Photophysics of Bis(chlorophyll)cyclophanes: Models of Photosynthetic Reaction Centers

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Abstract: The title cyclophanes are dimers of methyl mesopyropheophorbide *a* that are connected by two covalent linkages. Insertion of zero, one, or two magnesium ions in the cyclophane provides a series of compounds that are useful in exploring artificial photosynthesis. In contrast to recently studied cofacial porphyrins, the macrocycles of these dimers have orthogonal transition moments. This precludes strong interaction in spite of their close distance. The ground-state absorbance and emission spectra of the dimetalated and nonmetalated cyclophanes are similar to those of the corresponding monomers but show small red shifts, broadening, and hypochromism of the lowest energy ($\pi \rightarrow \pi^*$) transition. Difference spectra for absorbance of the excited state are presented for the monomers and the monometalated cyclophane. A weak vibronic coupling mechanism is proposed to account for the absorbance band broadening and is indicated by the circular dichroism observed. The fluorescence yields of the cyclophanes are quenched by a factor of 2 with respect to the monomers. This is due primarily to a decrease in the radiative rate. As the dielectric strength of the solvent is increased, further quenching of the fluorescence and triplet yields of only the monometalated cyclophane is found. The data presented elucidate the photophysics of these chlorophyll dimers and provide the basis for further study of the photochemistry of a donor-acceptor system with restricted conformational freedom.

Introduction

In both plants and in photosynthetic bacteria a small number of chlorophyll molecules contained in reaction center proteins carry out the primary charge separation of photosynthesis. A great deal of work has been carried out to ascertain the structural and mechanistic details of the primary photosynthetic act.[1] One of the most important questions regarding the initial charge separation is the precise spatial orientation of the primary donor with the primary acceptor molecule. The geometry in the natural organism is such that the forward electron transfer occurs in a few picoseconds, while the back electron transfer is several orders of magnitude slower. In the reaction center protein of purple photosynthetic bacteria, the most readily isolable and characterizable such protein, a bacteriochlorophyll *a* dimer, $(BChl\ a)_2$, serves as the primary donor, while a bacteriopheophytin *a* molecule functions as the first acceptor that remains reduced on a nanosecond time scale. In order to understand photoinduced charge separation in this system, several groups have prepared model systems involving one or two chlorophyll molecules covalently linked to a pheophytin molecule.[2-8] While all these model systems restrict the average distance between the chromophores, only a few of the models attempt to restrict the geometry of the chromophores relative to each other by using additional covalent linkages.[5,8] Knowledge of the basic photophysics and hypothetical electron transfer characteristics of these systems remains quite preliminary.

We have previously synthesized a bis(chlorophyll)cyclophane in which two mesopyrochlorophyllide *a* macrocycles are joined by two covalent linkages to form a C_2 symmetric structure in which the motion of the two macrocycles is confined to primarily a "jawing" motion along one axis (Figure 1).[5] Since this cyclophane can be prepared with zero, one, or two magnesium atoms, this model readily allows the study of chlorophyll-chlorophyll, chlorophyll-pheophytin, and pheophytin-pheophytin interactions in a spatially constrained system. Our investigations of the photophysics of these molecules will be presented in this paper.

Experimental Section

The cyclophanes were synthesized by use of the techniques outlined in ref 5. The cyclophanes were further purified through the use of high-pressure liquid chromatography (HPLC) (Waters Associates) with a reverse phase column (C_{18}-μ-bondapak) and a differential refractometer as a detector. Methanol was used as the solvent. Samples with solvents other than methanol were produced by evaporating the methanol with dry nitrogen and redissolving in the appropriate solvent. HPLC of these samples after the picosecond measurements were made indicated at most a 2% impurity. For the monometalated cyclophane, the impurity co-chromatographed with the metal free cyclophane while for the dimetalated cyclophane the impurity co-chromatographed with the monometalated cyclophane. The estimate of the sample purity was based on the area of the pure component peak compared to that of the impurity.

The solvents used were all reagent or spectral grade with the exception of the butyronitrile. Butyronitrile (Aldrich, 98%) was purified by refluxing the solvent with a mixture of potassium permanganate and sodium carbonate. The butyronitrile was then distilled. A second distillation from P_2O_5 was used to dry the solvent. To obtain the desired absorption spectrum indicative of pentacoordinate magnesium, pyridine, tetrahydrofuran, or ethanol was added.

