ratory has observed that, if the light from this source is filtered through a solution of 75 g of sodium nitrite per 100 mL of water, 1 can be epoxidized with as little as 10% photodestruction of the epoxide, while epoxidation with light from a G.E. sodium lamp proceeds in good yield with no more than traces of anthracene and anthraquinone being formed.

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Photochemical Electron Transfer in Monolayer Assemblies. 1. Spectroscopic Study of Radicals Produced in Chlorophyll *a*/Acceptor Systems

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Abstract: Chlorophyll monolayers together with an acceptor species such as sublimed chloranil cause a light-induced electron paramagnetic resonance (EPR) signal. Under steady-state illumination, the rise and decay of this signal were of the order of minutes. Under flash illumination, the decay time of this signal was 0.6 ms and was temperature independent. An experiment using deuterated chlorophyll monolayers with bromanil resulted in a narrow light-induced signal with a *g* factor of 2.0025 and a broad signal with a *g* factor near 2.009. These signals were attributed to the chlorophyll radical cation and the bromanil anion, respectively. In a separate experiment we generated the chlorophyll radical cation in monolayers using iodine vapor. The resulting EPR signal had a *g* factor of 2.0025 and the life width indicated that the signal was due to monomeric chlorophyll species. We also measured the magnetic circular dichroism (MCD) spectrum of monolayer assemblies of chlorophyll with surface-active acceptor species. We found light-induced bleaching at 680 nm with enhancement occurring at 660 and 672 nm.

Introduction

Although the details of photosynthesis are not yet fully understood, the concept of a functional unit, such as a reaction center, containing a donor and an acceptor is central to the mechanism of photosynthesis. Monolayers are often studied in an attempt to mimic the aggregation states of chlorophyll (Chl) and the donor–acceptor functional unit of photosynthesis. It is believed that thin barriers of less than 100 Å in thickness are instrumental in mediating the primary charge separation.[1,2] The monolayer model systems are attempts to mimic such a barrier. A number of studies have characterized the surface properties of the Chl monolayer,[3-5] as well as its spectroscopic properties.[6,7]

In this paper, we have constructed monomolecular films of Chl together with acceptors in an attempt to model the donor–acceptor electron transfer reaction found in photosynthesis. In part 1, we describe the electron paramagnetic resonance (EPR) results and the magnetic circular dichroism (MCD) results of this study. In part 2,[8] we describe the photoelectric phenomena in these monolayer assemblies.

Experimental Section

Monolayer Preparation. Great care is required in the preparation of monolayer systems, particularly in Chl monolayer systems.[5,9,10] To eliminate vibrations, the film balance was placed below ground level in the basement of the building; elsewhere in the building vibrations were too disruptive. The balance was covered with a Plexiglas box at all times to prevent dust contamination. Nitrogen gas was admitted to the balance chamber in an attempt to minimize degradation

of the chlorophyll film by atmospheric oxygen. The film balance was a Cenco torsion balance. The trough, coated with Bakelite, was carefully washed with Decon 75 (BDH) detergent, rinsed thoroughly with doubly distilled water, and dried. The entire surface was coated with a film of paraffin wax dissolved in benzene to leave the surface hydrophobic. The torsion barrier was made of Teflon with flexible Teflon tape closing off the ends. The subphase was triply distilled water. House distilled water was further distilled from $KMnO_4$, then from glass. The pH of the subphase was adjusted to 7.5 by adding phosphate buffer (10^{-4} M).

The pressure-area curve of the chlorophyll *a* monolayer is shown in Figure 1. This curve agrees well with that reported in the literature by Hirsch et al.[11] The experiments involving Chl were carried out in a dim green light, just bright enough to permit the manipulation of the apparatus. The Chl was spread with a benzene solvent.[4] After the benzene had evaporated, the surface pressure was very gently increased to 20 dyn cm⁻¹, which is below the collapse point of the Chl monolayer.[9] Then the sample slides were dipped. After the downward dip, the surface pressure was readjusted and the upward dip proceeded. In this way, we attempted to eliminate random fluctuations in the surface pressure during the dipping procedure. The Chl thus was deposited in the pressure range of 17.5–20 dyn cm⁻¹. The glass substrates used were relatively small, less than 5% of the water surface area covered with Chl.

