find a different distribution of photoproducts with more extensive fragmentation occurring in gas phase. Experiments reported here focus on the effect of the medium on the photodissociation of $Cr(CO)_6$.

In solution, on the picosecond time scale, no evidence is found for solvent cage recombinations of small fragments with CO. The primary photoproduct in condensed phase is shown to be $Cr(CO)_5$ whose formation and subsequent interaction with solvent molecules occurs within 25 ps.

Collisional effects on the gas-phase photodissociation of this metal carbonyl are shown to be important. Various added gases (a) affect intermediates of high internal energy content in the photodissociation pathway, (b) promote quenching of excited atomic photoproducts, and (c) lead to recombination with unsaturated intermediates in the case of added CO.

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Picosecond Spectroscopic Study of Chlorophyll-Based Models for the Primary Photochemistry of Photosynthesis

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A series of covalently linked dimers and trimers of chlorophyllide derivatives was investigated by time-resolved absorption and fluorescence spectroscopy (3-10^4 ps). For these compounds, the free energy difference between the singlet excited state of the electron donor and the anticipated cation–anion photoproduct (ΔG_{ET}) is estimated to range from +200 to −400 meV. For the dimers studied, the singlet-excited-state lifetimes range from 1 to 7 ns and depend inversely on the solvent's static dielectric constant. Since no decrease in lifetime or fluorescence quantum yield was found as ΔG_{ET} became more negative, this effect is unlikely to be due to slow electron transfer. It may be a result of fluctuating intramolecular association of the nonpolar macrocycles in solvents with a high dielectric constant. We also studied two trimers, each having the same chlorophyllide *a* dimer as the electron donor, but with pyropheophorbide *a* or pheophorbide *a* as the electron acceptor (the latter is 90 meV easier to reduce than the former). For the trimer with pheophorbide *a* as the acceptor, there is evidence for a new path of radiationless decay which may involve an electron-transfer product. However, the rate of formation of this product is slow ($\leq 10^{10}$ s^{-1}), and its yield is low (≤50%). Taken together, these results suggest that chlorophyll-based, donor–acceptor pairs connected by flexible chains longer than five atoms are not likely to duplicate the highly efficient excited-singlet-state electron-transfer reactions characteristic of the primary photochemistry of photosynthetic organisms.

Introduction

The initial chemical reaction in bacterial photosynthesis following photoexcitation is electron transfer (ET) to form a moderately stable cation–anion radical pair.[1-4] This reaction in photosynthetic bacteria is remarkable: the forward rate constant[5-7] is greater than 2×10^{11} s^{-1}, leading to a quantum yield close to unity, while the recombination back-reaction[8] is more than 3 orders of magnitude slower, providing sufficient time for further charge separation through reduction of other electron acceptors. The time scale of the forward reaction and the weak dependence of this rate on temperature between 4 and 300 K[9,10] suggest that molecular diffusion plays an insignificant role in the reaction. This focuses mechanistic investigations on the particular translational and angular coordinates of the reactants and unique characteristics of the intervening medium.

Extensive picosecond absorption and ESR studies have shown that the photoexcited electron donor in bacterial photosynthesis is a pair of bacteriochlorophylls[1,11] (BChl), while the electron acceptor is a bacteriopheophytin monomer[5,6,12] (bacteriochlorophyll where two H atoms replace

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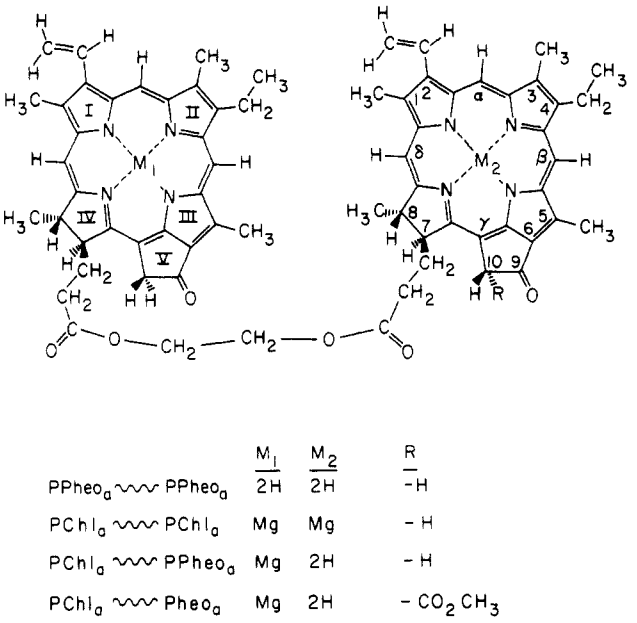

Figure 1. Structure, numbering system, and abbreviations for the dimers studied in this work. Chl*a* and Pheo*a* denote the chlorophyllide *a* and pheophorbide *a* fragments, respectively (R = CO_2CH_3). These symbols are preceded by P to denote the pyrolyzed chromophore where R = H (e.g., PChl*a* or PPheo*a*).

the central Mg, BPheo). It has been estimated that this reaction is exergonic by 50–130 meV from an analysis of the delayed fluorescence in *Rps. spheroides*;[13,14] electrochemical titrations suggest a value of about 100 meV in *Rps. viridis*.[15] These values are subject to considerable experimental and theoretical uncertainty. A further complication is the growing body of evidence suggesting the intermediacy of another electron acceptor, prior to BPheo, possibly a monomeric BChl.[7,16,17]

A sizable body of data has developed on the relative orientations of components in bacterial photosynthetic reaction centers,[18,19] but much less is known about the distance between reactants. Dutton et al.[20] estimate that the BChl pair and BPheo have an edge-to-edge separation of at least 9 Å; also, on the basis of circular and linear dichroism studies, Shuvalov and Asodov[21] suggest that this distance is 10–15 Å. These estimates should be considered cautiously, as the underlying theoretical bases for these analyses are subject to debate.