Steady-state absorption spectra were measured with an absorption spectrometer (Cary 219). Circular dichroism (CD) spectra were measured on a Jasco J40A. Uncorrected emission spectra were recorded with a spectrofluorometer (Perkin-Elmer MPF 44A) equipped with a red sensitive photomultiplier (Hamamatsu R928). Emission spectra were taken at 10^{-6} to 10^{-5} M in "I cell" (0.2 × 1 cm) cuvettes. The long path of the cuvettes was parallel to the excitation beam. Relative yields were obtained by integrating the emission spectrum with a planimeter. Fluorescence quantum yields were also measured with a photon counting apparatus.[9] Wavelength correction factors for the photon counting apparatus were obtained with a standard lamp from the National Bureau of Standards. In these experiments a 1 × 1 cm cuvette was used and the absorbance at the excitation wavelength was 0.01. The samples were excited with 380-nm light. Quantum yields were taken relative to chlorophyll *a*, which has a quantum yield of 0.32.[10] Absolute quantum yields were found to be reproducible to ±10% in these experiments and agreed well with the relative yields measured with the MPF 44A.

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Table I

	toluene				dichloromethane				butyronitrile			
	A_{max}	fwhm	F_{max}	fwhm	A_{max}	fwhm	F_{max}	fwhm	A_{max}	fwhm	F_{max}	fwhm
meso-methyl pyrochlorophyllide *a*	650	15	655	14	650	16	655	17	650	15	653	15
meso-methyl pyropheophorbide *a*	659	15	662	14	657	16	661	16	654	15	658	16
nonmetal cyclophane	660	22	664	20	659	19	660	18	658	22	662	22
monometal cyclophane	657	21	664	21	656	19	659	19	653	21	660	18
dimetal cyclophane	652	16	657	17	652	17	568	17	652	16	655	17

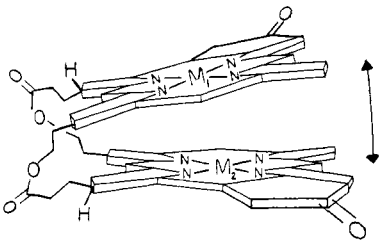

Figure 1. Structure of the bis(chlorophyll)cyclophanes: $M_1 = M_2 = Mg$; $M_1 = M_2 = H$; $M_1 = Mg$; $M_2 = H$.

Time-resolved fluorescence data for singlet lifetimes less than 3 ns were obtained with a streak camera (Hamamatsu C979). The output phosphor of the streak camera was imaged onto a silicon intensified vidicon (SIT) camera (RCA) which was digitized. The digital output of the optical multichannel analyzer (OMA) recording system was transferred to a NOVA 3 (Data General) computer for averaging. Further analysis of the data was carried out on a VAX 11/780 (Digital Equipment) computer using the program DISCRETE developed by Provencher.[11] The time base of the streak camera was calibrated with an etalon while the uniformity of response was checked with a sample having a long fluorescence lifetime (e.g., *meso*-methyl pyropheophorbide *a* (*meso*-MePPh *a*)). Sample cells had a 0.2-cm pathlength. Sample fluorescence was collected and collimated with a 50-mm focal length lens. After passing through color filters which blocked the excitation, the fluorescence was focused onto the input slit (30 μm) of the streak camera. A spatial filter was also used to block the excitation light. The laser was attenuated with neutral density filters to give typically 50% saturation. To eliminate the effect of rotational reorientation of the cyclophane on the fluorescence decay curves, the fluorescence from several samples was monitored with a polarizer placed between the sample and the streak camera. The results were not affected by having this polarizer either parallel or perpendicular to the excitation light. For singlet decay times longer than 3 ns a photomultiplier (Hamamatsu R928) coupled to an oscilloscope (Tektronix 7834) was employed. Only the first five dynodes of the photomuliplier were used to improve the time resolution. The time response of the photomultiplier–oscilloscope combination was 2 ns full width at half height (fwhh). Lifetimes between 2.5 and 4.5 ns measured with the streak camera and the photomultiplier agreed to within 20%. Signal averaging was used with the streak camera either by manually matching the maximum of the signal rise or by using a prepeak that went around the sample.