The monolayers were deposited on Corning microscope slide covers. These were first cut to size to fit into the EPR cavity (10 × 22 mm). They were washed in ethanol or acetone, then boiled in concentrated nitric acid for 3–4 h. The slides were then washed with doubly distilled water repeatedly, then with absolute ethanol, and were then dried. The substrates were then placed in a chloroform solution containing dimethyldichlorosilane[12] for a period of 15 min. After further washing with chloroform, the slides were dried. Only those slides which shed water perfectly were used for depositing monolayers. The slides were then suspended vertically from a system of levers driven by a phase tracking motor via a cardioidal cam resulting in an approximately

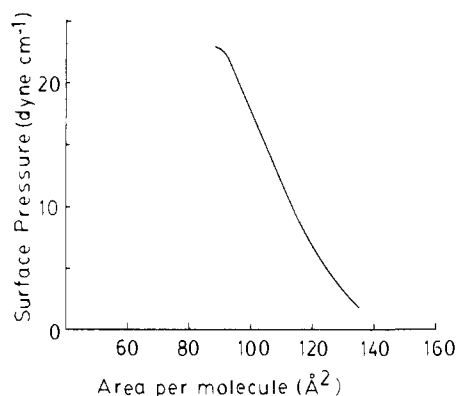† Member of the Centre for Interdisciplinary Studies in Chemical Physics at the University of Western Ontario.

Figure 1. The pressure–area diagram of Chl *a*. The subphase was 10^{-4} M phosphate buffer at pH 7.5.

constant dipping speed. The slides were dipped down and up, a distance of 1.8 cm each way, in 3 min resulting in a dipping speed slightly over 1 cm min^{-1}. We estimated the deposition ratio to be greater than 0.9, which is consistent with the data of Iriyama.[9] This figure indicates that the film may have been somewhat less densely packed on the glass substrate than it was on the water surface.

The fatty acids were deposited under a surface pressure of 25 dyn cm^{-1}. For these depositions, $CdCl_2$ was added to the subphase (10^{-4} M).[10] The compound N,N-distearoyl-1,4-diaminoanthraquinone (AQ), whose monolayer properties were characterized by Fukuda et al.,[13] could not be satisfactorily deposited by the dipping technique. The dipped samples were visibly nonuniform. Instead, the horizontal lift method[13] was used. The surfactant was compressed to a pressure of 25 dyn cm^{-1}. The glass substrates, suspended in a horizontal position, were lowered very slowly until they just touched the surface. The surface pressure was then released, the surface was cleaned, and the substrates were removed very gently.

In those experiments involving both Chl and chloranil, the Chl was deposited on the glass substrate first; the substrate was then suspended in a sublimation vessel vertically. The chloranil at the lower end of the vessel was warmed with hot water while the upper portion of the vessel where the Chl samples were located was cooled with ice. The temperature at the Chl sample as measured with a thermocouple remained below 20 °C. After 10–20 min in the sublimation vessel, a thin film (nonuniform) of chloranil was visible on the sample slides.

The EPR spectra were recorded on a Varian E-12 spectrometer. Seven sample slides were stacked in the dark, resulting in an optical density of 0.7, and were attached to a quartz tissue cell by Scotch tape. A rectangular TE$_{102}$ EPR cavity was employed and was flushed with nitrogen gas during the experiment. The *g* factors were measured by simultaneously recording the Mn^{2+} spectrum in SrO^{14a} and the sample spectrum.

The chlorophyll cation was generated by exposing the sample slides bearing the chlorophyll monolayers to iodine vapor for 10–20 s. The sample was then inserted in the EPR cavity. The same results, however, were obtained when chlorophyll was exposed to atmospheric oxygen.

The samples were illuminated by a custom-designed illuminator employing ellipsoidal optics and a General Electric sun gun 600-W lamp. The light was filtered by water as well as by a red filter (Corning CS2-62). For the flash-photolysis EPR experiments, a Photochemical Research Associates Model 610A pulsed light source with a flash width at half-maximum of 50 μs was used. The signal was recorded on a Fabritek 1072 computer of averaged transients (Nicolet Corp.).

The magnetic circular dichroism (MCD) experiments were performed on a Japan Spectroscopic Co. Jasco-ORD/UV-5 spectrometer. The magnetic field of 50 kG was supplied by an Oxford Instrument Co. (Oxford, England) superconducting magnet. The calibration and sign of the MCD signal agreed with conventional use.[15] Optical absorption spectra were recorded with a Cary 118 UV/vis spectrophotometer.