In order to deepen our understanding of natural photosystems and the mechanism of photoinduced ET reactions in the solid state, we have synthesized a large number

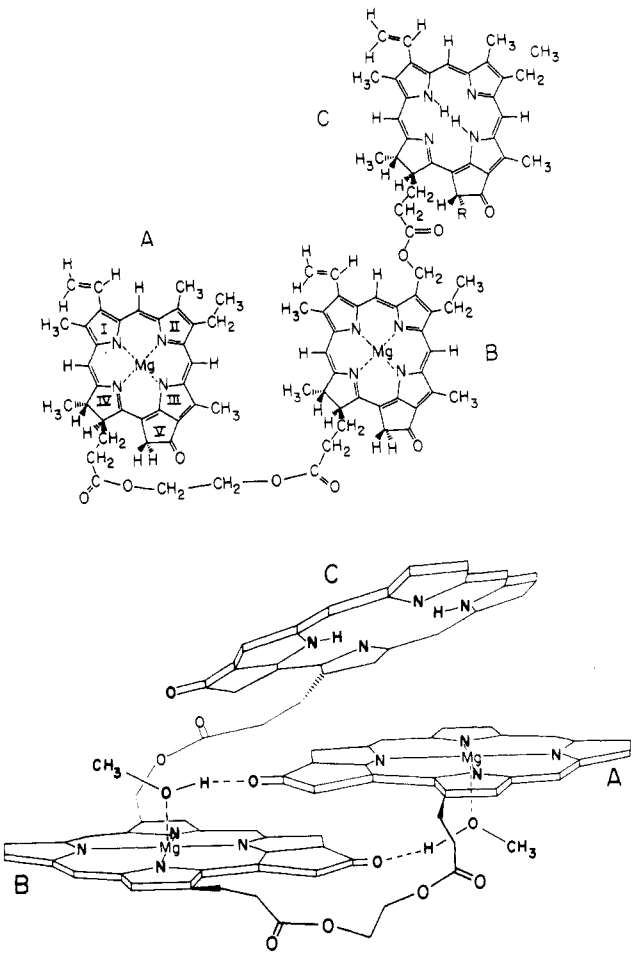

Figure 2. Structure and numbering system for the trimers studied in this work (R in ring C was either H or CO_2CH_3).

of analogues of the bacterial system. Synthetic models allow the distance of separation and redox potentials of the donor and acceptor, as well as properties of the surrounding medium, to be systematically varied. The model compounds in this work have been prepared by using chlorophyll *a* and *b* derivatives, rather than bacteriochlorophylls, because of their greater chemical stability and availability.

Attempts to prepare synthetic chlorophyll-based analogues of reaction center components began with the work of Boxer and Closs on the covalently linked pyrochlorophyllide *a* dimer,[22] PChl*a*~PChl*a* (see Figure 1 for structures and abbreviations; throughout this paper, the words "dimer" and "trimer" will be used to denote molecules containing two or three macrocycles, respectively). Addition of hydroxylic ligands, such as ethanol, "folds" this dimer into an intramolecular aggregate in which the macrocycles are held parallel by two bridging ligands, each of which hydrogen bonds to the carbonyl at position 9 of one macrocycle and coordinates to the central metal of the other. Compounds "folded" this way will be denoted as $(PChla)_2$, as opposed to PChl*a*~PChl*a*, which is used to symbolize "open" conformations enforced by addition of a non-hydrogen-bonding, strongly coordinating ligand like pyridine. Subsequently, covalently linked chlorophyllide and bacteriochlorophyllide dimers were prepared and exhibited identical aggregation.[23,24] Recently several groups

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have covalently linked porphyrin or chlorophyll derivatives with two or four bridges to produce both relatively rigid cofacial[25-28] and more loosely held hinged[29] structures.

Given the role of BPheo as an electron acceptor, it seemed reasonable to prepare dimers where one member of the pair contained Mg and the other did not (e.g., PChl*a*~PPheo*a*, where PPheo*a* is Mg-free pyropheophorbide *a*). In a preliminary picosecond spectroscopic investigation of cofacial diporphyrins, composed of Mg and free-base subunits, Netzel et al.[30] found evidence for the production of a cation–anion biradical within 6 ps of photoexcitation. This ET reaction proceeded from the singlet excited state and was exergonic by about 150 meV in CH_2Cl_2.

In order to study the electron-donating properties of a chlorophyll dimer, we have covalently linked the dimeric fragment to a metal-free macrocycle.[31] This trimer (Figure 2) has been characterized in detail by NMR in benzene-d_6. In the presence of hydroxylic ligands, the chlorophyll dimer folds as would be the case in the absence of the metal-free macrocycle, which is found to be positioned above the other two, (PChl*a*)$_2$~PPheo*a*.[31] Structural characterization of this and all other synthetic chlorophyll aggregates in solution relies heavily on NMR analysis. It is important to note that the measured NMR chemical shift is due to an average of structural conformations which fluctuate more rapidly than the inverse of the largest chemical shift differences (~milliseconds). On the other hand, picosecond kinetics measurements probe a much wider array of structures available to the aggregate.

Experimental Section

The apparatus used to measure the picosecond absorbance spectra has been described in detail elsewhere.[32] Here we summarize the key aspects of these measurements. The two probe beams of the system are monitored by a SIT-vidicon detector. The change-in-absorbance (ΔA) spectra taken at a designated time after excitation at 527 nm with a 6-ps laser pulse are the average of 20 pairs of laser shots. One laser shot of a pair records the probe beam ratios at 250 wavelengths when the sample is not excited; the other laser shot of a pair makes the same measurement when the sample is excited. The log of the ratio of these probe beam ratios yields the reported ΔA values. The errors in ΔA reported in this paper are the standard deviations of the mean ΔA values for the set of ΔA's taken at a given time after excitation.

Most of the samples in this study yield detectable fluorescence. Under our excitation conditions the spectral shape of this fluorescence is constant and the intensity varies directly with excitation pulse power. Measurements in which the probe pulse precedes photolysis (fluorescence can be detected, but ΔA changes cannot occur) show that the fluorescence spectrum can be accurately subtracted from the spectrum of the probe light passing through the sample before any ratios are calculated. The intensity of the subtracted fluorescence is adjusted for the measured photolysis pulse power. In this way, we eliminate all artifacts in the ΔA measurements due to spontaneous emission. This procedure does not correct for emission stimulated by the probe light.

The white probe light is generated by focusing 1054-nm laser light into a 5-cm cell of D_2O. The duration of the probe pulse is 8 ps (fwhm), and the spectral resolution of the detection system is 4.8 nm. The 6-ps excitation pulse at 527 nm contains 0.8 ± 0.2 mJ of energy (1.5-mm diameter). A Laser Precision energy meter coupled to a sample-and-hold circuit and a PDP 11/03 controlled A-to-D converter ensures that data from pulses outside this energy interval are rejected.

For optical transients with lifetimes less than 25 ps, the effects of temporal dispersion in the white probe light are important. In our apparatus there is about 1 ps of delay for each 35 nm of spectral increment in the 550–775-nm region. We adopt the procedure of specifying the time of arrival of 775-nm light at the sample relative to the excitation pulse; positive time means that the 775-nm light arrives after the excitation pulse. The actual arrival time of any other wavelength is obtained by adding the appropriate delay at that wavelength to the 775-nm arrival time. We define $t = 0$ as the earliest detectable point of full excitation of the sample, as verified both by the maximum transmission point of a CS_2 Kerr shutter[33] and by the time of full bleach of several polypyridine-substituted Fe(II) compounds.[32,34]

Fluorescence lifetimes were measured by using single-photon counting equipment after excitation with a 400-ps (fwhm) pulse of synchrotron light at the Stanford Synchrotron Radiation Laboratory.[35,36] An RCA 8852 or a Hamamatsu R1333 photomultiplier tube detected the fluorescence at 90° to the excitation beam. The excitation beam was passed through a monochromator and filtered producing narrow-band excitation (420 ± 5 nm), and the emission was detected through long-pass or interference filters. The lifetimes were obtained by deconvolution of the synchrotron pulse profile (measured at the detection wavelength), combined with nonlinear least-squares analysis.[37,38] Time-resolved fluorescence excitation spectra were obtained by scanning the monochromator, while detecting fluorescent events occuring only at a fixed time after excitation.