Time-resolved absorption difference spectra were measured with a mode-locked Neodymium glass laser (pulse width ~10 ps) in a point by point fashion as described in ref 12. An echelon was used in the spectral studies. Absorbance changes were averaged over five echelon segments from 10 to 50 ps after excitation. Each data point consists of four excitation and four nonexcitation shots. Typical uncertainty is <0.03 A. A SIT or silicon vidicon (RCA) was used to detect the probe light. The peak absorbance of the sample at the red-most band was typically set to 1.0–1.5. The laser was found to be 70–80% saturating by attenuation of the exciting light with neutral density filters. Absorbance at longer times was measured by addition of a 30-ft optical delay line for the probe pulse. Triplet quantum yields were estimated by the ratio of the bleaching in the red-most absorption band of the molecules at long times (30 ns) with that measured immediately after excitation (10 ps).

Results

The absorption spectra of the three cyclophanes in dichloromethane with 1% (v:v) pyridine are shown in Figure 2a. For comparison the absorption spectra of the monomers are shown in Figure 2b. The extinction coefficients were measured in toluene with 1% (v:v) pyridine. The red-most band (Q(0,0)) was found to have an extinction of 4.8×10^4 M^{-1} cm^{-1} for monomeric *meso*-methyl pyrochlorophyllide *a* and 3.9×10^4 M^{-1} cm^{-1} for monomeric *meso*-methyl pyropheophorbide *a*. In comparison, the dimetalated cyclophane extinction was 8.2×10^4 M^{-1} cm^{-1} and the nonmetalated was 5.4×10^4 M^{-1} cm^{-1}. These agree well with the previous determination.[5] The Soret (B(0,0)) electronic transitions and the vibrational overtones of the red-most (Q(0,0)) electronic transition are increased in relative strength in the cyclophanes as compared to the monomers.

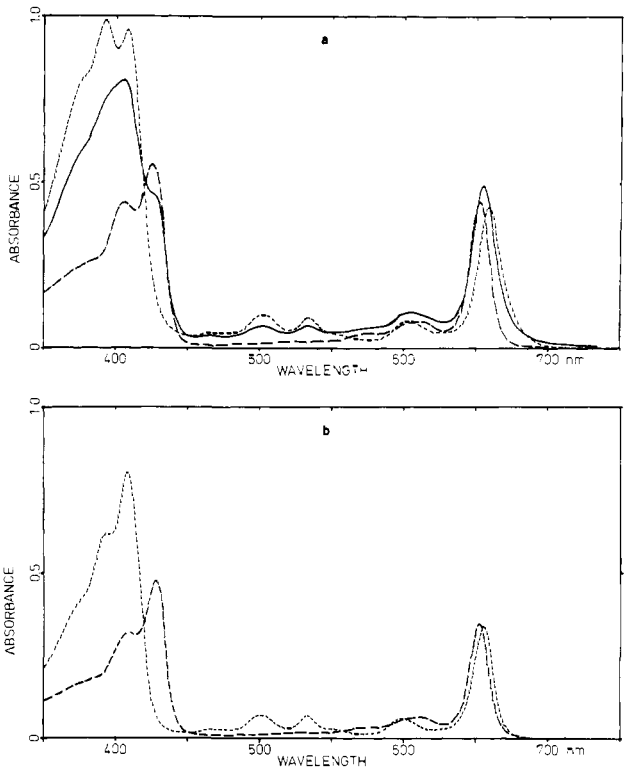

Figure 2. (a) Absorption spectra of the nonmetalated (----), monometallated (—), and dimetallated (--) cyclophanes. (b) Absorption spectra of *meso*-methyl pyropheophorbide *a* (----) and *meso*-methyl pyrochlorophyillide *a* (--). All spectra were taken in dichloromethane with 1% (v:v) pyridine. Path length was 0.1 cm.

The circular dichroism (CD) of the lowest excited singlet state of the monomers and the monometalated cyclophane is shown in Figure 3. An amplification of the monomer negative rotation was seen in the cyclophane in toluene without any accompanying positive band.

