

Chlorophyll-Porphyrin Heterodimers with Orthogonal π Systems: Solvent Polarity Dependent Photophysics

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Abstract: The synthesis and properties of a series of fixed-distance chlorophyll-porphyrin molecules are described. These molecules consist of a methyl pyrochlorophyllide *a* moiety which is directly bonded at its 2-position to the 5-position of a 2,8,12,18-tetraethyl-3,7,13,17-tetramethyl-15-(*p*-tolyl)porphyrin. Steric hindrance between adjacent substituents rigidly positions the π systems of both macrocycles perpendicular to one another. The macrocycles were selectively metalated with zinc to give the four possible derivatives, HCHP, ZCHP, HCZP, and ZCZP, where H, Z, C, and P denote free base, Zn derivative, chlorin, and porphyrin, respectively. The lowest excited singlet states of HCHP and ZCHP, which are localized on HC and ZC, respectively, exhibit lifetimes and fluorescence quantum yields that are solvent polarity independent and do not differ significantly from those of chlorophyll itself. ZCZP, however, displays a lowest excited singlet state lifetime and fluorescence quantum yield that are strongly solvent polarity dependent. The fluorescence lifetime is 3.4 ns in toluene and decreases to 119 ps in butyronitrile. Since the fluorescence quantum yield of ZCZP is proportional to its fluorescence lifetime, nonradiative decay is strongly enhanced for ZCZP in polar media. However, picosecond transient absorption measurements show no evidence for a distinct ion-pair intermediate. This is consistent with the fact that the energy levels of hypothetical charge-separated states within ZCZP, estimated from redox potentials, lie above that of S_1 and are therefore virtual states. HCZP also displays distinctive solvent dependent photophysics. Once again, nonradiative decay is strongly enhanced as solvent polarity increases. However, in HCZP picosecond transient absorption measurements show clear evidence of ion-pair formation in butyronitrile in 4 ps. The ion pair recombines in 43 ps. HCZP is the only compound in the series for which redox potentials in polar solvents predict that an ion-pair state, HC^-ZP^+ , lies below S_1 and is therefore a real ion-pair state. Thus, the influence of both virtual and real charge-transfer states on donor-acceptor photophysics can be directly observed in similar molecules.

Introduction

The electron donors and acceptors in photosynthetic reaction centers are positioned at precise distances and orientations relative to one another to promote efficient photoinduced charge separation and to impede charge recombination.¹⁻³ However, the nature of the medium that lies between each donor-acceptor pair is thought to have a large influence on the observed rates of electron transfer. For example, in the bacterial photosynthetic reaction center a bacteriochlorophyll (BChl) molecule lies between the dimeric bacteriochlorophyll donor (BChl₂) and the bacterio-*p*-heophytin (BPh) acceptor. The π systems of these chromophores lie at large angles relative to one another (about 70°) in an approximate edge-to-edge configuration. It is thought that superexchange, which mixes low-lying, ionic, virtual states involving the intermediate BChl with the locally excited state of the donor, may lead to a greatly increased rate of charge separation.⁴⁻⁷ Recently, both photochemical holeburning experiments⁸⁻¹¹ and Stark effect spectroscopy^{12,13} on reaction centers have been reported. The results of these experiments suggest that excitation of BChl₂ produces an excited state with significant charge-transfer (CT) character. A recent study of reaction centers from the His^{M200} → Leu mutant of *Rb. capsulatus* in which the BChl₂ donor is replaced by a BChl-BPh heterodimer shows that excitation of the heterodimer results in a 50% quantum yield of nonradiative decay to ground state with a 30 ps time constant.¹⁴ Several femtosecond transient absorption experiments on native reaction centers show no evidence for intradimer charge-separated intermediates.¹⁵⁻¹⁷ However, a recent femtosecond experiment suggests that an electron may reside for a short time on the BChl that lies between the dimer and the BPh acceptor in reaction centers.¹⁸

Recent papers have presented model systems which address the issue of whether superexchange results in increased rates of electron transfer in multichromophore donor-acceptor molecules.¹⁹⁻²¹ However, the impact of low-lying virtual states possessing CT character on the photophysics of porphyrin and chlorophyll donor-acceptor molecules remains unclear. We re-

cently demonstrated that a chlorophyll dimer can undergo solvent-induced symmetry breaking within the excited singlet manifold.²² The result of this symmetry breaking is enhanced nonradiative decay of the excited state without the appearance of distinct charge-separated intermediates as monitored by transient absorption spectroscopy. Strictly speaking, CT state formation within a symmetric dimer is symmetry forbidden. However, charge resonance states which result from a linear combination of the two dimer CT states can be populated.²³

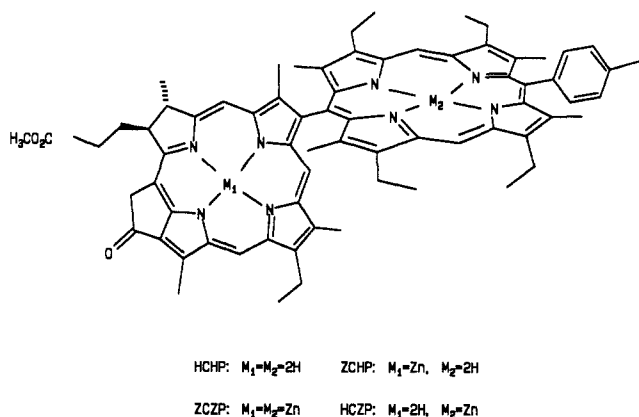
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Selective solvation of dimers can break their symmetry by providing a different electronic environment for each of the two chromophores and thereby promote the population of CT states. A well-characterized example of a molecule which undergoes solvent-induced symmetry breaking is the symmetric bichromophore 9,9'-bianthryl.^{24,25} Since solvation is adequate to destroy the symmetry and promote the population of CT states in model systems, it is reasonable that similar environmental asymmetries¹ in the reaction center protein surrounding the dimeric donor can promote mixing of CT states with the locally excited singlet state of the dimer. However, mixing of charge resonance states of the dimer with its lower exciton state would not depend strongly on these local asymmetries.²³

In order to better understand the influence of low-lying CT states on the observable photophysics of chlorophyll and porphyrin donor-acceptor molecules we have prepared a series of chlorophyll-porphyrin molecules in which the two macrocycles are positioned at a fixed distance and orientation relative to one another. Molecules HCHP, ZCHP, HCZP, and ZCZP possess a chlorophyll molecule rigidly bound to a porphyrin such that the π systems of both macrocycles are constrained by steric interactions to be perpendicular to one another. This geometry was chosen to mimic approximately the geometric relationship between the BChl₂ donor and the intermediary BChl within photosynthetic reaction centers.



Results

Synthesis. The structures of HCHP, HCZP, ZCHP, and ZCZP are shown in the labeled drawing. The porphyrinogen of HCHP was prepared from methyl pyropheophorbide *d* and *p*-tolualdehyde in a condensation reaction with the appropriate dipyrromethane.²⁶ Favorable conditions to promote the condensation reaction were based on the method presented recently by Lindsey for sterically hindered porphyrins.²⁷ Formation of HCHP from the porphyrinogen was carried out by room-temperature oxidation with chloranil.