All compounds and their variations were synthesized as previously described.[22,31] In the picosecond absorption experiments, the samples were held in 2-mm path length, optical cells. All samples were outgassed and sealed under vacuum. The range of sample concentrations was 3×10^{-5}–7×10^{-5} M. All samples were thoroughly mixed after each laser shot. Careful comparison of their ground-state absorption spectra before and after the picosecond kinetic measurements showed no differences, indicating that the laser excitations did not cause any irreversible photochemical changes. The relative fluorescence quantum yields were measured in 1 × 1 cm cells in an MPF-4 spectrofluorimeter with the excitation and observation beams at 90° to each other. The samples were excited at 420 ± 5 nm, and the absorbance in this region was less than

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TABLE I: One-Electron Reduction Potentials for the Chromophores in the Model Compounds

compd[a]	$E_{1/2}$,[b] V	electrolyte[c]
PChl$a^{+}\cdot$/PChl$a$	+0.84	ClO_4^-
	+0.74	Cl^-
PChl$a$/PChl$a^{-}\cdot$	−1.03	ClO_4^-
PPheo$a^{+}\cdot$/PPheo$a$	+1.15	ClO_4^-
PPheo$a$/PPheo$a^{-}\cdot$	−0.87	ClO_4^-
	−0.75	Cl^-
Pheo$a$/Pheo$a^{-}\cdot$	−0.78	ClO_4^-
	−0.64	Cl^-

[a] All compounds are the methyl esters. [b] $E_{1/2}$ vs. NHE at 25 °C. [c] 0.1 M of the indicated tetraethylammonium chloride (Cl^-) or tetrabutylammonium perchlorate (ClO_4^-) salt in CH_2Cl_2.

0.05. The sample absorbance at wavelengths above 600 nm was less than 0.02, so reabsorption of fluorescence was negligible. All of the midpoint potentials ($E_{1/2}$) were determined by previously described cyclic voltametric techniques.[39]

Results and Discussion

Electrochemical Data. The one-electron reduction potentials of the monomer fragments of the dimers and the trimers studied in this work are presented in Table I. The observation that pheophorbides are 90 meV easier to reduce than the corresponding pyropheophorbides (lack of carbomethoxy at position 10) provides a convenient method for varying donor–acceptor redox potential differences, without significantly changing the ground- and excited-state absorption spectra, singlet-state lifetime, or geometry of the aggregate. The addition of Cl^- can also be used to alter the reduction potentials; however, this cannot be done with the intramolecular aggregates.

An estimate of the free energy change of an ET reaction (ΔG_{ET}) can be made from the one-electron reduction potentials of the donor ($E(D^{+}\cdot/D)$) and acceptor ($E(A/A^{-}\cdot)$) couples and the first-excited-singlet energy ($E(S_1)$)[40] as follows:[41]

$$\Delta G_{ET} = E(D^{+}\cdot/D) - E(A/A^{-}\cdot) - E(S_1)$$

Values of ΔG_{ET} are presented in Table II. While junction potentials complicate the interpretation of monomeric midpoint potentials in different media, their effects can be avoided in estimates of ΔG_{ET} if $E(D^{+}\cdot/D)$ and $E(A/A^{+}\cdot)$ are measured under the same conditions in the same solvent. If this is done, the junction potentials cancel in calculations of ΔG_{ET}, since only the difference in midpoints of reduction potentials is required. The expression for ΔG_{ET} neglects Coulomb interactions and solvation effects, which have been discussed at length in the literature.[42-44] Consideration of these effects leads to the prediction that ΔG_{ET} should be more favorable as the solvent static dielectric constant increases. The relationship between ΔG_{ET} and the rate constant for ET has been widely discussed, debated theoretically, and tested experimentally.[45,46] On the basis of this literature,[47,48] we expect ET to occur for $-\Delta G_{ET} > 150$ meV and the rate to increase with increasing exergonicity over the range of values in Table II.

TABLE II: Estimates of the Excess Free Energy for ET Reactions from the Excited Singlet States of Several Dimers[a]

compd no.	dimer[b]	$E(S_1)$,[c] eV	$E_{1/2}$,[d] eV	ΔG_{ET}, meV
1	PPheo$a$~PPheo$a$ + Py	1.81	2.02	+210
2	PChl$a$~PChl$a$ + Py	1.82	1.87	+50
3	$(PChla)_2$ + EtOH	1.75	1.80[e]	+50
4	PChl$a$~PPheo$a$ + Py	1.81	1.71	−100
5	PChl$a$~PPheo$a$ + Cl^-	1.81	1.49	−320
6	PChl$a$~Pheo$a$ + Py	1.81	1.62	−190
7	PChl$a$~Pheo$a$ + Cl^-	1.81	1.38	−430

[a] Neglecting electrostatic corrections (see text). [b] py = 0.5 M pyridine; EtOH = 0.5 M ethanol; Cl^- = 0.1 M tetraethylammonium chloride. The solvent is CH_2Cl_2. [c] Estimate of the 0-0 energy of lowest excited singlet state taken ca. 20% up the long-wavelength edge of the lowest-energy ground-state absorption band (±0.03 eV).[39] [d] Algebraic sum of the midpoint potential for reducing the oxidized electron donor minus that for reducing the electron acceptor. [e] Wasielewski et al.[34] have shown that a doubly linked, hinged *meso*-PChl$a$ dimer is 70 meV easier to oxidize than Chl$a$. We take this as a reasonable correction to $E_{1/2}$ for formation of a typical dimer cation.