The emission spectra of the cyclophanes are shown in Figure 4a. For comparison, the emission spectra of the two monomers and their mixture are presented in Figure 4b. The maximum in the emission spectra and the absorption spectra of the monomers and the cyclophanes as well as the full width at half height are summarized in Table I. The three solvents were chosen for their range of dielectric constant. Toluene, methylene chloride, and butyronitrile have dielectric constants of 2.4, 9, and 20, respectively. The most striking feature in this table is the fact that there is only a small amount of broadening in both the absorption and the emission spectra of the cyclophanes with respect to the mo-

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Table II

	toluene				dichloromethane				butyronitrile			
	τ_f, ns	ϕ_f	$k_R \times 10^{-7}$ s^{-1}	ϕ_T	τ_f, ns	ϕ_f	$k_R \times 10^{-7}$ s^{-1}	ϕ_T	τ_f, ns	ϕ_f	$k_R \times 10^{-7}$ s^{-1}	ϕ_T
meso-methyl pyrochlorophyllide *a*	7.5	0.60	8.0		7.0	0.56	8.0[a]		11.0	0.50	6.0	0.40
meso-methyl pyropheophorbide *a*	8.0	0.40	6.0		7.0	0.46	5.0		10.0	0.43	3.9	0.65
nonmetalated cyclophane	8.0	0.20	3.5	0.45	6.0	0.31	4.2	0.3	6.0	0.33	3.5	0.40
monometalated cyclophane	6.5	0.17	2.8	0.45	1.3[b]	0.06	3.3	0.02	0.5[b]	0.04[c]	2.26	0.10
dimetalated cyclophane	8.0	0.26	4.6	0.45	6.3	0.36	6.3	0.40	3.5	0.22	3.8	0.15

[a] This value was calculated from ϕ_f and τ_f and used as a normalizing factor. [b] Best single exponential fits. [c] This value represents only an upper limit due to the presence of a long-lived fluorescent impurity.

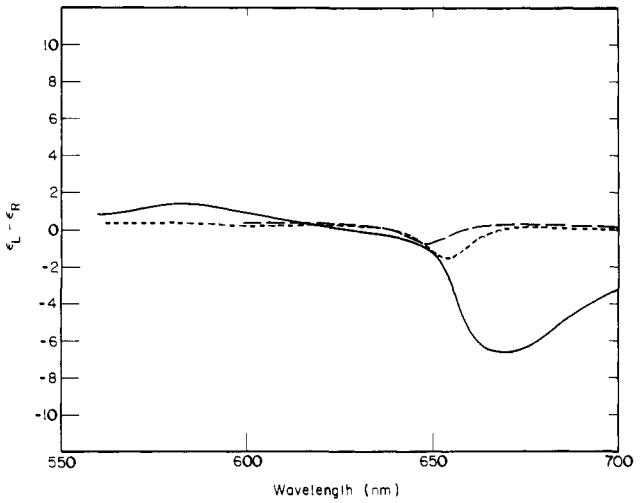

Figure 3. Circular dichroism of the monometalated cyclophane (—), *meso*-methyl pyrochlorophyllide *a* (– –), and *meso*-methyl pyropheophorbide *a* (- - - -). The solvent was toluene and 1% (v:v) ethanol. Path length was 2 cm. The concentration was adjusted so all compounds had an absorbance of 1.0 for the red-most band.

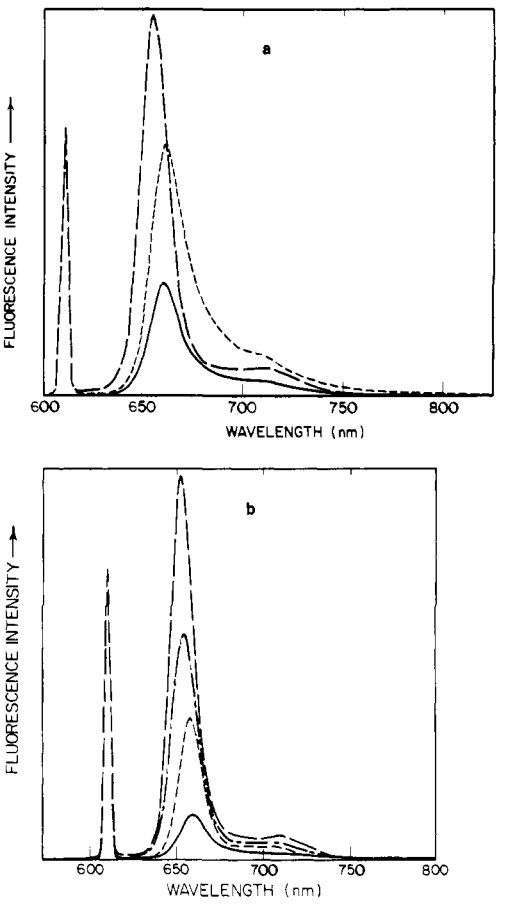

Figure 4. (a) Emission spectra of the monometalated (—), dimetalated (– –), and nonmetalated (- - - -) cyclophanes. (b) Emission spectra of *meso*-methyl pyrochlorophyllide *a* (– –), *meso*-methyl pyropheophorbide *a* (- - - -), a 1:1 mixture of these two monomers (– – –), and monometallated cyclophane (—). The solvent was butyronitrile with 2% pyridine. The cuvette was an I cell 1.0 × 0.2 cm. All samples were adjusted in concentration to have an absorbance of 0.1 in the red-most band for the 0.2-cm path. Excitation wavelength was 610 nm; Rayleigh scattering is shown.