We found that the porphyrin ring in HCHP metalates selectively with $ZnOAc_2$ in $CHCl_3/MeOH$ at room temperature to yield HCZP. Warming the same solution to reflux results in double metalation to yield ZCZP. If ZCZP is treated with small amounts of dichloroacetic acid, the porphyrin loses its Zn atom much more rapidly than the chlorin ring. Thus, ZCHP is readily obtained from ZCZP. Varying the metalation state of the macrocycles results in well-defined changes in the redox potentials of the macrocycles.

The proton NMR spectra of HCHP, ZCHP, HCZP, and ZCZP are solvent independent. The methyl groups at the 3 and 7 positions of the porphyrin buttress the chlorophyll and fix the plane of the chlorophyll macrocycle perpendicular to that of the porphyrin.²⁸ Rotation about the single bond joining the porphyrin

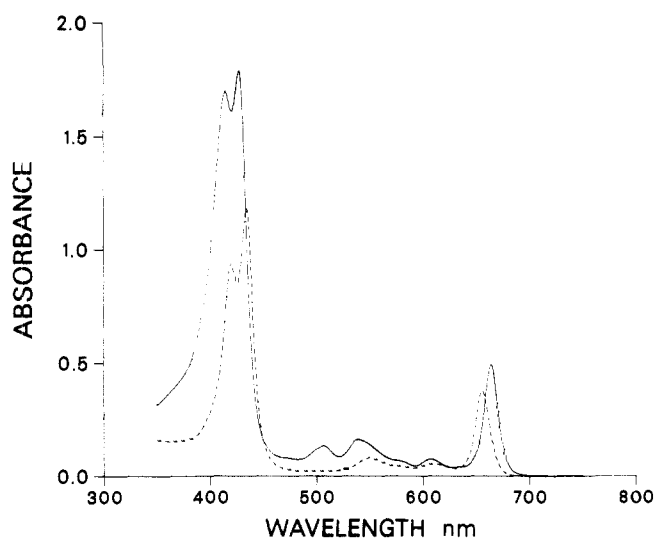


Figure 1. Ground-state absorption spectra of HCZP (—) (10^{-5} M) and ZCZP (---) (6×10^{-6} M) in butyronitrile.

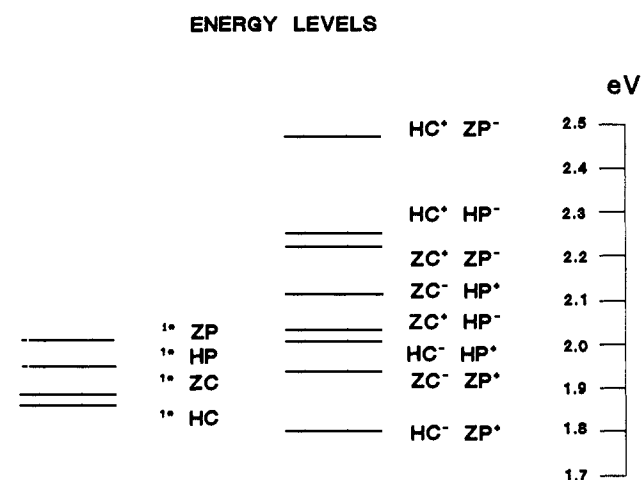


Figure 2. Energy level diagrams for low-lying locally excited singlet states and charge-transfer states of HCHP, HCZP, ZCHP, and ZCZP in butyronitrile.

to the chlorin is completely restricted.

Photophysics. The ground-state optical absorption spectra of ZCZP and HCZP are shown in Figure 1. It is immediately apparent that the spectra of both molecules are a superposition of the respective spectra of the porphyrin and chlorin moieties with two Soret bands and distinct Q bands for each macrocycle. Since the energy levels of the chlorin and porphyrin macrocycles are nonresonant, exciton splittings of the optical absorption bands are not observed. The Q_y band of the chlorin rings in HCZP and ZCZP occur at 669 and 654 nm, respectively, and are only 1–2 nm blue-shifted from the respective bands in free base and zinc methyl pyropheophorbide *a*. Similarly, the (0,0) fluorescence emission bands of HCZP and ZCZP occur at 674 and 660 nm, respectively, and are also only 1–2 nm blue-shifted from the corresponding bands in free base and zinc methyl pyropheophorbide *a*. Thus, the π systems of the two macrocycles are only weakly coupled. The prominence of the Q bands of the chlorin make it possible to selectively excite the chlorin in our experiments. At 610 nm, the wavelength of our laser excitation experiments, the ratio of chlorin/porphyrin absorbance is >25 for ZCZP and about 8 for HCZP. In addition, we can use the distinct spectroscopic signature of the Soret bands to detect the involvement of chlorin or porphyrin states in the overall excited state description of these molecules.

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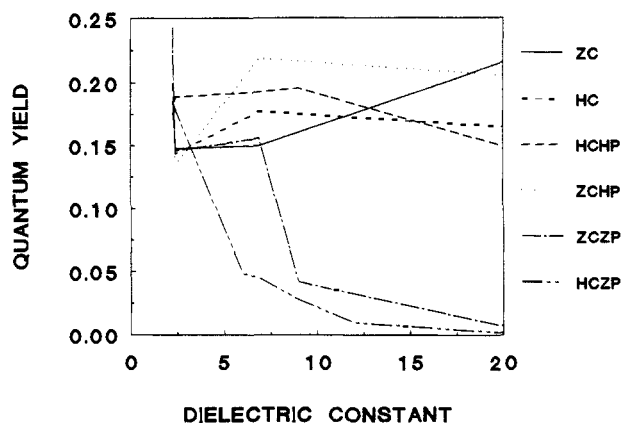


Figure 3. Dependence of fluorescence quantum yields on solvent dielectric constant for the indicated compounds.

Table I. Fluorescence Decay Times (ns)^a

solvent	ZC	HC	ZCZP	HCZP
dioxane	7.68 ± 0.04	11.5 ± 0.5	4.66 ± 0.03	8.2 ± 0.3
toluene	3.14 ± 0.01	10.5 ± 0.5	3.43 ± 0.01	8.5 ± 0.3
ether	5.97 ± 0.01	10.3 ± 0.5	3.69 ± 0.01	11.9 ± 0.9
EtOAc	5.94 ± 0.01	10.2 ± 0.5	2.61 ± 0.01	1.49 ± 0.01
MTHF	5.90 ± 0.01	10.8 ± 0.5	3.22 ± 0.01	2.06 ± 0.01
CH ₂ Cl ₂	3.33 ± 0.01	9.0 ± 0.4	0.87 ± 0.01	0.41 ± 0.01
pyridine	6.18 ± 0.02	10.7 ± 0.5	0.29 ± 0.01	0.0161 ± 0.0006
butyro-nitrile	6.00 ± 0.01	9.4 ± 0.4	0.119 ± 0.001	0.0070 ± 0.0006
DMF	6.63 ± 0.01	7.9 ± 0.3	0.052 ± 0.001	0.0049 ± 0.0008

^a Fluorescence was detected between 650 and 700 nm. No wavelength dependences of the lifetimes were observed.

