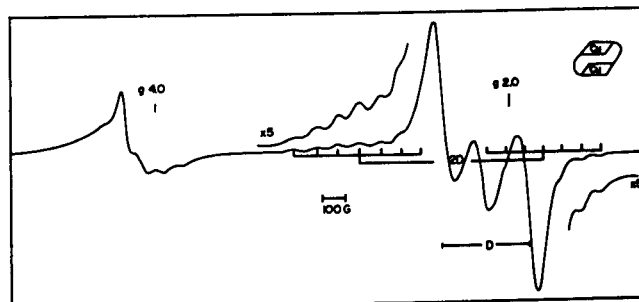


Figure 1. Epr spectrum of Cu(II)-Cu(II) diporphyrin-5 in dichloromethane/toluene at 77°K, concentration = 1mM. Since the two unpaired copper electrons are localized largely in the porphyrin plane and cannot pair, a triplet spectrum results.

Table 1
Characteristic data of Cofacial Diporphyrins

Compound	Soret band (a)	Nmr N-H (Deuteriochloroform)	Fluorescence (b) Q(0,0)	Φ_F (c)	Cu-Cu Zero-field Splitting (d)	Interplanar (e) Separation
4 Me ester	398 nm (169.9 ϵ mM)	-3.8 δ	619 nm	0.094	--	--
1 dimer-7	383 nm (191)	-6.2 δ	628 nm	0.035	0.011 cm^{-1}	6.4 \AA
2 dimer-6	381 nm (209)	-6.6 δ	630 nm	0.021	0.0205 cm^{-1}	5.4 \AA
3 dimer-5	373 nm (201)	-8.5 δ	630 nm	0.007	0.0415 cm^{-1}	4.2 \AA

(a) Absorption spectra recorded in dichloromethane at 23°. (b) 77°K in toluene glass. (c) Fluorescence quantum yields assuming yield for etioporphyrin I = 0.09 (reference 10). (d) Epr spectra were recorded on a Varian E-4 spectrometer, 77°K in dichloromethane/toluene. (e) Calculated according to reference 19.

(17,18) of the two Cu^{2+} nuclei ($I = 3/2$). From the apparent zero-field splitting obtained from the full-field lines one can calculate the separation between the coppers to be 4.2 \AA (19), nearly identical to the distance estimated from a CPK molecular model. Epr data for other Cu-Cu diporphyrins are tabulated in Table 1. Comparisons of the inner nitrogen proton chemical shift of various diporphyrins are also given. It is evident that the upfield shift caused by mutual diamagnetic ring current interactions may be used as an index of the ring separation.

This series of diporphyrins with well-defined structure and ring separation offers an unusual opportunity to study exciton interaction in porphyrin aggregates. Several modes of exciton couplings have currently been advocated to account for the spectral shift of the P700 (5,7). A comparison of the absorption spectra of our dimeric and monomeric porphyrins (Figure 2 and Table 1) reveals the following abnormalities for the dimer: 1) a relative large blue shift of the Soret band, 2) a slight red shift of the visible bands and 3) the Soret band shows a prominent red tail extending out to 500 nm region (20). In order to understand these spectral differences, let us first consider porphyrin electronic states in the dimer. If a pair of degenerate dipolar states X, Y on porphyrin A is to interact with a similar pair X', Y' on porphyrin B, the nature of the exciton coupling will depend on the dimer geometry (21). In our doubly linked dimer, these dipoles are most likely parallel to each other, with some possibility of slight tilting and/or shifting. The exciton coupling between two parallel transition dipoles is basically set by (22,23)

$$V = \frac{e^2 \mu^2}{R^3} G \quad (1)$$

where μ , R are the dipole moment and the perpendicular distance between the two porphyrin planes, respectively. G is a geometric factor which should close to unity since

in our case any severe distortion from the parallel conformation is likely to be small (24). The dipole moment can be estimated (25) by

$$\mu^2 = \frac{\epsilon_{\text{max}}}{2500 M} \cdot \frac{\Delta\lambda}{\lambda_{\text{max}}} \quad (2)$$

where M is the degeneracy and $\Delta\lambda$, the band width at half maximum. From available spectral data we can estimate a range of magnitudes for the exciton coupling in our diporphyrins: 2000 cm^{-1} - 6000 cm^{-1} .