Computer simulations of the EPR spectra were performed using the program ESRALL (University of Western Ontario) using Gaussian line shapes.

Chemicals. Chlorophyll (Chl) was prepared from algae, spinach, fresh corn leaves, or other grasses by the dioxane precipitation
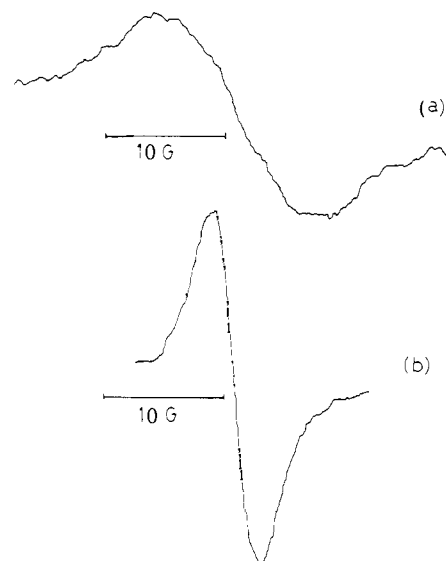

Figure 2. The EPR signals due to normal Chl$^+$ (a) and DChl$^+$ (b) in monolayer assemblies. The signals were recorded under a modulation amplitude of 2 G, 15-mW power, a time constant of 1 s, a gain of 8×10^3, and a scan time of 2 min. The *g* factor was 2.0025. The lines did not narrow under lower power settings.

method.[16,17] The extract was then purified by column chromatography using type II alumina. The Chl preparation was rapid (3–5 h) to minimize decomposition of Chl. The Chl was stored in benzene solution under dry ice. The purity of the Chl was checked by the optical absorption spectrum. Fresh Chl was prepared every few days. Fully deuterated Chl (DChl) was prepared from *Scenedesmus obliquus* algae grown in 99% D_2O.

N,N'-Distearoyl-1,4-diaminoanthraquinone (AQ) was prepared by the acylation reaction as described by Fukuda.[13] Chloranil was obtained from Eastman and was used as received. Bromanil was synthesized from bromine and benzoquinone according to the method of Jackson and Bolton.[18] The structure was confirmed by a mass spectrum. Saturated fatty acids were obtained from Serdary Research Labs.

Results and Discussion

Chl Cation. After the Chl samples were exposed to iodine vapor and inserted into the cavity of the EPR instrument, an EPR signal was detected. Figure 2 shows the signals arising from the Chl and DChl cations in monolayers without any other acceptor species after exposure to iodine vapor or atmospheric oxygen. The observed *g* factor is 2.0025. The EPR line widths are 12.6 ± 0.4 G for normal Chl and 4.4 ± 0.2 G for DChl. Deuteration narrows the line by a factor of 2.8 indicating that the EPR line width is largely due to hyperfine coupling between the unpaired electron and the hydrogen nuclei. The narrowing effect of deuteration is limited to a maximum of 3.26, which is the ratio of the total hyperfine splitting of a proton vs. a deuteron.[14b] Fajer[19] has reported that, in a solid solution matrix using a methanol–methylene chloride mixed solvent, the monomeric Chl cation has an EPR line width of 9 G, where the line width is largely due to hyperfine interaction with the β protons on the saturated ring IV (see Figure 3). For dimeric species such as the synthetic dimer cation of chlorophyllide, the EPR signal has a line width of 7 G as reported by Wasielewski et al.[21]

The observed width of the EPR signal in the monolayer assembly is probably due to crowding in the monolayer environment. Hirsch et al.[11] have reported spectroscopic evidence for six different aggregation states in the Chl monolayer. Since an EPR line narrows as the number of molecules sharing the unpaired electron increases, the line width of 12.6 G which we observed could be due to a Chl monomer species. To account for the fact that it is wider than the 9-G width of the monomer
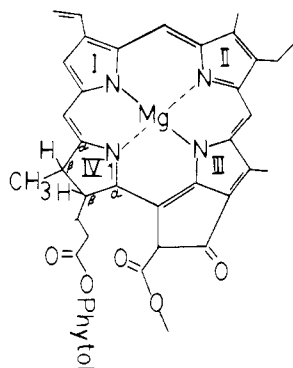
Figure 3. The molecular structure of Chl *a*. The hyperfine interaction occurs in the saturated ring IV. The dihedral angle is the angle made by the p_z orbital on the β-carbon atom with the plane containing the C_α-C_β H bonds on ring IV. Phytol stands for -CH$_2$CH=C(CH$_3$)-[CH$_2$CH$_2$CH$_2$CH-(CH$_3$)]$_3$CH$_3$.
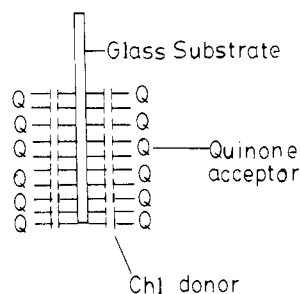