Figure 2 shows the energy levels of the locally excited states of the chromophores within HCHP, ZCHP, HCZP, and ZCZP and several hypothetical CT states. The energies of the excited states are determined from the position of the (0,0) band of the fluorescence emission, while the hypothetical CT state energies are estimated from a simple sum of the one-electron oxidation and reduction potentials of the chromophores in butyronitrile. These CT state energies are reasonable estimates only in highly polar media, where the ions are strongly solvated and the coulombic interaction between the ions is small. Two important features of the energetics of these molecules can be noted from these data. First, most of the predicted CT states are low-lying, i.e., energetically close to S₁. Second, only HC⁻ZP⁺ is below the locally excited singlet states of the chromophores. The next lowest lying state belongs to ZC⁻ZP⁺. Thus, one might expect HCZP and ZCZP to show the greatest perturbation of their locally excited singlet states by mixing with the CT states.

Figure 3 gives the fluorescence quantum yields of HCHP, ZCHP, HCZP, and ZCZP along with the zinc and free base methyl pyropheophorbide *a* reference compounds. Since we found that energy transfer from the porphyrin to the chlorin in each of these molecules proceeds in times <1 ps, the locally excited singlet state resides on the chlorin. The only compounds in the series that show solvent polarity dependent fluorescence quantum yields are HCZP and ZCZP. The emission from both molecules is strongly quenched in polar media. The static dielectric constant required to diminish the emission yield of ZCZP is somewhat higher than that of HCZP. Table I presents fluorescence lifetime data for ZCZP and HCZP in the same solvents used to obtain the quantum yield data. It is immediately obvious from Figure 3 and Table I that the reduction in emission quantum yield closely parallels the observed decrease in fluorescence lifetime as the solvent polarity increases. This suggests that increasing the solvent polarity results in a new nonradiative channel that competes with radiative decay. The nature of this channel can be examined by looking for transient spectral changes which arise following excitation of HCZP and ZCZP.

Figure 4A,B shows the transient absorption difference spectrum of ZCZP in toluene ($\epsilon = 2.4$) and in butyronitrile ($\epsilon = 20$) obtained

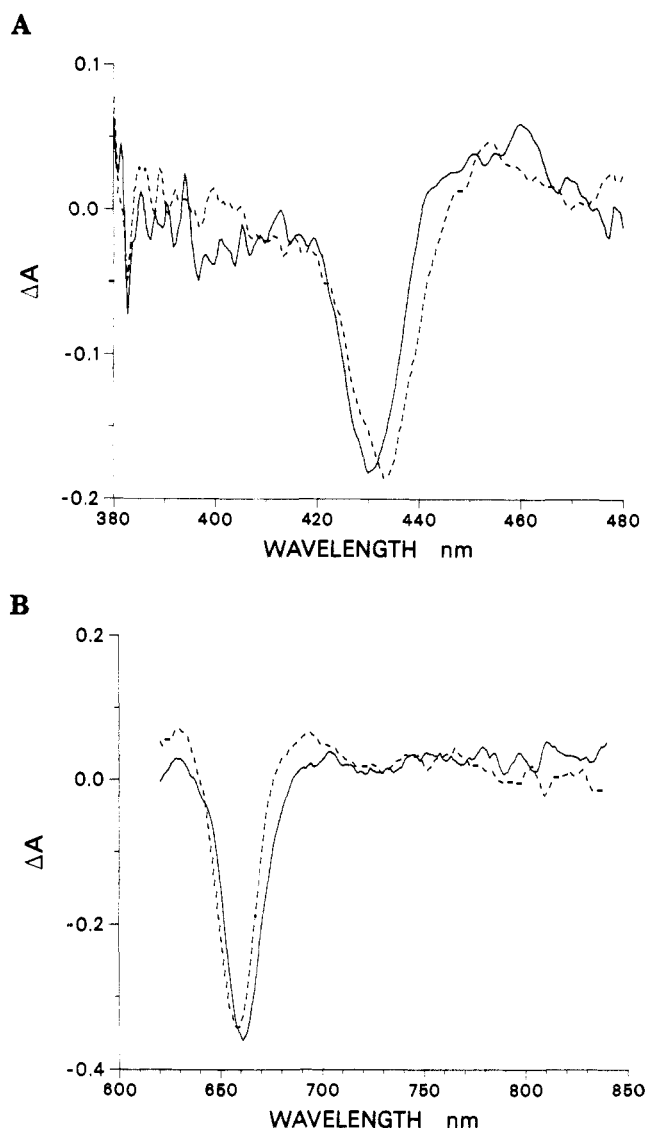


Figure 4. (A) Transient absorption spectrum of ZCZP in toluene (—) and butyronitrile (---) at 20 ps following a 1-ps laser flash at 610 nm. (B) Transient absorption spectrum of ZCZP in toluene (—) and butyronitrile (---) at 20 ps following a 1-ps laser flash at 610 nm.

20 ps after a 1 ps laser flash at 610 nm. In both solvents the Soret band due to the chlorin chromophore at 430 nm bleaches within the 1 ps time of the laser flash. There is no evidence for bleaching of the porphyrin Soret band at 414 nm. Similarly, in both solvents, Figure 4B, the Q_y band of the chlorin bleaches immediately upon excitation. There is no evidence of significant absorption in the near-infrared region of the spectrum, where the radical ion states of both porphyrins and chlorins have absorbances.²⁹⁻³¹

Figure 5 shows the recovery of the Q_y band bleach as a function of time. The data show that the excited state recovers much faster in polar media than in nonpolar media, 119 ps vs 3.4 ns, respectively. The excited-state recovery times obtained via transient absorption agree well with those obtained from fluorescence emission decays shown in Table I. Throughout the recovery time of the absorption changes the spectral features illustrated in Figure 4A,B only diminish. No new features or changes in band shape or structure are observed.

Figures 6A,B shows the corresponding transient absorption changes for HCZP in both toluene and butyronitrile. In toluene the transient absorption spectra shown in Figure 6A,B appear with

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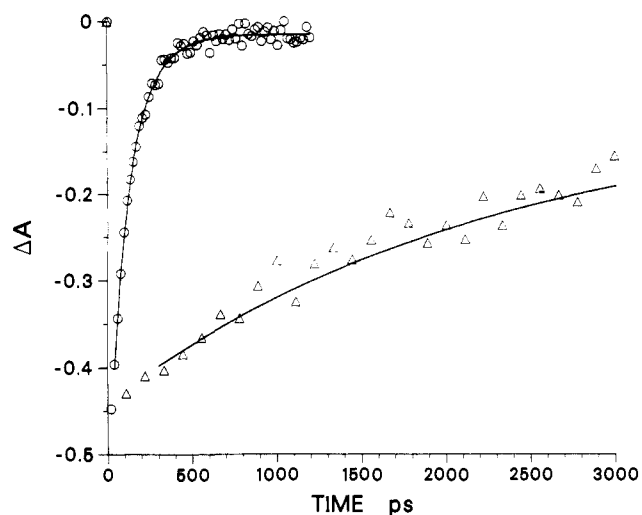


Figure 5. Transient absorption recovery at 660 nm for ZCZP in toluene (Δ) and butyronitrile (O) following a 1-ps, 610-nm laser flash.