nomers. The broadening is <3 nm for the dimetalated and <7 nm for the nonmetalated cyclophane. The absorption spectra of both the monomers and the cyclophanes are very weakly solvent dependent. The Stokes shift is only a few nanometers for both the monomers and the cyclophane.

The fluorescence yields and other photophysical parameters for the cyclophanes and the monomers are given in Table II. The fluorescence yields for the monometalated cyclophane represent an upper limit due to the presence of a small amount of fluorescent impurity. The fluorescence yield of nonmetalated cyclophane in butyronitrile is about 0.3. Thus, at a concentration of 2% the metal-free cyclophane impurity would contribute 0.006 to the overall yield. Since the yield of monometalated cyclophane in butyronitrile is 0.04, the impurity may contribute as much as 15% to the total yield.

The radiative rate for the singlet excited state is the fluorescence quantum yield divided by the fluorescence lifetime. Relative radiative rates were obtained by monitoring the instantaneous emission from samples of known absorbance at the excitation wavelength of the laser (530 nm). The laser energy was monitored with a prepulse. The absorption of the sample at the red peak (near 656 nm) was kept below 0.1 to minimize the effect of self-absorption on the relative radiative rates. The relative radiative rates measured in this way were normalized to a radiative rate of 8×10^7 s^{-1} for *meso*-methyl pyrochlorophyllide *a* (*meso*-MePchl *a*) in methylene chloride, which was obtained from the fluorescence lifetime and the fluorescence quantum yield. When the radiative rate of *meso*-MePPh *a* was measured relative to *meso*-MePChl *a* in this way it was found to agree to within 20% to that calculated from its lifetime and fluorescence yield. The absolute rates obtained from normalization to *meso*-MePchl *a* are found in Table II for various samples under different solvent conditions. Possible errors in the determination of radiative rates by this method could arise from impurities, residual polarization, and wavelength-dependent detector efficiency. These were all checked and found to be small compared with experimental error (20%). The fluorescence lifetimes of the three cyclophanes were measured in three solvents. The fluorescence decays for the three cyclophanes in butyronitrile are shown in Figure 5. The best single exponential fits to the data are reported in Table II.

In all the samples studied there was a long-lived component in the absorbance decay whose lifetime in all of the solvents at 10^{-4} M concentration was found to be longer than 1 μs. This component is believed to be the triplet state. The yields of the long-lived state for various samples are summarized in Table II.

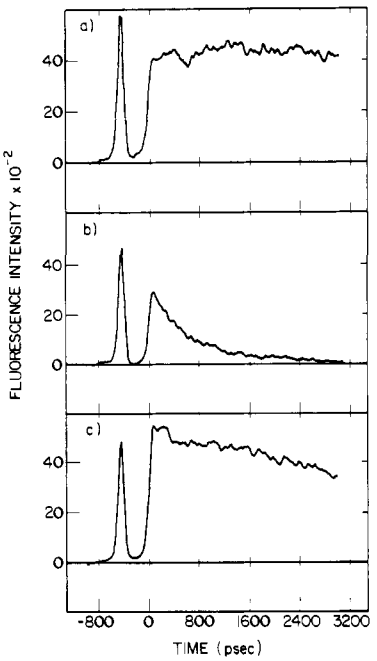

Figure 5. Time-resolved fluorescence from (a) nonmetalated, (b) monometalated, and (c) dimetalated cyclophanes. Solvent was butyronitrile and 2% pyridine. Path length was 0.2 cm. All samples had absorbance in red-most band of 0.3. The prepulse shown at −500 ps went around the sample and was used for signal averaging. Excitation wavelength was 630 nm.