Figure 4. The Chl-quinone model system. The glass substrate bears the Chl monolayers. These are then covered by a film of sublimed quinone acceptor.
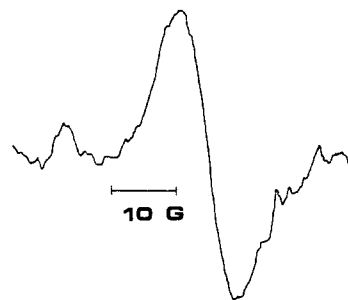

Figure 5. Light minus dark difference EPR spectra (four scans light on and four scans light off averaged) of DChl with sublimed chloranil. Seven slides were used with four layers of DChl on each side of each slide. The instrument settings were as follows: magnetic field, 3390 G; microwave frequency, 9.512 GHz; modulation amplitude, 6.3 G; microwave power, 20 mW; gain, 1.25×10^4; time constant, 0.3 s; scan time, 4 min; scan width, 100 G.
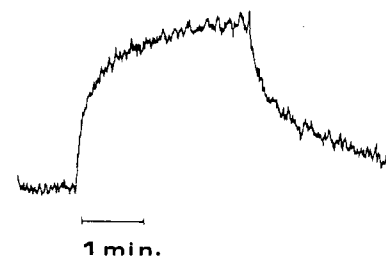

Figure 6. The rise and decay of the EPR signal of the DChl-chloranil system under steady-state illumination with red light. The magnetic field was positioned at the low-field maximum (see Figure 1). Illumination was by a General Electric sun-gun lamp with filtering through water and a red Corning filter CS2-62. The instrument settings were as follows: magnetic field, 3384 G; microwave frequency, 9.513 GHz; gain, 2×10^4; microwave power, 20 mW; modulation amplitude, 12.5 G; time constant 1 s; scan time, 16 min.

cation signal observed in a solid solution matrix by Fajer,[19] we may postulate that the crowding of the monolayer leads to skeletal stress resulting in changes to the dihedral angle θ (the angle made by the p_z orbital on the β-carbon atom and the C_α-C_β-H plane). Assuming that θ is 45° in the solid solution case,[19] by applying the equation $a_H = \rho_C(-9.2 + 96.7 \cos^2 \theta)$, where a_H is the hyperfine coupling constant and ρ_C is the electron density on the α-carbon atom,[19,20] we may estimate that the dihedral angle has changed to 36°. This change corresponds to crowding the C-H bond out of the plane of the ring, thereby increasing the overlap with the p_z orbital on the α-carbon atom.

The EPR data suggest that it is only the monomeric species which donates an electron even though a large variety of aggregation states are probably present. It would appear that the aggregated forms of Chl in the monolayer system do not behave as donor species; they may very well behave as quenching sites instead. In view of the fact that the optical absorption of the Chl aggregates occurs to the red of the monomeric form[11] it seems reasonable to assign a quenching role to the aggregates. In all likelihood, then, it is the monomeric form which is photochemically active.

Chl-Chloranil and Chl-Bromanil Systems. As a first model for the reaction center, DChl monolayers covered with sublimed chloranil were studied by EPR. This model is shown in Figure 4. Several of these assemblies were stacked and placed in the cavity of an EPR spectrometer. Upon irradiation with red light, a light-induced EPR signal was detected (see Figure 5). The signal was a single line of width $\sim$10 G, $g = 2.0043$, and hence the DChl and quinone signals could not be resolved. The rise and decay of this signal shown in Figure 6 were of the order of minutes, but depended on sublimation conditions. The quantum yield (DChl$^+$ *or* quinone generated per red photon absorbed) was $1.0 \pm 0.5 \times 10^{-5}$.

To assist in the interpretation of these data, we repeated this experiment with bromanil instead of chloranil. Bromanil has a g factor quite different from that of chloranil or Chl, thereby permitting the resolution of the EPR signals due to the Chl cation and the quinone anion. We now observed a narrow signal with $g = 2.0025$ due to the Chl cation and a very broad signal with $g \sim 2.009$ due to the bromanil anion. The dark- and light-induced spectra are shown in Figure 7.