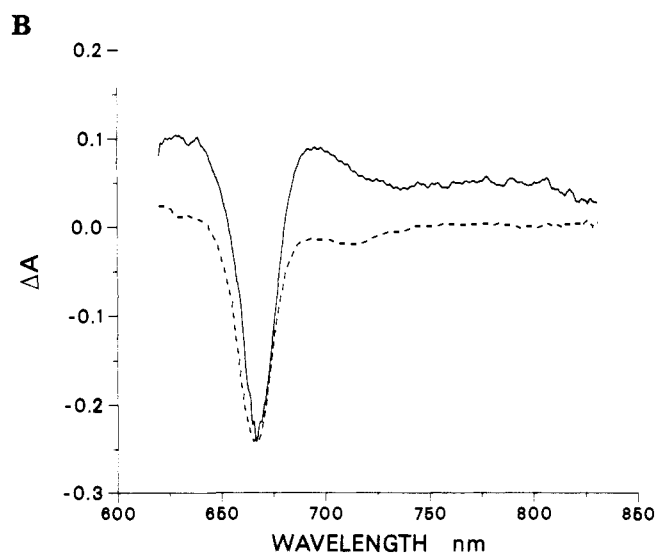
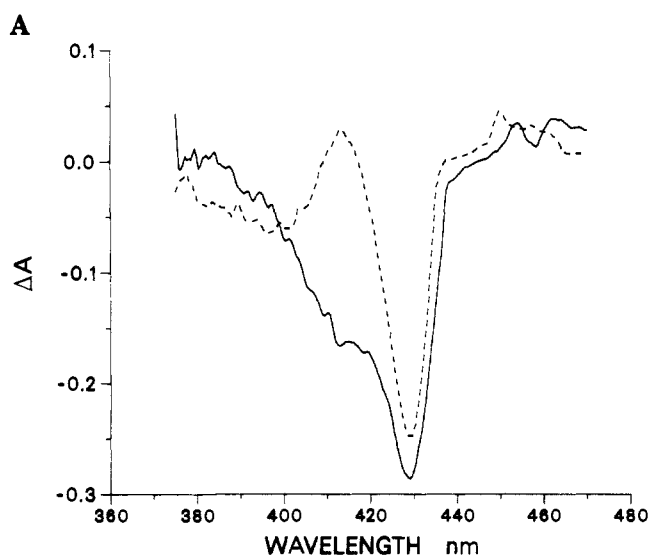


Figure 6. (A) Transient absorption spectrum of HCZP in toluene (---) and butyronitrile (—) at 20 ps following a 1-ps laser flash at 610 nm. (B) Transient absorption spectrum of HCZP in toluene (---) and butyronitrile (—) at 20 ps following a 1-ps laser flash at 610 nm.

the laser flash and decay with an 8.5 ns time constant. The spectral features show only involvement of the chlorin ring in the excited state and no evidence of ion-pair intermediates in the

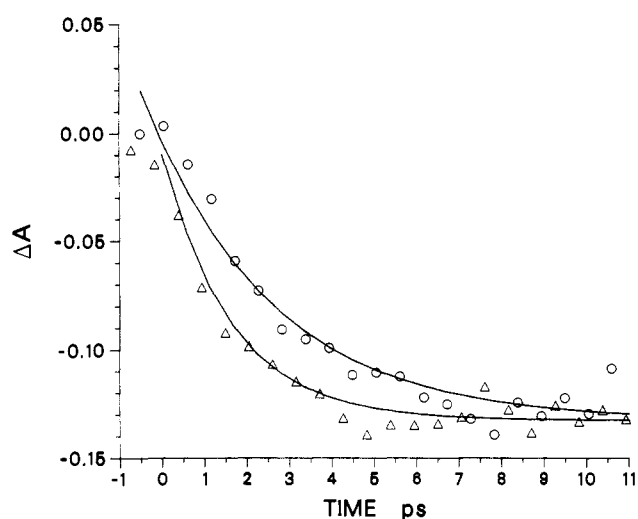


Figure 7. Transient absorption changes at 414 nm (O) and at 430 nm (Δ) for HCZP in butyronitrile following a 1-ps laser flash at 610 nm.

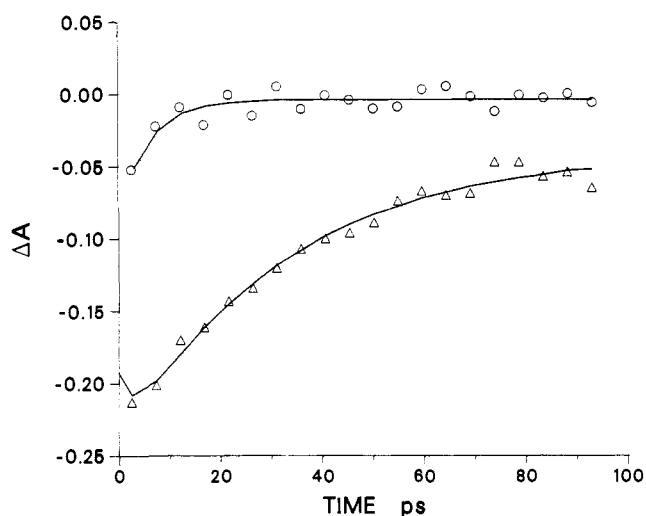


Figure 8. Stimulated emission decay at 685 nm (O) and transient absorption decay at 670 nm (Δ) for HCZP in butyronitrile following a 1-ps, 610-nm laser flash.

near-infrared region of the spectrum. On the other hand, when HCZP is excited in butyronitrile, it is apparent that the Soret bands from both the porphyrin and the chlorin are bleached. The chlorin bleach at 430 nm appears within the 1-ps laser flash and is followed by the appearance of the porphyrin bleach at 414 nm with a time constant of 4 ± 1 ps, Figure 7. We attribute this longer time constant for the appearance of the bleach at 414 nm to the reaction ${}^1\text{HCZP} \rightarrow \text{HC}^-\text{ZP}^+$. The transient absorption changes in the Q_y band region of the spectrum also differ substantially from those observed in toluene. The spectrum of HCZP in toluene, Figure 6B, is similar to that of ZCZP in Figure 4B and gives no indication of significant ion-pair character. On the other hand, in butyronitrile, the broad absorption feature between 625 and 700 nm is characteristic of the porphyrin cation radical,³¹ while the absorption feature at near 800 nm is characteristic of the chlorophyll anion radical.³⁰ Thus, a real ion-pair intermediate is formed following excitation of HCZP in a polar solvent.

Further evidence for the formation of the ion-pair state of HCZP in polar media is presented in Figure 8. The disappearance of ${}^1\text{HCZP}$ can be obtained from the decay of its stimulated emission.³² The weak stimulated emission recovers with a 5 ± 1 ps time constant and is within experimental error of fluorescence lifetime of HCZP under these conditions, Table I, and the ap-

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pearance of the porphyrin Soret band bleach at 414 nm, Figure 7. On the other hand, the absorption changes in the Q_y region of the spectrum attributable to $HC^{\cdot-}ZP^+$ decay with a 43 ± 1 ps time constant, Figure 8. No longerlived states are observed.