Pulse Energy Dependence and Photobleaching. Studies of the dependence of the sample emission and change in absorbance (ΔA) on pulse energy show that neither is saturated, and calculations of the variation of fractional change in absorbance, $\Delta A/A$, with energy after the first 100 ps agree with the observed $\Delta A/A$ values. Since dimeric and trimeric samples with added pyridine show no NMR evidence of close association, we expect their chromophores to absorb independently. In this situation, $\Delta A/A$ values greater than 50% for symmetric dimers (e.g., PChl$a$~PChl$a$ or PPheo$a$~PPheo$a$) imply that some molecules have more than one chromophore excited. Multiple excitation of any given chromophore within a dimer is also possible under these excitation conditions. To assure that the photochemistry of the S_1 states of the chromophores is being studied in the absorption experiments, we compared the fluorescence lifetimes obtained under photon-counting conditions to the absorption kinetics. For samples with an open configuration, the agreement between the two measurements is excellent. Therefore, the chromophores of these samples must quickly relax to the S_1 state and absorb and decay independently of whether an adjoining chromophore is in an excited or ground state. Work by Shepanski and Anderson suggests that electronic and vibrational relaxations to the lowest vibrational level of S_1 occur on a time scale shorter than 10 ps for Chl$a$ excited at 355 nm.[49] For samples with a folded configuration, differences between fluorescence and absorption kinetics are observed and discussed. Finally, comparison of the ΔA spectra at 3 ps after excitation for chlorophyll and pheophytin monomers and all of the dimers with their corresponding ground-state absorption spectra shows an exact agreement between the shape and location of the maximum bleaching and the shape and location of the maximum ground-state absorbance. This result provides an important check on the accuracy of the

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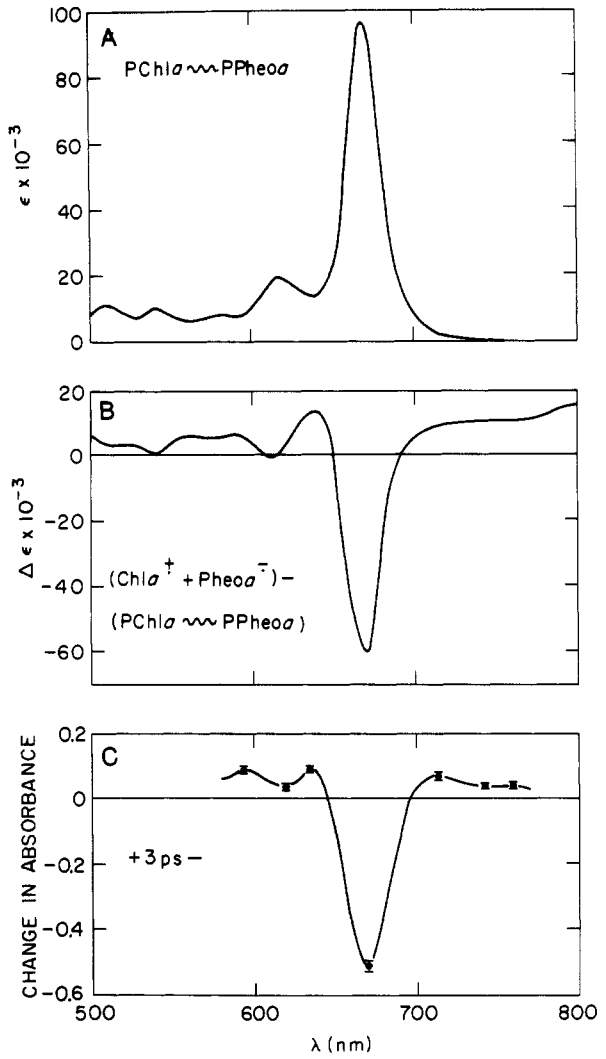

Figure 3. Comparison of (A) ground-state absorbance of PChla ~ PPheoa (4×10^{-5} M), (B) the hypothetical change-in-absorbance spectra *if radical ions were formed* constructed from the known absorption spectra of $Chla^{+\cdot}$ and $Pheoa^{-\cdot}$[51,52] minus the spectrum in A, and (C) the change-in-absorbance spectrum of A 3 ps after photoexcitation. Because spectrum C is due to formation of singlet excited states and not ion pairs, it is evident that the similarity of B and C is deceptive, and the picosecond change-in-absorbance data in this wavelength region are inadequate to demonstrate ion-pair formation.

picosecond change-in-absorbance measurements.

A principal objective of this work is to learn about the chemical factors governing ET reactions from the S_1 states of photosynthetic pigments and their aggregates. In particular we want to explore the limits of donor–acceptor distance requirements in achieving rapid ($k > 10^{11}$ s^{-1}) ET reactions. Work on a cofacial diporphyrin with a 4-Å interplanar separation between the Mg porphyrin donor and the free-base porphyrin acceptor demonstrates ET from the diporphyrin's S_1 state in <6 ps.[30,50] In the present work we test the hypothesis that the donor and the acceptor must be so close. To answer this question it is necessary to be able to recognize the ΔA spectra produced by an internal ET reaction (e.g., $(PChla{\sim}PPheoa)^{S_1} \rightarrow PChla^{+\cdot}{\sim}PPheoa^{-\cdot}$).

Figure 3 compares a change-in-absorbance spectrum for PChla~PPheoa in toluene with ethanol to a *calculated* change-in-extinction-coefficient spectrum for forming the desired $PChla^{+\cdot}{\sim}PPheoa^{-\cdot}$ from PChla~PPheoa, using

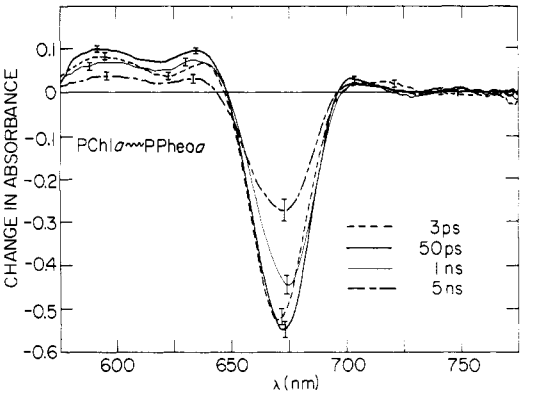

Figure 4. Picosecond transient absorption kinetics for 3×10^{-5} M PChla ~ PPheoa in toluene with 0.5 M pyridine at the indicated times. The ground-state absorbance at 665 nm was 0.65.

the known absorption spectra of $Chla^{+\cdot}$ and $Pheoa^{-\cdot}$.[51,52] These two spectra are quite similar; however, the change-in-absorbance spectrum in Figure 3 is *also* nearly identical with the picosecond change-in-absorbance spectra for the pyromethylchlorophyllide *a* (PMeChla) and pyromethylpheophorbide *a* (PMePhoea) *monomers* (data not shown). Thus, it is nearly impossible to distinguish the excited singlet states of PChla and PPheoa from their respective cations and anions by means of the transient absorption in the 570–770-nm region. For this reason we combine measurements of picosecond absorbance kinetics, fluorescence lifetimes, and fluorescence quantum yields to decide whether excited singlet states or ET products are formed following photoexcitation of the chlorophyll-based models.

Survey of Fluorescence Quantum Yields and Lifetimes. Fluorescence quantum yield and lifetime results for the monomeric chromophores, PMeChla, PMePheoa and MePheoa, are shown in Table IIIA. The relative quantum yields are about the same for all of the monomers and show no major variation upon substitution of pyridine for ethanol as ligand or upon a change of solvent.