These values are accurate to within 10%. The monomers each showed yields of approximately 0.5 in butyronitrile. For monometalated cyclophane the yield substantially decreased as the dielectric strength of the solvent increased. Thus, although a triplet yield of 0.45 was found in toluene, the yield was only 0.1 ± 0.05 in butyronitrile. The dimetalated cyclophane showed a decrease in triplet yield only in butyronitrile, while for the nonmetalated cyclophane the triplet yield was not affected by higher dielectrics. Thus, the triplet yield was found to parallel changes in the fluorescence yield.

Time resolved excited-state difference spectra of monomeric *meso*-MePChl *a* and *meso*-MePPh *a* in butyronitrile were averaged from 10 to 50 ps after a flash. They are shown in Figures 6a and b. A difference spectrum of the monometalated cyclophane in butyronitrile averaged between 10 and 50 ps after excitation is shown in Figure 6c.

Discussion

An examination of the absorption and emission spectra of the cyclophanes, Figures 2 and 4, with reference to those of the monomers indicates that the two macrocycles act as nearly isolated chromophores despite their proximity. A small red shift, 2–4 nm, and broadening of the first excited singlet Q(0,0) bands near 656 nm was found. The band broadening was about 2 nm for dimetalated cyclophane, 4 nm for monometalated cyclophane, and 5–7 nm for nonmetalated cyclophane (Table I). The lack of electronic interaction in the cyclophane excited states which is evident from the data can be discussed in terms of the zero-order exciton model.[13] This model predicts that two molecules with distinct dipole transition moments will form an excited state which is a linear combination of the monomer excited states when the monomers are in close proximity. As is shown in Figure 1 when the two macrocycles are coplanar and their transition moments are perpendicular, the model predicts no interaction. A twisting motion of the macrocycles which would decrease the angle between the transition moments but keep the macrocycles coplanar would produce a splitting of the exciton (+ −) states. This would lead to band broadening and red shifting of the band. Exciton (+ −) states would immediately appear in the CD spectrum as the

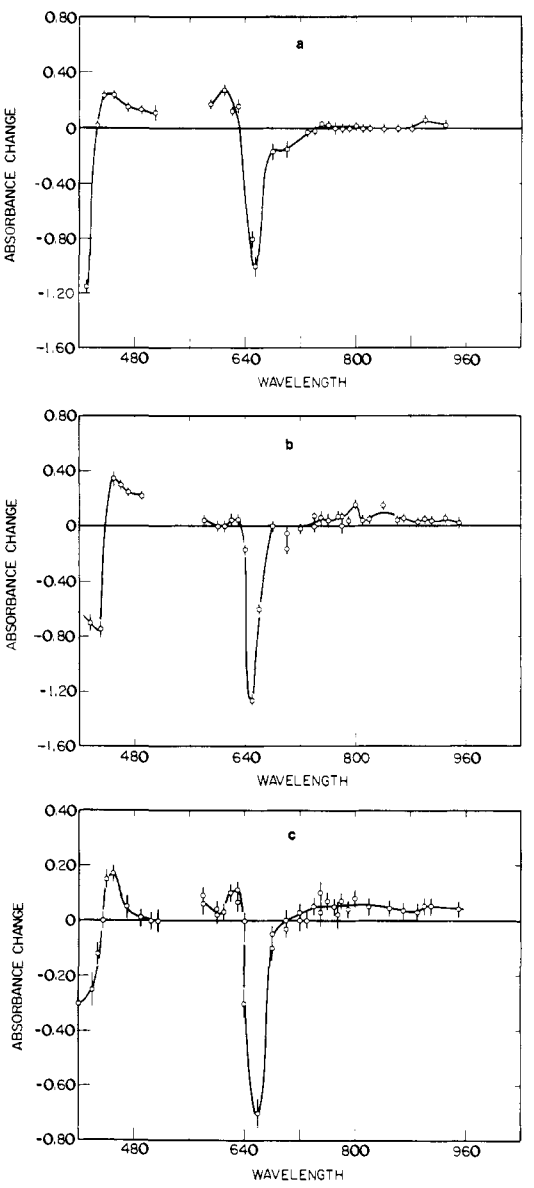

Figure 6. Excited-state absorbance difference spectra taken 10–50 ps after excitation with a 530-nm laser pulse: (a) *meso*-methyl pyropheophorbide *a*; (b) *meso*-methyl pyrochlorophyllide *a*; and (c) monometalated cyclophane. The solvent was butyronitrile and 5% (v:v) tetrahydrofuran. The path length was 0.1 cm. The data in each trace is taken from several different samples whose absorbance of the red-most band was 1.0–1.5 and corrected for differences in ground-state absorbance.