Discussion

The photophysical data suggest that rapid, nonradiative decay pathways for the lowest excited singlet states of HCZP and ZCZP are dominant in polar solvents but relatively unimportant in nonpolar media.

In polar solvents electron transfer from ZP to 1HC occurs within HCZP. Placing either HCZP or ZCZP in nonpolar media substantially increases the energies of the CT states. An estimate of this increase can be made by using dielectric continuum theory to obtain the solvation energy of the ions as a function of solvent polarity,³¹ eq 1

$$(\Delta G_{CT})_x = (E_{1/2}^+ - E_{1/2}^-) + (e^2/\epsilon_x)(1/r - 1/r_{12}) - (e^2/\epsilon_m r) \quad (1)$$

where $(\Delta G_{CT})_x$ is the CT state energy in solvent x , $E_{1/2}^+$ and $E_{1/2}^-$ are the half-wave potentials for one-electron oxidation of the donor and reduction of the acceptor, respectively, in polar solvent m , e is the electronic charge, ϵ_x and ϵ_m are the static dielectric constants of solvents x and m , respectively, r is the ionic radius of both ions (assumed to be equal), and r_{12} is the distance between the ions. For two ions with 5 Å radii separated by 10 Å in toluene the CT state energies should lie about 0.46 eV higher than those depicted in Figure 1. Thus, in toluene one expects the energies of $HC^{\cdot-}ZP^+$ and $HC^+ZP^{\cdot-}$ to be at least 0.36 eV above that of 1HCZP , so that ion-pair formation is precluded.

For ZCZP in both toluene and butyronitrile the energies of $ZC^{\cdot-}ZP^+$ and $ZC^+ZP^{\cdot-}$ should be above that of 1ZCZP . In toluene the energies of the CT states should be sufficiently above that of the locally excited singlet state to preclude significant interaction between these states. Two types of mechanism may account for the data: first, the fluorescence quenching in ZCZP may be explained by postulating the formation of a pure CT state of ZCZP. Alternatively, solvent polarity dependent mixing of CT character into the locally excited state of ZCZP may enhance nonradiative transitions between the mixed excited state and the ground state.

The formation of intramolecular charge-transfer states in symmetric bichromophoric molecules is a well-known phenomenon.^{24,25} For example, excitation of 9,9'-bianthryl in nonpolar solvents results in a fluorescence emission spectrum similar to that of anthracene. However, as the polarity of the solvent increases, a second emission band appears at a wavelength which is red-shifted relative to that of the original band. The red-shifted emission band moves to longer wavelength as the solvent polarity increases. In addition, the quantum yield of the red-shifted emission grows at the expense of the quantum yield of the original band. The red-shifted emission results from an intramolecular charge-transfer state of 9,9'-bianthryl that is stabilized by the polar solvent. Formation of this CT state is a result of rotation about the 9,9' single bond joining the two anthracenes. This rotation results in minimal overlap between the π systems of both anthracenes. The term "twisted intramolecular charge-transfer" (TICT) state has been used to describe this type of CT state. The criterion for TICT state formation within a bichromophoric molecule has been described as the "rule of minimum overlap".³⁴ In a symmetric bichromophore, TICT state formation is favored when the two chromophores are unable to adopt a conformation in which their π systems are face-to-face but are able to twist into a conformation in which the two π systems are orthogonal. This criterion is opposite to that for excimer formation, where the greatest stabilization is generally obtained when the two chromophores are able to maximize their π overlap. The structures of HCHP, ZCHP, HCZP, and ZCZP are all ideal for TICT state formation. The methyl groups at the 3- and 7-positions on the

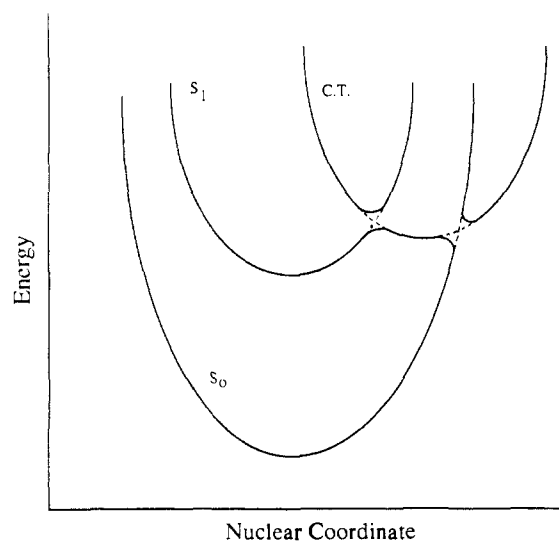


Figure 9. Potential energy surfaces for ZCZP.

porphyrin hold the chlorin ring perpendicular to the porphyrin. Therefore, it is sterically impossible for the π systems of the chlorophyll and the porphyrin in these molecules to achieve large overlap.

In a CT or TICT state the asymmetric charge distribution in the molecule results in a dipole moment that interacts strongly with solvent dipoles. As solvent polarity increases, the CT or TICT state is stabilized. Since the λ_{max} of emission from ZCZP is essentially independent of solvent polarity, the fluorescence of ZCZP at 660 nm is not due to an emissive CT or TICT state. Yet, as the solvent polarity increases, the quantum yield of emission from the 660-nm band decreases greatly. Despite intensive efforts, we have never observed emission from charge-separated states involving chlorophyll or porphyrin containing donor-acceptor molecules that are known to form radical ion pairs in high quantum yield.³⁵ Therefore, we hypothesize that the TICT state of ZCZP decays entirely nonradiatively. However, this hypothesis requires the energy of the TICT state to be below that of S_1 . An estimate of the energy of a hypothetical TICT state in ZCZP can be obtained from our electrochemical data and is shown in Figure 2. The sum of the one-electron redox potentials of ZCZP in polar media suggests that the TICT state energy is probably no lower than about 1.95 eV. This is 0.08 eV above the observed lowest excited singlet state energy of ZCZP. Dissolving ZCZP in low polarity media such as toluene serves only to increase the energy of the TICT state, thereby increasing the energy gap between this state and S_1 . Placement of the TICT state of ZCZP above S_1 is consistent with the transient absorption and emission data obtained for ZCZP. The transient spectra of ZCZP shown in Figures 4A,B show no evidence of ion pairs as the solvent polarity increases.

It is possible that nonradiative transitions between S_1 and S_0 in ZCZP are enhanced by mixing of a low-lying CT (or TICT) state at about 1.95 eV into S_1 at 1.87 eV. A small amount of mixing could result in significant enhancement of the nonradiative decay rate in ZCZP without the appearance of large changes in the excited-state absorption spectrum. Nonradiative decay from $S_1 \rightarrow S_0$ in chlorophylls is relatively inefficient. Internal conversion accounts for no more than 15% of excited-state decay. Ab initio SCF-MO-CI calculations of both S_0 and S_1 for ethyl chlorophyllide *a* show that the π electron populations at each atom in the π system do not differ significantly between S_0 and S_1 .³⁶ The similar electron distributions for S_0 and S_1 suggest that the potential surfaces of these states form a nested pair, Figure 9. The absence of a crossing point between the surfaces of S_0 and S_1

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results in a very small Franck-Condon factor with a consequent low rate of internal conversion.