Figure 8 shows the individual EPR spectra of the DChl$^+$ and bromanil anion species. The DChl spectrum has a g factor of 2.0025 and a line width of 4.4 G. The EPR signal due to the bromanil anion in an ethanol matrix was recorded at 77 K. It has a g factor of $\sim$2.009 and a line width of $\sim$22 G. The experimental EPR signal of Figure 7 was simulated by summing two Gaussian curves having these experimentally determined g factors and line widths and the same spin concentration. Since the sample is in the solid state, the EPR lines are more likely to be Gaussian than Lorentzian in shape. The result is shown in Figure 7 below the experimental spectrum. The two spectra are in reasonable agreement taking into account that the experimental spectrum of Figure 7 is broadened due to overmodulation. This result indicates that the DChl monolayer acts as the donor and the quinone acts as the acceptor in a light-induced electron transfer reaction.

Upon flashing the DChl-chloranil system, a rapidly decaying EPR signal was observed with $t_{1/2} \simeq 0.6$ ms. This decay was temperature independent down to 100 K. The kinetic profile is shown in Figure 9. An attempt was made to slow the back reaction by interspersing fatty acid monolayers between the DChl and the chloranil. As a result, the intensity of the EPR signal was reduced, but the decay time remained unchanged. This result would be expected if the chloranil diffuses through the fatty acid buffer layers.
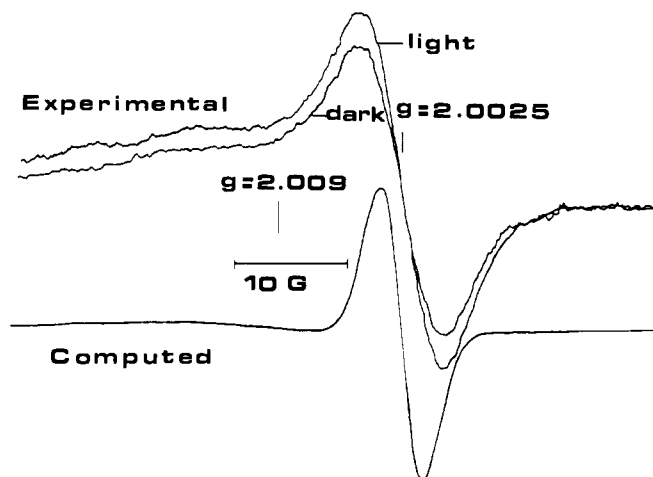
Figure 7. The EPR signal of the DChl–bromanil system in the dark and under illumination. The bromanil signal has a *g* factor of 2.009. The DChl cation signal is visible at *g* = 2.0025 and is broadened somewhat by overmodulation. The bromanil signal is barely visible because of its broadness. The instrument settings were as follows: modulation amplitude, 6.3 G; microwave power, 20 mW; time constant, 1 s; scan time, 8 min. Below, a computed spectrum using the experimental *g* factors and line widths of the DChl cation signal and the bromanil anion signal.
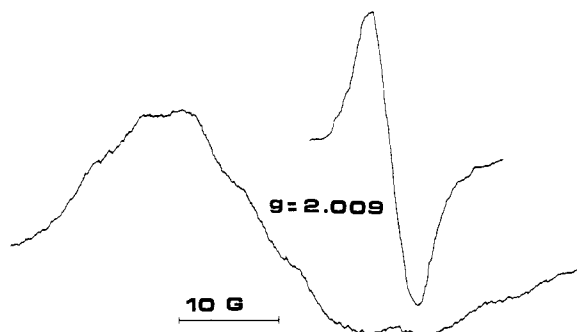

Figure 8. The EPR signal due to the DChl cation, above, in monolayer assemblies after exposure to iodine vapor. The signal was recorded under 2 G modulation amplitude, 15 mW power, a time constant of 1 s, a gain of 8 × 10³, and a scan time of 2 min. The *g* factor was 2.0025. The line did not narrow under lower power settings. The EPR signal due to the bromanil anion in an ethanol glass at 77 K is shown below. The observed *g* factor was about 2.009 and the signal was about 22 G wide. The instrument settings were as follows: modulation amplitude, 2 G; gain, 2.5 × 10³; microwave power, 0.2 mW; microwave frequency, 9.136 GHz.