Table IIIB summarizes the results of fluorescence quantum yield, fluorescence lifetime, and absorbance kinetic measurements (see below) for a series of dimers. Because the free energy change of the desired ET reaction is likely to depend on the static dielectric constant (ϵ) of the solvent, toluene ($\epsilon = 2$), methylene chloride ($\epsilon = 9$), and acetonitrile ($\epsilon = 39$) were used. The data show that open PChla~PChla and PChla~PPheoa in toluene with pyridine have fluorescence lifetimes and quantum yields that are similar to those of their monomeric subunits. In contrast to the monomers, all of the dimers show a trend of decreasing fluorescence quantum yield with increasing solvent static dielectric constant.

Table IIIC contains the corresponding data for the two trimers. The data for the open trimers in the three solvents with added pyridine are very similar to those of the dimers. However, neither of the two trimers in CH_2Cl_2 CH_2Cl_2. with ethanol yields a fluorescence decay which can be described by a single exponential. This is also true for $(PChla)_2$ folded in CH_2Cl_2. For these samples, each decay is better fitted by a sum of two decays, with lifetimes of ~100 ps (~90% of the emission) and 4–5 ns (~10% of the emission). However, time-resolved fluorescence excitation spectra indicate that the two components of the fluorescence decay are due to different species: excitation

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TABLE III: Relative Fluorescence Quantum Yields[a] and Lifetimes[b]

compd	ligand[c]	solvent: toluene	solvent: CH_2Cl_2	solvent: CH_3CN
		A. Monomers[d]		
PChl*a*	EtOH	93	95 [6.0 ± 0.1]	96
PChl*a*	Py	97 [6.9 ± 0.1]	76	82 [7.1 ± 0.1]
PPheo*a*	EtOH	92	89 [6.3 ± 0.1]	72
PPheo*a*	Py	100 [7.6 ± 0.1]	78	77 [7.6 ± 0.1]
Pheo*a*	EtOH		[5.2 ± 0.1]	
Pheo*a*	Py	[6.3 ± 0.1]		
		B. Dimers		
PPheo*a*~PPheo*a*	Py	[5.1 ± 0.1]	[4.5 ± 0.1]	[0.80: 2.0 ± 0.1; 0.20: 4.7 ± 0.1]
PChl*a*~PChl*a*	Py	98 (6.2 ± 0.8) [5.2 ± 0.1]	69 [3.8 ± 0.1]	21 [0.56: 0.8 ± 0.1; 0.44: 1.9 ± 0.1]
$(PChla)_2$	EtOH	62	12 (110 ± 20 ps)[e] [0.97: 0.1 ± 0.03; 0.03: 3.0 ± 0.1]	14
PChl*a*~PPheo*a*	Py	99 (7.5 ± 1.0) [6.1 ± 0.1]	32 (1.8 ± 0.2) [2.1 ± 0.1]	14 (0.85 ± 0.1) [0.84: 0.9 ± 0.1; 0.16: 6.6 ± 0.1]
PChl*a*-PPheo*a*	EtOH	45 (3.8 ± 0.8)[f] [3.9 ± 0.2]	33 [3.0 ± 0.2]	14
PChl*a*~Pheo*a*	Py	80	34	19
PChl*a*~Pheo*a*	EtOH	53	37	21
PChl*a*~PPheo*a*	Cl^-		34	16
PChl*a*~Pheo*a*	Cl^-		34	20
		C. Trimers		
$(PChla)_2$~PPheo*a*	EtOH	41 (3.4 ± 0.4)[g] [2.8 ± 0.1]	9 [0.93: 0.1 ± 0.03; 0.07: 4.8 ± 0.1][h]	6
PChl*a*~PChl*a*~PPheo*a*	Py	51 (7.0 ± 1.0) [5.9 ± 0.3]	20	7
$(PChla)_2$~Pheo*a*	EtOH	47	13 [0.89: 0.1 ± 0.03; 0.11: 4.4 ± 0.1][i]	10
PChl*a*~PChl*a*~Pheo*a*	Py	81	27	12

[a] Arbitrary Units (±10%). Quantum yields are corrected for the refractive index of the solvent (see Hermans, J. J.; Levinson, S. *J. Opt. Soc. Am.* **1951**, *41*, 460). [b] Fluorescence lifetimes (1/*e*) are given in square brackets in nanoseconds. The fraction of each decay component is listed preceding its lifetime for fits requiring two exponentials. Lifetimes obtained from picosecond absorption data (1/*e*) are given in parentheses in nanoseconds. [c] Py = 0.5 M pyridine, EtOH = 0.5 M ethanol, Cl^- = 0.1 M tetrabutylammonium chloride. [d] Measurements were made on the methyl esters. [e] A long-lived bleach is also observed which persists for longer than 5 ns and is attributed to the formation of PChl*a* ~ ^{3}PChl*a* (see text). [f] For data taken more than 1 ns after photolysis. Earlier data show a more rapid ground-state recovery that may be due to intramolecular excited-state annihilation. [g] The reported lifetime is for the decay of the apparent bleach at 709 nm. A 60 ± 10 ps transient is observed at 670 nm in the early spectra (see text and Figure 6). [h] A fast transient (~100 ps) and a long-lived bleach (>5 ns) are observed in the picosecond transient absorption spectra (see text and Figure 7). [i] A fast transient (~100 ps) and a decay with a lifetime of 3 ns are observed in the picosecond transient absorption spectra (see text and Figure 7).

spectra of the longer-lifetime components lack the spectral features of the folded-dimer portion of each sample, while these features dominate the excitation spectra of the early fluorescence.[53] The following sections compare these emission results to the transient absorption properties of these samples.

Absorption Kinetics for Dimers. PChla~PPheoa in Toluene with Pyridine. Figure 4 shows picosecond kinetic data for the PChl*a*~PPheo*a* in toluene with pyridine using 0.8 mJ of excitation light. Assuming the ΔA asymptote for the absorbance growth is zero, the data at 670 nm for 0.05, 1, and 5 ns after excitation yield a lifetime of 7.5 ± 1 ns. This is in reasonable agreement with the fluorescence decay measurement of 6.1 ± 0.2 ns. (Note that a shorter absorbance growth lifetime results if a slightly negative ΔA asymptote is chosen. This is almost certainly appropriate since some triplet-state population is very likely.) Additionally, short-lived spectral changes between 3 and 50 ps are present. To check whether the short-lived transient is due to high excitation energy, we collected data on the same sample with 0.3 mJ of 527-nm exciting light. These data still show band shifting and a growth in the bleach at 670 nm between 3 and 50 ps.