On the other hand, addition or removal of an electron from either the chlorophyll or metalloporphyrin ring in ZCZP results in significant changes in the overall π electron distribution within these macrocycles.^{37,38} Moreover, these changes in π electron distribution also differ from the π electron distribution in both S_0 and S_1 . In particular, for the CT state ZC^-ZP^+ the π electron distribution within the reduced chlorophyll ZC^- is very asymmetric with most of the unpaired electron density concentrated along the ring A-C axis. Rings B and D have relatively little π electron density. Within the oxidized porphyrin ZP^+ the π electron density is more or less evenly distributed around the periphery of the macrocycle. The changes in electron density distribution in ZC^-ZP^+ relative to both ZCZP and 1ZCZP should result in a corresponding displacement of the nuclei in the CT state relative to those in the excited and ground states, Figure 9.

If the CT state of ZCZP is low-lying in polar solvents as is suggested by our electrochemical data, the potential energy surface for the CT state may intersect the surfaces of both S_1 and S_0 . Semiclassical electron-transfer theory³⁹ can be used to calculate the magnitude of the electronic coupling between the chlorin and porphyrin. By using the free energy and electron-transfer rate data for HCZP in butyronitrile the electronic coupling between these two macrocycles is on the order of 25–50 cm^{-1} . Thus, the surface crossings may be avoided resulting in a relatively smooth pathway for nonradiative deactivation of S_1 to S_0 .

The photophysical properties of ZCZP and HCZP can be compared directly with those of the BChl₂ dimer in wild-type reaction centers and the BChl-BPh heterodimer in the His^{M200} → Leu mutant of *Rb. capsulatus*. As mentioned in the Introduction there is no evidence for the formation of BChl⁻-BChl⁺ ion pairs in the BChl₂ dimer. However, both Stark spectroscopy and photochemical hole-burning experiments suggest that a low-lying, virtual CT state of the dimer is mixed with the lowest excited singlet state of the dimer. Our results on the ZCZP molecule show that the presence of a low-lying CT state about 0.1 eV above the lowest excited singlet state of ZCZP strongly influences the rate of nonradiative decay of ZCZP without the appearance of an ion-pair state. Some years ago Holten et al. measured the lifetime of 1BChl_2 in *Rp. viridis* reaction centers for which the BPh_L acceptor was prerduced.⁴⁰ They found that the lifetime of 1BChl_2 was only 20 ps. This contrasts with the typical 2 ns lifetimes of bacteriochlorophyll excited singlet states in vitro.⁴¹ Thus, it appears that the BChl₂ dimer in reaction centers may also possess an enhanced nonradiative decay path similar to that found in ZCZP. Holten et al. have shown that the heterodimer BChl-BPh in the mutant reaction centers undergoes internal electron transfer to yield the spectroscopically observable intermediate BChl⁻-BPh⁺.⁴² The decay of this intermediate partitions between about 50% charge recombination to ground state and about 50% further electron transfer from the BPh⁺ within the heterodimer to the BPh_L electron acceptor in the reaction center. The 30 ps charge recombination reaction $BChl^+-BPh^- \rightarrow BChl-BPh$ is similar to that found in HCZP which undergoes rapid charge recombination $HC^-ZP^+ \rightarrow HCZP$ in 43 ps. In both BChl-BPh and HCZP real ion-pair states of these heterodimers are observed directly by transient absorption spectroscopy. This suggests that both species form ion pairs with energies that are slightly below the energies of their respective lowest excited singlet

states. The strong photophysical analogies between the reaction center dimers and heterodimers with ZCZP and HCZP, respectively, suggest that it will be useful to further study ZCZP and HCZP by using Stark spectroscopy and photochemical hole-burning techniques. These techniques can be used to examine in more detail the influence of low-lying CT states on the photophysics of these molecules.

Conclusion

The chlorophyll-porphyrin molecules described in this paper are sensitive probes of their solvation environment. Our data show that two large π macrocycles, which are electronically coupled, may exhibit enhanced rates of nonradiative decay as a function of increasing solvent polarity. Enhanced nonradiative decay need not require the formation of real, spectroscopically observable ion-pair states. It is sufficient to mix CT character into the excited-state description of the macrocycles. Our ability to manipulate the energy level of the CT state within these model dimers allows us to gain further insight into the photophysics of both the wild-type and mutant primary donors in photosynthetic bacteria.

Experimental Section

Physical Measurements. Solvents for all spectroscopic experiments were dried and stored over 3 Å molecular sieves. HPLC grade toluene was distilled from LiAlH₄ (LAH). Butyronitrile was refluxed over KMnO₄ and Na₂CO₃ and then twice distilled retaining the middle portion each time. 2-Methyltetrahydrofuran (MTHF) was freshly distilled from LAH before each experiment.

Proton NMR spectra were obtained on a 300-MHz Bruker spectrometer. UV-visible absorption spectra were taken on a Shimadzu UV-160. Fluorescence spectra were obtained by using a Perkin-Elmer MPF-2A fluorimeter interfaced to a PDP 11/34 computer. All samples for fluorescence were purified by preparative TLC on Merck silica gel plates. Samples for fluorescence measurements were 10⁻⁷ M in 1-cm cuvettes. The emission was measured 90° to the excitation beam. Fluorescence quantum yields were determined by integrating the digitized emission spectra from 600 to 800 nm and referencing the integral to that for chlorophyll *a* in diethyl ether.⁴³

Redox potentials for HCHP, HCZP, ZCHP, and ZCZP were determined in butyronitrile containing 0.1 M tetra-*n*-butylammonium perchlorate by using a Pt disc electrode at 21°. These potentials were measured relative to a saturated calomel electrode by using ac voltammetry.⁴⁴ Both the one-electron oxidations and reductions of these molecules exhibited good reversibility.

The transient absorption spectra were obtained by using a Rh-6G dye laser synchronously pumped by a frequency-doubled, mode-locked CW Nd:YAG laser. The 1.0-ps pulses of 610-nm light were amplified by a four-stage dye amplifier (Rh-640) pumped by the frequency doubled output (532 nm) of a Nd:YAG laser. Malachite green saturable absorber dye jets between stages 2 and 3 and between stages 3 and 4 of the amplifier chain minimized the amplified stimulated emission generated in the amplifier. The amplification produced a 1 mJ/pulse at 10 Hz. This beam was sent through a 60/40 beam splitter. The smaller portion was focused down to a 2-mm diameter beam and used as the excitation pulse. The larger portion was tightly focused into a 2-cm path length cell containing either 2/1 CCl₄/CHCl₃ or 1/1 H₂O/D₂O. This generated a continuum which was used as the probe light. The arrival at the sample of the probe beam was delayed relative to the excitation beam by an optical delay. The probe beam was divided into reference and measuring beams by a 50/50 beam splitter. Both probe beams passed through the sample. The reference beam passed through an area that was not illuminated by the excitation beam, while the measuring beam passed through the same portion of the sample through which the excitation beam passed. Both beams were then focused onto the slit of a monochromator. The monochromator dispersed the beams onto the face of an intensified SIT detector which was part of an optical multichannel analyzer (PAR OMA 11). Solutions with an absorbance of about 0.15 at 610 nm (2-mm path length cells) were used.