That a dark signal was observed may indicate the presence of Chl–quinone radical pairs which probably are photochemically inactive. The light-induced EPR signal clearly demonstrates an electron transfer reaction from Chl to quinone. That the signal is small and the quantum yield low is consistent with the idea that only a small portion of the Chl present in the monolayer is photochemically active.

Chl–AQ System. To avoid the possible diffusion of the acceptor species into the donor layer, we turned to surface-active quinones. As we were unable to find a good analogue of chloranil, we used the surface-active derivative of 1,4-diaminoanthraquinone (AQ).[13] With this acceptor, the EPR experiments were repeated. Again, under illumination with red light, an EPR signal was observed, as shown in Figure 10. The observed *g* factor was 2.0028 ± 0.004, with a line width of ~13 G. As this signal was weaker than the previous DChl–chloranil signal, the signal was overmodulated to maximize sensitivity, and hence no further resolution of the observed signal was possible. The EPR spectrum of the AQ anion can be generated with sodium vapor. It has a *g* factor of 2.0053 and a line width of 7 G. The EPR signal of DChl was shown previously in Figure 2. Because the AQ⁻ signal is broader than that of the
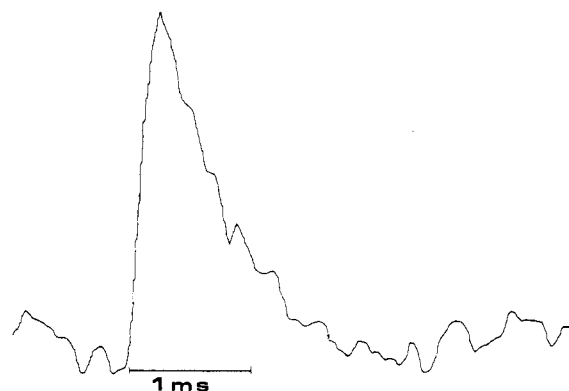

Figure 9. The rise and decay of the EPR signal in the DChl–chloranil system under flash illumination. The magnetic field was positioned at the low-field maximum. This signal is the result of 3072 flashes. The instrument settings were as follows: magnetic field, 3384 G; microwave frequency, 9.511 GHz; microwave power, 20 mW; gain, 6.3 × 10³; modulation amplitude, 12.5 G; the time constant was out. The scans were recorded in 256 points at intervals of 20 µs. Off resonance no signal was detectable.
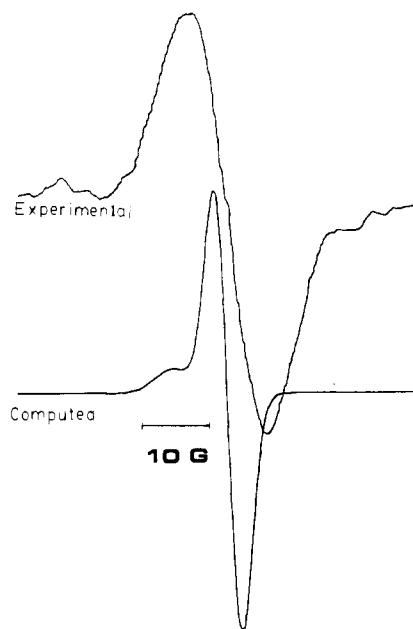

Figure 10. The light-induced EPR signal of the DChl–AQ system. Six light minus six dark scans are shown. The donor and acceptor were separated by the phytol chain of Chl, and one stearate chain resulting in a nominal separation of about 40 Å. The instrument settings were as follows: magnetic field, 3540 G; microwave frequency, 9.5 GHz; gain, 8 × 10³; modulation amplitude, 12.5 G; time constant, 1 s; scan time, 1 min; microwave power, 15 mW. This signal is broadened by overmodulation. The computed spectrum using experimental *g* factors and line widths is shown below.

DChl⁺, the latter should dominate the spectrum. To confirm that this is indeed the case, the spectrum was simulated by computer, and the result is shown in the lower part of Figure 10, using the experimental *g* factors and line widths. Indeed, the signal due to AQ would be likely to disappear under conditions of overmodulation. A flash experiment was also attempted. However, with this weaker electron acceptor, no consistent flash-induced signal could be detected.