PChla~PPheoa in CH_2Cl_2 with Pyridine. Figure 5A shows picosecond kinetic data for PChl*a*~PPheo*a* in methylene chloride with pyridine as the ligand. When a ΔA asymptote of −0.14 at 660 nm is selected, a good fit to a lifetime of 1.8 ± 0.2 ns is found, in agreement with the 2.1 ± 0.1 ns fluorescence decay measurement. The residual bleaching at 5.2 ns is probably due to molecules that have intersystem crossed to the triplet state. Because the singlet excited state of PChl*a* is only 0.01 eV higher in energy than that of PPheo*a*, excited states of both of the chromophores of the dimer should be populated at room temperature. Since about 75% of the dimers have *both* macrocycles excited, it is striking that the fluorescence decay (measured when very few chromophores are excited) agrees so well with the lifetime measured from absorbance-change data. The absorption data again show a band shift between 3 and 100 ps.

PChla~PPheoa in CH_3CN with Pyridine. Figure 5B shows kinetic data for PChl*a*~PPheo*a* in acetonitrile with pyridine. If the change-in-absorbance value found 5.2 ns after excitation is taken as the asymptote of the absorbance increase at 665 nm, the preceding points yield a lifetime of 0.85 ± 0.10 ns, in agreement with the 0.9 ± 0.1 ns fluorescence lifetime. We note that a small fraction (15%)

(53) Loss of Mg from a very small fraction of trimers could produce this result, because the fluorescence quantum yields and lifetimes of open fragments are much greater than those of the folded dimer. This type of time-resolved excitation spectroscopy is greatly facilitated by tunable synchrotron radiation.

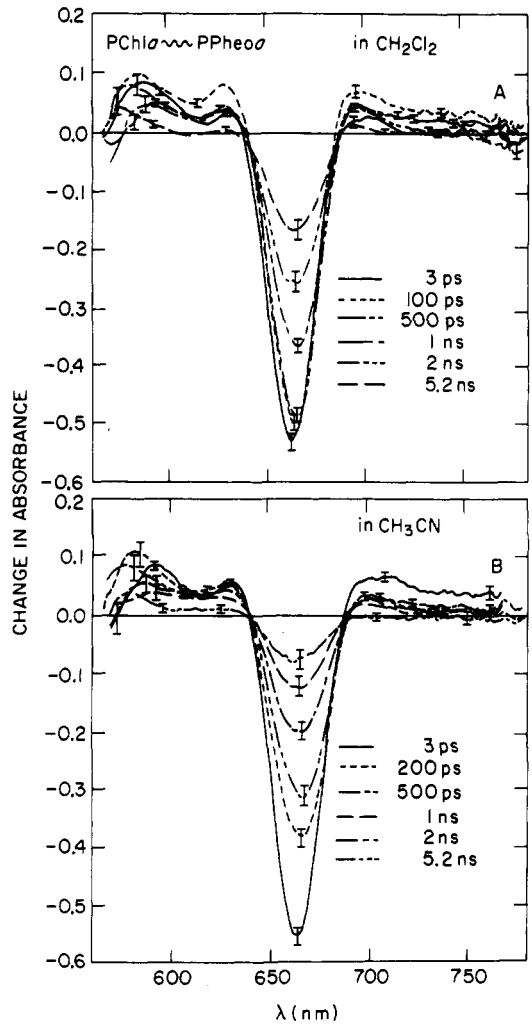

Figure 5. Picosecond transient absorption kinetics for 3×10^{-5} M PChla ~PPheoa in (A) CH_2Cl_2 with 0.5 M pyridine and (B) CH_3CN with 0.5 M pyridine.

of the emission from this sample decays with a lifetime of 6.6 ± 0.1 ns. This is comparable with the singlet lifetimes of the monomers that comprise this dimer. However, the same sample in CH_2Cl_2 showed no long-lived component. This small decay component is not detected in the transient absorption data, and we are uncertain of its origin.

PChla~PChla in Toluene with Pyridine. The data (not shown) for the symmetric PChla~PChla dimer shows an absorbance growth in the 670-nm region which has a lifetime of 6.2 ± 0.8 ns, assuming a ΔA symptote of zero. Allowing for some triplet-state formation by choosing a negative ΔA symptote brings the lifetime from absorbance measurements into excellent agreement with the 5.2 ± 0.1 ns singlet-state lifetime found in fluorescence measurements. The data also show a band shift between 3 and 50 ps.

Discussion. The correspondence of the lifetimes from fluorescence and absorption experiments shows that the same states are being monitored in both experiments. If ET occurred in <6 ps, we would expect the fluorescence and absorption kinetics to be very different, unless an emitting charge-transfer state were populated. This is unlikely because the shape and the energy of the fluorescence spectra are quite similar to those of the monomers. Rather, the energy of charge-transfer-state emission should vary both with the redox properties of the sample and with the polarizability of the solvent. Therefore, all of the emitting states are assigned to be $\pi\pi^*$ singlets.

A trend of decreasing S_1 lifetimes with increasing solvent static dielectric constant is noted for mixed dimers comprising Mg and free-base macrocycles. Surprisingly, fluorescence lifetime data for symmetric dimers (e.g., PChla~PChla and PPheoa~PPheoa) show a similar trend (Table III). In these cases ΔG_{ET} for ET is definitely unfavorable (see Table II). A possible explanation of this solvent effect for all of the open dimers is that the average distance between the macrocycles is likely to be smaller in high-dielectric solvents. This is reasonable, because the macrocycles are nonpolar and will tend to associate as the dielectric constant is increased.[54] Such an increase in effective chromophore concentration may lead to effects which are analogous to "concentration quenching" (a well-known phenomenon for chlorophylls and a variety of dyes).[55-57] Increased association may enhance the radiationless decay of the singlet excited state to the ground state by increasing the number of configurational fluctuations available for such decay. In contrast, we note that the fluorescence lifetime of a doubly covalently linked dimer of a pyropheophorbide derivative is nearly identical with that of the monomer.[28] Thus, it appears that large amplitude conformational fluctuations are required for this pathway of deactivation to be important.

Slow ET followed by immediate (<1 ps) recombination has also been proposed as a mechanism to account for concentration quenching.[42,58] We note that the magnitude of the reduction in lifetime and quantum yield with increased solvent dielectric constant is more pronounced for PPheoa~PChla (ΔG_{ET} = −100 meV) than for PPheoa~PPheoa (ΔG_{ET} = +210 meV) or PChla~PChla (ΔG_{ET} = +50 meV). However, the remaining dimers (compounds 4–7 in Table II) show no correlation between the magnitudes of their reduction in quantum yield and their ΔG_{ET} values. Thus, ET quenching does not appear to be the dominant cause of the shortened singlet lifetime in these dimers in high-dielectric solvents. While the effects of structural rigidity and subunit orientation on this phenomenon are currently being investigated,[59] the clear result is that the distance requirements for efficient and rapid ($k > 10^{11}$ s^{-1}) photoinduced ET between chlorophyll and pheophytin macrocycles are sufficiently demanding that a single 10-membered linking chain does not bring them close enough together for it to occur.