Fluorescence lifetime measurements used 1.0-ps, 2-mm diameter, 200- μ J pulses from the same source as described for the transient absorbance experiments. The samples were placed in 0.5-cm cells (optical density ca. 0.03 at 610 nm), and emission 90° to the excitation was

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collected and focused onto the slit of a Hamamatsu C979 streak camera. The temporally dispersed image was recorded by the intensified SIT vidicon of the PAR OMA 11. The geometry of the experimental setup determined the 15-ps instrument response. Decay times were obtained by iterative reconvolution of the data with least-squares fitting by using the Levenberg-Marquardt algorithm.

Syntheses. Methyl Porphoporphorbide *d*. A solution of 4.75 g of NaIO₄ in 30 mL of H₂O and 2 mL of acetic acid was added with a syringe pump at a rate of 1 mL/min to 400 mL of dioxane containing 2.0 g of methyl pyroporphorbide *d*⁴⁵ and 40 mg of OsO₄. The reaction mixture was stirred overnight at room temperature. The reaction was poured into water, extracted with chloroform, dried over Na₂SO₄, and filtered, and the solvents were evaporated. The residue was chromatographed on silica gel in 15% acetone/CCl₄ to yield 1.3 g (65%) methyl pyroporphorbide *d*: ¹H NMR (CDCl₃) δ -2.34 (br s, N-H), δ 1.60 (t, 4b-H), δ 1.85 (d, 8a-H), δ 2.58 (m, 7a-H), δ 2.70 (m, 7b-H), δ 3.12 (s, 3-Me), δ 3.52 (m, 4a-H), δ 3.59 (s, 5-Me), δ 3.63 (s, 1-Me or CO₂Me), δ 3.68 (s, 1-Me or CO₂Me), δ 4.35 (m, 7a-H or 8-H), δ 4.54 (m, 7a-H or 8-H), δ 5.23 (dd, 10-H), δ 8.75 (s, δ-H), δ 9.33 (s, β-H), δ 10.00 (s, α-H), δ 11.38 (s, 2a-H); electronic spectrum (acetone), λ_(max) (rel ε) 689.5 nm (0.74), 628.5 (0.08), 549.5 (0.14), 517.5 (0.15), 423.5 (1.00), 384.5 (0.83).

4,4'-Diethyl-3,3'-dimethyldipyrromethane. Dibenzyl 4,4'-diethyl-3,3'-dimethyldipyrromethane-2,2'-dicarboxylate²⁴ (4.0 g, 8.02 × 10⁻³ mol) was dissolved in 150 mL of tetrahydrofuran, 0.5 g of 10% Pd/C was added, and the mixture was purged with nitrogen for 5 min. Triethylamine (0.5 mL) was added, and the mixture was hydrogenolyzed in a Parr shaker at 40 psi for 2 h. The mixture was purged again with nitrogen, 0.5 g more of catalyst was added, and the mixture was further hydrogenolyzed at 40 psi for another 2 h. The process was repeated a third time after which the mixture was purged with nitrogen and suction filtered on a medium frit to remove the 1.5 g of catalyst. The organic layer was stripped on a rotary evaporator leaving a white solid, which could be stored in a freezer without decomposition. This solid was dissolved in dried ethanolamine (70 mL) and refluxed for 30 min. It was then cooled to room temperature, 100 mL of methylene chloride was added, and the solution was poured into water. The organic layer was washed 4 times with 300 mL of water each time and dried over anhydrous potassium carbonate. It was stripped to dryness leaving an oil which was quickly chromatographed on Merck silica gel 60 with methylene chloride. All fractions which turned grey when spotted on a silica gel TLC plate and viewed under a short wavelength UV lamp were combined and stripped on a rotary evaporator: yield 1.44 g, 78%; NMR (CDCl₃) δ ~ 7.38 (br s, ~2 H), 6.365 (s, 2 H), 3.823 (s, 2 H), 2.441 (q, 4 H, *J* = 7.6 Hz), 2.050 (s, 6 H), 1.099 (t, 6 H, *J* = 7.4 Hz).

HCHP. A 2.5-mL portion of a stock solution of 4,4'-diethyl-3,3'-dimethyldipyrromethane (1.44 g in 10 mL chloroform) (0.36 g, 1.5 × 10⁻³ mol), *p*-tolualdehyde (0.18 g, 1.5 × 10⁻³ mol), and methyl pyroporphorbide *d* (0.4 g, 7.25 × 10⁻⁴ mol) was added to 150 mL of chloroform under nitrogen with stirring at room temperature. The solution was purged with nitrogen for ~2 min. Boron trifluoride etherate (0.2 mL) was added, and the mixture was stirred for 2 h. The reaction was conveniently followed by TLC in 10% acetone in chloroform (v/v). A greenish-brown band (*R_f* ~ 0.7) formed quickly. This was the porphyrinogen precursor to the product. Chloranil (0.35 g, 1.5 × 10⁻³ mol) was added, and the mixture was stirred for 0.5 h. The organic layer was then stripped on a rotary evaporator and column chromatographed with 5% acetone in methylene chloride (v/v). All fractions containing the product were rechromatographed with 2% acetone in methylene chloride (v/v) 0.105 g isolated, 12% yield: electronic spectrum (CH₂Cl₂) λ_(max) (rel ε) 412 (1.000), 427 (0.923), 509.5 (0.138), 537 (0.065), 571.5 (0.045), 608.5 (0.048), 667.0 (0.296); NMR (CDCl₃) δ (*p*-tolyl group) 8.01 (d, 1 H, *J* = 7.9 Hz), 7.95 (d, 1 H, *J* = 7.8 Hz), 7.58 (d, 2 H, *J* = 7.8 Hz), 2.75 (s, 3 H); (porphyrin) 10.34 (s, 2 H), 4.07 (q, 4 H, *J* = ~7.4 Hz), ~3.92 (m, 4 H), 2.57 (s, 6 H), 1.91 (s, 3 H), 1.87 (s, 3 H), 1.82 (t, 6 H, *J* = 7.6 Hz), 1.68 (t, 6 H, *J* = 7.13 Hz); (phorbin) 9.50 (s, 1 H), 8.89 (s, 1 H), 8.84 (s, 1 H), 5.40 and 5.24 (AB quartet, 2 H, *J* = 20.1 Hz), 4.47 (d, 1 H, *J* = 8.6 Hz), 4.69 (q, 1 H, *J* = 7.1 Hz), 4.47 (d, 1 H, *J* = 8.6 Hz), 3.71 (s, 3 H), 3.68 (s, 3 H), ~2.80 (m, 3 H), ~2.48 (m, 2 H), 2.23 (s, 3 H), 2.03 (d, 3 H, 7.2 Hz); ring NH's -1.00 (br s, 2 H).