MCD Experiments. Although the donor species is probably monomeric, the absorption spectrum of Chl monolayers would indicate the presence of large aggregates.[11,22] The absorption spectra are broader and are red shifted with respect to the solution spectrum. Illumination of the Chl monolayer results in bleaching near 700 nm in the red absorption band.[22] MCD experiments were attempted in an effort to help clarify the role of aggregates in the photochemistry of Chl monolayers.
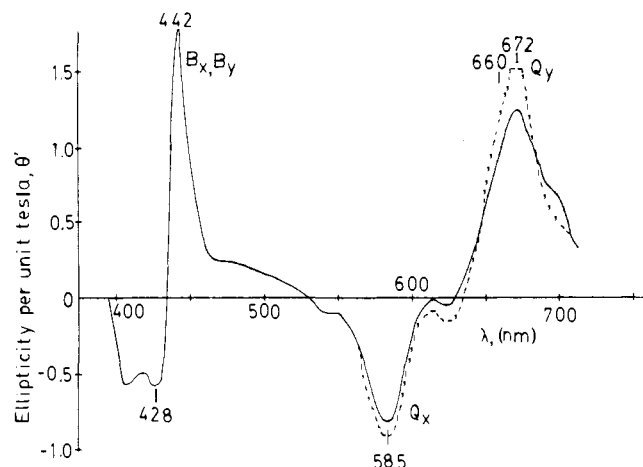
Figure 11. The MCD spectrum of 96 layers at Chl alternated with 48 layers of AQ. The zero field spectrum has been subtracted out. The scan was started at 710 nm. The first scan was completed in 10 min (solid line) and the second scan followed immediately (dotted line). In ether solution, the red maximum occurs at 662 nm and the blue maximum occurs at 420 nm. Monolayers of Chl alone consistently showed the solid line spectrum. The instrumental settings were as follows: sensitivity, 6.8×10^{-3} degree cm^{-1}; slit width, 0.6 mm; magnetic field, 5.0 T. A multialkali, red-sensitive phototube was used, Hamamatsu R 955.

The MCD spectrum is more sensitive to changes in the electronic configuration of the excited state than is the absorption spectrum. Because the ground state is diamagnetic in these monolayer samples, there is no temperature dependence of the MCD signal intensity down to 20 K (vide infra), and the MCD spectrum shows changes that have occurred to the excited state *g* factor, This technique can be considered as an optical complement to the EPR technique. An example of the sensitivity of the MCD spectrum to changes in the configuration of the 18 π-electron ring can be seen in the data measured for phthalocyanine thin films compared with the solution spectra for the same species.[23]

Ninety-six Chl monolayers were alternated with 48 layers of the acceptor AQ. Figure 11 shows the resulting MCD spectrum before and after illumination. The AQ shows no MCD activity between 500 and 710 nm. This spectrum thus is due to the Chl chromophore. Compared to the MCD spectrum of Chl in ether solution,[24] the red peak is broadened and red shifted from 662 to 672 nm, These effects are similar to those observed in the visible absorption spectrum[22] of the Chl monolayers. After illumination, however, the red band bleaches at 680 nm with enhancement occurring at about 660 and at 672 nm. By analogy to the ether solution spectrum, the 660-nm band is possibly due to the presence of monomeric species. The enhancement at 660 nm then could arise from a breakdown of the large aggregates resulting in an increased concentration of monomeric species. Samples comprising monolayers of Chl which had no AQ layers exhibited a spectrum similar to the unbleached envelope shown in Figure 11. There was no change in these spectra upon illumination or when spectra were recorded at 20 K, No temperature dependence was observed. The bleaching and enhancement effect may be caused by stress resulting from the electric field due to electron transfer from the donor to the acceptor. This spectrum represents the first example of a light-induced bleaching effect with a concomitant enhancement effect in Chl monolayer assemblies,

Recently, Periasamy and Linschitz[25] have demonstrated a similar disaggregation effect. They flashed a methylcyclohexane–methanol solution containing Chl at −78 °C with a ruby laser. They observed a bleaching of the dimer absorption band with a concomitant absorption enhancement to shorter wavelength.

Conclusions

By EPR, we have shown that monolayers of Chl can absorb red light and donate an electron to a nearby quinone species resulting in the formation of the Chl^{+}· radical cation and the semiquinone radical anion. This reaction is fairly inefficient, probably owing to concentration quenching. Also by EPR, we have shown that the donor species probably is a monomeric unit of Chl in the monolayer assembly. By MCD experiments, we have found evidence that the concentration of monomeric Chl may increase as the layer experiences stress.

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