The band shifting observed at early times (<50 ps) following excitation can be explained by several mechanisms, none of which is completely satisfactory. Directional energy transfer following the preferential excitation of the PPheoa half of the dimers at 527 nm is a possibility, but the data for the symmetric PChla~PChla dimer also show this band-shifting phenomenon. Molecular reconfiguration during the first 50 ps could change the singlet-excited-state absorption spectrum. The observed red shift in the bleach would require a change in the spectrum of S_1 at approximately 680 nm. While this does correspond to a feature in the absorption spectrum of S_1 reported by Shepanski and Anderson,[49] our data show a rather flat S_1

(54) This association has been noted in work on unlinked high-spin ferric complexes of tetraarylporphyrins. See: Snyder, R. V.; La Mar, G. N. *J. Am. Chem. Soc.* **1977**, *99*, 7178.

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(59) We find that rigid doubly linked dimers of chlorophylls[28] or porphyrins[26] have lifetimes which are comparable with those of the corresponding monomers. This contrasts sharply with the results on singly linked, conformationally mobile dimers reported in this paper.

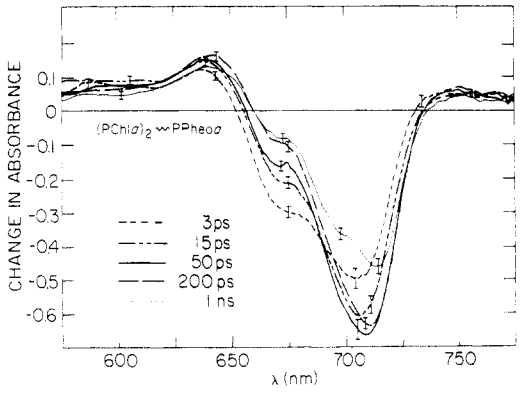

Figure 6. Picosecond transient absorption kinetics for 6×10^{-5} M $(PChla)_2 \sim PPheoa$ in toluene folded with 0.5 M ethanol.

absorption in this region with no such feature. We conclude that changes in the S_1 absorption spectrum are not a likely cause of the band shifting. Stimulated emission caused by the probe pulse would account for the red shift in the bleach. However, the time delay in observation of the red shift requires that a relatively slow relaxation process occur before the excited state can emit or that a molecular reconfiguration occur which changes the stimulated emission probability. The later may well be the most likely explanation, as Hindman et al.[60] have shown that the molecular configuration can have a large effect on the stimulated light-emission properties of the PChl*a*~PChl*a* dimer.

Picosecond Absorption Kinetics for Trimers. Since the electron donor in bacterial reaction centers is a dimer, we were interested to determine whether a dimeric PChl*a* complex, such as $(PChla)_2$, facilitates an ET reaction. In the trimers a five-atom chain joins the $(PChla)_2$ fragment to the metal-free macrocycle. As noted earlier, the addition of ethanol folds the $(PChla)_2$ part of the trimer with two alcohol bridges[31] (see Figure 2). This leads to a shift in the absorption maximum of the PChl*a* dimer fragment from 667 nm (open configuration) to 696 nm (folded configuration).

$(PChla)_2$~PPheoa in Toluene with Ethanol. Figure 6 presents picosecond absorbance data for $(PChla)_2$~PPheo*a* folded in toluene by the addition of ethanol. The early spectra (<1 ns) show a rapid absorbance increase at 670 nm with a lifetime of 60 ± 10 ps. A parallel increase of apparent bleaching at 709 nm is also present; however, 709 nm corresponds to the emission rather than the absorption region of $(PChla)_2$. The absorbance increase at 670 nm is due to repopulation of the ground state of PPheo*a*. Since the extinction coefficient of PPheo*a* at 527 nm is larger than that of the $(PChla)_2$ fragment, preferential excitation of PPheo*a* is expected. The increase of apparent bleaching at 709 nm shows that the excited-state energy of PPheo*a* is rapidly transferred intramolecularly to the lower-energy singlet excited state of $(PChla)_2$ ($k = 2 \times 10^{10}$ s^{-1}, very likely determined by the rate of folding and unfolding of the $(PChla)_2$ fragment).

The bleaching at 709 nm is excessive because of probe-light amplification through stimulated emission from the S_1 state of $(PChla)_2$. This apparent bleaching persists for >5 ns. Attempts to eliminate it by reducing the excitation energy from 0.8 to 0.1 mJ were unsuccessful. In this case the apparent bleaching due to stimulated emission is absent at times of <10 ps, becomes the dominant feature by 500 ps, and persists beyond 4 ns. In contrast, fluorescence lifetime measurements under photon-counting conditions show only a single emission decay time of 2.8 ± 0.1 ns. These results demonstrate that the photophysical properties of this trimer include energy transfer, S_1 decay, and the ability to amplify probe light. They rule out rapid ($k > 3 \times 10^8$ s^{-1}) electron-transfer reactions.

When Pheo*a* is substituted for PPheo*a* as the electron acceptor in the above trimer in toluene with ethanol, the free energy change for an ET reaction from the S_1 state of the dimer fragment becomes more favorable. However, there is essentially no difference in the fluorescence quantum yield due to this substitution. This result indicates that the improvement in ΔG_{ET} is not enough to produce the appreciable fluorescence quenching that must accompany a fast ET from the S_1 state of $(PChla)_2$. Therefore no picosecond absorption measurements were made on this trimer in toluene. These covalently linked trimers folded with ethanol in toluene are quite similar to the tetrameric aggregate proposed by Pellin et al.[61] in which the ethylene glycol ester of PPheo*a* is used to fold $(PChla)_2$ in toluene. We find no evidence for ET rates of $>3 \times 10^8$ s^{-1} in our systems and suggest that the results reported by Pellin et al.[61] can likewise be explained as S_1-state formation and decay, *without invoking rapid ET* ($k > 10^{11}$ s^{-1}).

$(PChla)_2$~PPheoa vs. $(PChla)_2$~Pheoa in CH_2Cl_2 with Ethanol. In this solvent, the ΔG_{ET} estimates for ET from the S_1 state of $(PChla)_2$ are respectively −40 and −130 meV. In order to interpret the excited-state dynamics of these two trimers, it is first necessary to establish the excited-state characteristics of the potential electron donor, $(PChla)_2$.

The fluorescence lifetime and the quantum yield of $(PChla)_2$ folded with ethanol in CH_2Cl_2 have been studied by Pellin et al.[62] using picosecond streak camera measurements. They found a lifetime at room temperature of 110 ps and a striking dependence of the lifetime on temperature. Freed[63] interprets these effects in terms of the interplay of two slightly separated exciton states. Under our experimental conditions, 97% of the sample's emission has a lifetime of 100 ± 30 ps and 3% has a lifetime of 3.0 ± 0.1 ns. The excitation spectrum of the short-lived emission corresponds to the absorption spectrum of folded (PChl*a*), while that of the long-lived emission corresponds to the absorption spectrum of open dimers and metal-free impurities. The picosecond absorbance kinetics for this molecule show a rapid ground-state repopulation with a lifetime of 100 ± 20 ps. A residual bleach at 695 nm of 70% of the original ΔA is observed 1 ns after excitation. This bleach persists longer than 5 ns with 45% of the original $\Delta A/A$. Periasamy et al.[64] have shown that photoexcited $(PChla)_2$ yields an open dimer comprising one triplet and one ground-state subunit, PChl*a* ~ ^{3}PChl*a*. Thus, the long-lived bleach is very likely due to this species.