In the Soret region (B state), the B^+ exciton state would occur at

$$E_B^+ = E_B^\circ + D + V \quad (3)$$

where E_B° is the monomer absorption, D is the "solvent parameter." D usually causes a red shift but its value is difficult to estimate. In diporphyrin 1, from the B^+ at 384 nm and the red tail where the center of B^- band probably occurred around 480 nm one can estimate the exciton coupling as half of this energy gap, or $V = 2500 \text{ cm}^{-1}$, comparable to the V set by Eq. 1. In diporphyrin 3, with a shortened R, V is enhanced more than 3 fold and this was reflected by the wider separation of the blue maximum and the red tail. In the visible region (Q state), since the dipole strength is much weaker than the B band, the exciton coupling is much smaller. The slight red shift and the more diffused band shape possibly is a result of the inhomogeneous solvent broadening. The red-shift of the visible bands and the red tail of the Soret band, albeit less conspicuous than the Soret blue shift, played a major role in enhancing the self-quenching of the dimer fluorescence yield (Table 1).

In addition to the free base diporphyrins, we have examined a large number of their di-metal complexes, e.g. Cu-Cu, Zn-Zn, Mg-Mg, etc. (26). In each case, a blue-shifted Soret maximum was observed. The magnitude of

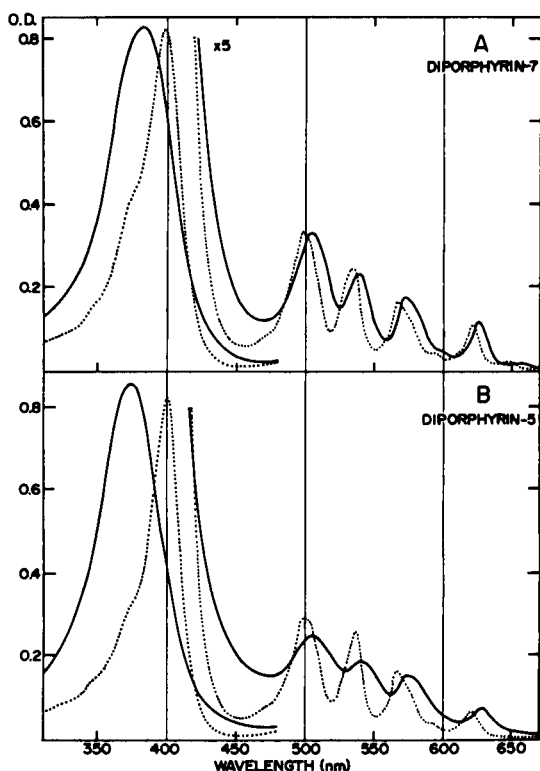


Figure 2. (A) Diporphyrin-7 (solid line) versus monomer 4 dimethyl ester (dotted line). (B) Diporphyrin-5 (solid line) versus monomer 5 dimethyl ester (dotted line). All absorption spectra were taken in dichloromethane at 23°. Concentrations were adjusted such that the peak heights of the Soret band were roughly the same.

exciton coupling varied from metal to metal (27). With Mg-Mg complexes, the spectral shift appeared to be moderate yet the principal features of the dimer spectra clearly remained unchanged (28). Solvent polarity and temperature seemed to have little effect on the absorption or excitation spectra. For example, the Mg-Mg complex of **1** in dry toluene at 23° gave absorption maxima: α 581, β 543, S402nm; while in aqueous dimethylformamide: α 583, β 546, S403nm (at RT) and α 581, β 545, S406nm (at 77° K). These results suggest that the Mg-Mg diporphyrin spectroscopically is quite different from the P700 dimer. This is expected if one considers the large difference of the electronic states between a Mg porphyrin and Chl a (29) plus the fact that the presence of carbonyl groups on the chlorophyll ring not only facilitates water complexation but restricts the orientation of the transition dipoles so that very specific exciton coupling would occur to give the spectral shift. The Mg-diporphyrins, nevertheless, are still attractive systems for studying excitation energy transfers in porphyrin-like materials (8). Further investigation into the singlet and triplet lifetimes of the dimer is needed to gain insight of these systems.

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$G=1+\sin^2\theta$, Y, Y' with shifting: $G=1-3 \sin^2\phi$.

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(27) Axial ligands also affect the spectral shift. For example, in the presence of triphenylmethylimidazole, the Fe(II)-Fe(II) diporphyrin-7 forms only 5-coordinate heme $[\text{Ph}_3\text{C-Im-Fe}]_2$ which has a Soret peak at 395nm, blue-shifted 16nm. Addition of pyrazine to this species gives a pyrazine bridged complex with the Soret at 411 nm, not much different from a monomeric 6-coordinate hemochrome. Also the dioxygen adducts exhibit

little shift. (C. K. Chang, manuscript in preparation).

(28) Absorption spectra in CH_2Cl_2 at 23° , MgOEP: α 579, β 541, S408 nm; and Mg-Mg diporphyrin-5: α 586, β 548, S391 nm. Mg-Mg diporphyrin-6: α 583, β 544, S402 nm.

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Note added in proof: In the light of the present work and reference 10, the dimer spectrum reported by Ogoshi *et al.* (ref. 11) clearly was incorrect. See also [Ichimura, *Chem. Letters*, 641 (1977)] for additional evidence.