transition moments became nonorthogonal. Such CD behavior has recently been observed in a cofacial bis(chlorophyll)-cyclophane[8] in which the transition moments are parallel. The circular dichroism of our monometalated cyclophane did not show a conserved negative and positive rotation (Figure 3). The small negative rotation for the monomers was amplified by a factor of three for the dimer. Thus, the small broadening seen in the absorbance and fluorescence spectra is probably not due to exciton interaction. A much more feasible motion for the two macrocycles is "jawing" as indicated in Figure 1. This motion consists of a change in angle between the planes of the two macrocycles and a concomitant increase in intermacrocyclic distance while the Q_y transition moments of the two macrocycles remain approximately perpendicular. In this instance the zero-order exciton model again predicts no electronic interaction.

The interaction which does take place between the monomers in the cyclophane may be attributed to weak vibronic coupling.[14]

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The fluorescence yields of the dimetalated and nonmetalated cyclophanes in a given solvent are roughly a factor of 2 less than those of their corresponding monomers (Table II). This result contrasts with that reported for singly linked pyrochlorophyll *a* dimers vs. their corresponding monomers.[15] In the latter case the singly linked dimers possess fluorescence lifetimes and quantum yields of fluorescence that are comparable to their monomers. The decrease in fluorescence lifetime for the dimetalated and nonmetalated cyclophanes is mainly due to a decrease in their radiative rate. This effect is also consistent with the observed hypochromism of the cyclophanes. The spectra of the cyclophanes also showed broader bands in both absorption and emission and the corresponding monomers (Table I). The ratio of the intensity of the vibrational overtones to the electronic transition in absorption and emission was found to increase for the cyclophanes with respect to the monomers (Figures 2 and 4). These observations suggest that weak vibronic coupling provides a mode of interaction between the macrocycles in the restricted conformation of the cyclophanes, but is either not present or unobservable in the singly linked pyrochlorophyll dimers which are much more conformationally labile.

The data in Table II show that the fluorescence yields of the dimetalated and nonmetalated cyclophanes do not vary significantly with increasing solvent dielectric strength. This reflects the fact that the radiative rates and triplet quantum yields also change only slightly as solvent dielectric strength changes. The only compound in the series that displays a strong dependence of both fluorescence and triplet quantum yield on solvent dielectric constant is the monometalated cyclophane. For this compound both the fluorescence yield and the triplet yield decrease with increasing solvent dielectric strength. Once again these results contrast strongly with the results obtained for singly linked pyrochlorophyll *a* dimers.[15] In the latter case each dimer irrespective of its degree of metalation displays a decrease in fluorescence quantum yield and lifetime as a function of increasing solvent dielectric strength. The authors suggest that this effect is due to the average distance between macrocycles being somewhat smaller in higher dielectric media due to the nonpolar nature of the compounds themselves. Clearly the situation must be different for the cyclophanes in which the conformation of the molecules is already restricted. It is therefore reasonable that the dimetalated and nonmetalated cyclophanes should display a minimum effect of solvent dielectric. This makes the dramatic decrease in fluorescence and triplet yields in the monometalated cyclophane highly suggestive of an independent route that is depleting S_1. In order to examine this interesting case more carefully, "excited state difference" spectra of the monomers and the monometalated cyclophane in high dielectric solvent were measured and are shown in Figure 6. These excited-state difference spectra represent differences in the extinction coefficient between the first excited singlet state and the ground singlet state. The Soret band and the $Q_y(0,0)$ band bleach respectively at 400–420 nm and 660 nm. Rather broad positive optical density changes are found for the monomers between 430 and 500 nm and between 580 and 620 nm. A positive absorbance change has also been reported for the excited singlet state of chlorophyll *a* between 450 and 500 nm.[16,17] In general, the excited-state difference spectrum of the monometalated cyclophane is similar to the spectra for the monomers. These spectra are also similar to the superposition of the spectra due to the chlorophyll *a* cation radical and the pheophytin *a* anion radical.[18,19]

The suggestive luminescence data and the somewhat ambiguous excited-state absorption data for the monometalated cyclophane led use to examine more carefully the possibility that the additional nonradiative pathway for deactivation of S_1 in this compound may be electron transfer. This study will be presented in a following paper.

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Registry No. Nonmetal cyclophane, 66230-02-2; monometal cyclophane, 85735-48-4; dimetal cyclophane, 66219-80-5.

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