Although the relative fluorescence quantum yields and fluorescence lifetimes for $(PChla)_2$~PPheo*a* and $(PChla)_2$~Pheo*a* folded in CH_2Cl_2 are about the same (Table III), we noted a striking difference in their picosecond absorption kinetics (Figure 7). The decay kinetics for $(PChla)_2$~PPheo*a* (Figure 7B) are very similar to those of $(PChla)_2$, including the formation of a long-lived tran-

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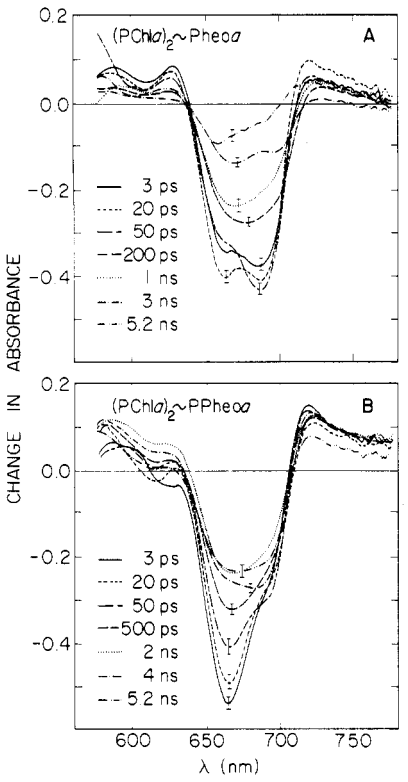

Figure 7. Comparison of the picosecond transient absorption decay kinetics for $(PChla)_2$~PPheo*a* and $(PChla)_2$~Pheo*a*, both (5×10^{-5} M) in CH_2Cl_2 folded with 0.5 M ethanol. It is apparent that the trimer with Pheo*a* as the acceptor returns to the ground state rapidly while that with PPheo*a* does not.

sient (lifetime > 5 ns) with about 50% of the original ΔA at t = 500 ps. Note that the fluorescence lifetime and time-resolved excitation data indicate that no more than 10% of the trimers are unfolded. This fraction of the sample cannot account for the large yield of the long-lived transient. In contrast, the $(PChla)_2$~Pheo*a* bleach (Figure 7A) decays much more rapidly (lifetime ~ 3 ns). Both trimers exhibit very similar subnanosecond fluorescence and absorption decay kinetics. Since the principal difference between these trimers is the estimated free energy change for ET from S_1, it is conceivable that ET occurs in $(PChla)_2$~Pheo*a*, but not in $(PChla)_2$~PPheo*a*. The rapid ($\sim 3 \times 10^8$ s^{-1}) loss of bleaching in the former would then be due to recombination of the ion pair to repopulate the ground state. This interpretation implies that the rate of the ET reaction from S_1 is slower than or comparable to the dimer fluorescence lifetime (100 ps) and that the yield is <50% (a conclusion supported by the magnitude of the bleaching at 1 ns). An alternative explanation is that intersystem crossing from the triplet state to the ground state is increased for $(PChla)_2$~Pheo*a* relative to that for $(PChla)_2$~PPheo*a*. This seems unlikely, since Chl*a* triplet lifetimes are typically in the microsecond range.[64]

Summary. We conclude that the dimers joined with a single 10-membered chain do not produce rapid ($k > 10^{11}$ s^{-1}) ET reactions from their S_1 states. Although they show a trend of fluorescence lifetime and quantum yield reduction with increased solvent static dielectric constant, there is no comparable trend of reduction in these quantities with decrease of ΔG_{ET} (−100 to −400 meV range). Thus, slow ET does not appear to be responsible for the lifetime changes.

The trimeric models use a dimeric electron donor and a shorter linking chain (only five members) to join the donor and acceptor subunits. Both of these changes with respect to the dimeric models should facilitate ET reactions. In CH_2Cl_2 the fluorescence and absorption kinetics for $(PChla)_2$~PPheo*a* are nearly identical with those for $(PChla)_2$, where only S_1 and T_1 states have been observed.[62,64] Thus, it is likely that only S_1 and T_1 states are formed by photoexciting this trimer. For $(PChla)_2$~Pheo*a* in CH_2Cl_2 the fluorescence quantum yield and lifetime are similar to those of $(PChla)_2$ and $(PChla)_2$~PPheo*a*, but the absorption kinetics are strikingly different. These results could be due to ET from S_1 ($k < 10^{10}$ s^{-1}) followed by reverse ET to re-form the ground state ($k \sim 3 \times 10^8$ s^{-1}). However, ΔA spectra in the visible are clearly insufficient to establish uniquely this possibility as the correct assignment. The present data do allow us to conclude that, if ET is occurring, its rate is ~25 times slower than the reduction of BPheo by the photoexcited BChl pair in bacterial photosynthesis and its quantum yield is <50%. Taken together, these results suggest that chlorophyll-based, donor–acceptor pairs connected by flexible chains longer than five atoms are not likely to duplicate the $>10^{11}$-s^{-1} excited-singlet-state ET reactions characteristic of the primary photochemistry of photosynthetic organisms.

An important difference between the models discussed in this paper and the natural photosynthetic system is that our models have considerable conformational flexibility. However, covalently connected donor–acceptor pairs, such as anthracene–dimethylaniline, provide convincing evidence for rapid (<7 ps) radical-ion pair formation and charge stabilization (500–600 ps), even though the reactive components are not rigidly connected.[65] In this case a very short linking chain (three methylene groups) may be the key to success. For large planar molecules, such as the chlorophylls and pheophytin, orientation may also be crucial. Work with cofacial diporphyrins suggests radical-ion pair formation when $-\Delta G_{ET} > 150$ meV and when the interplanar separation is about 4 Å.[30] While none of these synthetic systems produces radical-ion pair lifetimes which are as long as those in photosynthetic reaction centers (~10 ns), they do provide a starting point for future work. With this in mind, studies on cofacial chlorophyll analogues are in progress.[28]

Acknowledgment. This work was supported in part by the NSF under grant PCM7926677. Work at the Brookhaven National Laboratory was supported by the Division of Basic Energy Sciences of the US Department of Energy. Fluorescence lifetimes were obtained at the Stanford Synchrotron Radiation Laboratory supported by NIH 01209-01. S.G.B. is an Alfred P. Sloan and Camille and Henry Dreyfus Teacher–Scholar Fellow.

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