= 8.6 Hz), 3.72 (s, 3 H), 3.69 (s, 3 H), 3.47 (q, 2, *J* = 7.5 Hz), 3.18 (s, 3 H), ~2.80 (m, 3 H), ~2.48 (m, 2 H), 2.23 (s, 3 H), 2.03 (d, 3 H, 7.2 Hz); ring NH's -1.00 (br s, 4 H); mass spectrum (FAB) calcd 1088 (M), found 1092 (M + 4).

HCZP. HCHP (50 mg, 4.6 × 10⁻⁵ mol) was dissolved in a mixture of 3/1 v/v chloroform/methanol (25 ml) with stirring under nitrogen. Zinc acetate dihydrate (10 mg, 4.6 × 10⁻⁵ mol) was added, and a rapid color change from green-brown to red-brown occurred. The porphyrin ring now contains zinc. The reaction mixture was poured into water and extracted with chloroform, and the organic layer was washed twice with water, dried over anhydrous potassium carbonate, and stripped on a rotary evaporator. Preparatory TLC on C₁₈-reverse phase plates and elution with 20% chloroform in methanol separated the HCZP from minor amounts of HCHP, ZCHP, and ZCZP: yield 87%; electronic spectrum (CH₂Cl₂) λ_(max) (rel ε) 413.5 (1.000), 430 (0.928), 505.5 (0.062), 538 (0.097), 608.5 (0.026), 668.5 nm (0.280); NMR (CDCl₃) δ (*p*-tolyl group) 8.01 (d, 1 H, *J* = 7.9 Hz), 7.94 (d, 1 H, *J* = 7.9 Hz), 7.94 (d, 1 H, *J* = 7.8 Hz), 7.58 (d, 2 H, *J* = 7.8 Hz), 2.75 (s, 3 H); (porphyrin) 10.29 (s, 2 H), 4.07 (q, 4 H, *J* = ~7.4 Hz), ~3.87 (m, 4 H), 2.56 (s, 6 H), 1.90 (s, 3 H), 1.86 (s, 3 H), 1.81 (t, 6 H, *J* = 7.6 Hz), 1.67 (t, 6 H, *J* = 7.13 Hz); (phorbin) 9.51 (s, 1 H), 8.892 (s, 1 H), 8.72 (s, 1 H), 5.40 and 5.23 (AB quartet, 2 H, *J* = 20.1 Hz), 4.47 (d, 1 H, *J* = 8.6 Hz), 4.69 (q, 1 H, *J* = 7.1 Hz), 4.47 (d, 1 H, *J* = 8.6 Hz), 3.71 (s, 3 H), 3.68 (s, 3 H), 3.46 (q, 2 H, *J* = 7.5 Hz), 3.17 (s, 3 H), ~2.80 (m, 3 H), ~2.48 (m, 2 H), 2.23 (s, 3 H), 2.02 (d, 3 H, 7.2 Hz); ring NH's ~-1.00 (br s, 2 H).

ZCZP. HCHP (50 mg, 4.6 × 10⁻⁵ mol) was dissolved in a mixture of 3/1 v/v chloroform/methanol (25 ml) with stirring under nitrogen. Zinc acetate dihydrate (10 mg, 4.6 × 10⁻⁵ mol) was added, and the solution was refluxed for 1 h. A deep green color signified that both the chlorin and porphyrin rings were both metalated. The workup was identical with that of HCZP above: yield 98%; electronic spectrum (CH₂Cl₂) λ_(max) (rel ε) 414.5 (1.000), 428.0 (1.087), 543.5 (0.087), 607.5 (0.064), 654 (0.332); NMR (CDCl₃) δ (*p*-tolyl group) 8.01 (d, 1 H, *J* = 7.9 Hz), 7.94 (d, 1 H, *J* = 7.8 Hz), 7.58 (d, 2 H, *J* = 7.8 Hz), 2.75 (s, 3 H); (porphyrin) 10.29 (s, 2 H), 4.07 (q, 4 H, *J* = ~7.4 Hz), ~3.87 (m, 4 H), 2.57 (s, 6 H), 1.90 (s, 3 H), 1.86 (s, 3 H), 1.81 (t, 6 H, *J* = 7.6 Hz), 1.67 (t, 6 H, *J* = 7.13 Hz); (phorbin) 9.58 (s, 1 H), 8.73 (s, 1 H), 8.71 (s, 1 H), 5.40 and 5.24 (AB quartet, 2 H, *J* = 20.1 Hz), 4.47 (d, 1 H, *J* = 8.6 Hz), 4.69 (q, 1 H, *J* = 7.1 Hz), 4.47 (d, 1 H, *J* = 8.6 Hz), 3.71 (s, 3 H), 3.68 (s, 3 H), 3.46 (q, 2 H, *J* = 7.5 Hz), 3.17 (s, 3 H), ~2.80 (m, 3 H), ~2.48 (m, 2 H), 2.23 (s, 3 H), 2.03 (d, 3 H, 7.2 Hz).

ZCHP. ZCZP (10 mg, 9 × 10⁻⁶ mol) was dissolved in methylene chloride (10 mL). Dichloroacetic acid (10 μL) was added with stirring. A light green color occurred immediately signifying release of the zinc from the porphyrin ring. The solution was stirred for 1 h and then poured into dilute, aqueous potassium carbonate. The organic layer was washed twice with water, dried over anhydrous potassium carbonate, and stripped on a rotary evaporator. Preparatory TLC on C₁₈-reverse phase plates and elution with 20% chloroform in methanol resulted in a clean separation of ZCHP from residual HCHP, HCZP, and ZCZP: yield 7.2 mg, 75%; electronic spectrum (CH₂Cl₂) λ_(max) (rel ε) 413.5 (1.000), 430 (1.112), 508.5 (0.101), 575.0 (0.064), 610.0 (0.067), 659.0 nm (0.509). NMR (CDCl₃) δ (*p*-tolyl group) 8.01 (d, 1 H, *J* = 7.9 Hz), 7.94 (d, 1 H, *J* = 7.8 Hz), 7.58 (d, 2 H, *J* = 7.8 Hz), 2.751 (s, 3 H); (porphyrin) 10.34 (s, 2 H), 4.07 (q, 4 H, *J* = ~7.4 Hz), ~3.92 (m, 4 H), 2.57 (s, 6 H), 1.90 (s, 3 H), 1.86 (s, 3 H), 1.81 (t, 6 H, *J* = 7.6 Hz), 1.67 (t, 6 H, *J* = 7.13 Hz); (phorbin) 9.58 (s, 1 H), 8.73 (s, 1 H), 8.71 (s, 1 H), 5.40 and 5.24 (AB quartet, 2 H, *J* = 20.1 Hz), 4.47 (d, 1 H, *J* = 8.6 Hz), 4.69 (q, 1 H, *J* = 7.1 Hz), 4.47 (d, 1 H, *J* = 8.6 Hz), 3.71 (s, 3 H), 3.68 (s, 3 H), 3.46 (q, 2 H, *J* = 7.5 Hz), 3.17 (s, 3 H), ~2.80 (m, 3 H), ~2.48 (m, 2 H), 2.23 (s, 3 H), 2.03 (d, 3 H, 7.2 Hz); ring NH's -1.00 (br s, 2 H).

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