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ENERGY TRANSFER IN REAL AND ARTIFICIAL PHOTOSYNTHETIC SYSTEMS[†]J.C. Hindman, J.E. Hunt and J.J. Katz[‡]

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Fluorescence emission from the photosynthetic organisms *Tribonema aequale*, *Anacystis nidulans*, and *Chlorella vulgaris* and from some chlorophyll model systems have been recorded as a function of excitation wavelength and temperature. Considerable similarity was observed in the effects of excitation wavelength and temperature on the fluorescence from intact photosynthetic organisms and the model systems. The parallelism in behavior suggest that self-assembly processes may occur in both the *in vivo* and *in vitro* systems that give rise to chlorophyll species at low temperature that may differ significantly from those present at ambient temperatures.

Introduction

Despite major advances in the understanding of the primary light conversion events in photosynthesis resulting from the successful crystallization of the photoreaction center of photosynthetic bacteria, many aspects of the primary processes of photosynthesis, particularly in green plants, remain obscure. The current consensus has it that charge oxidation and reduction capacity in green plant photosynthesis takes place by serial operation of two photoreaction centers (PSI and PSII), which, like the light-harvesting apparatus, consist of chlorophyll-protein complexes. It is also widely assumed that the anomalous optical properties of *in vivo* chlorophyll can be attributed to chlorophyll-protein interactions. Further, it is generally accepted that fluorescence originating in the reaction centers or the antenna chlorophyll is an accurate indicator of energy flow. All of these statements may in fact be correct. However, in our view, the experimental bases for these postulates, though voluminous, are nevertheless, in our view, not commensurate with the importance of the propositions. We have therefore undertaken a comparison of the fluorescence emissions of three intact photosynthetic organisms with those of some model chlorophyll systems to address some issues that we feel are still unresolved.

Most of what is known or surmised about chlorophyll function in the primary light conversion events in green plants is derived from optical spectroscopy on intact living organisms or on (partially) functional fragments extracted from them. Even though such systems are considerably simplified relative to the intact organism, with the exception of crystalline reaction centers, they are still very complex. The precise relationships of the isolated thylakoid, reaction center preparation, or chlorophyll-protein complex to what is actually present in the intact

organism is for the most part enigmatic. While optical spectroscopy is a powerful tool for characterizing excited state energy levels, the amount of structural information that can be extracted from optical data is distressingly small, and the assignment of the spectra is not at all a straightforward matter. In this communication, we have attempted to increase the information content of optical experiments by conducting parallel experiments on intact or fragmented photosynthetic systems, and on simple laboratory systems of well-defined composition and structure.

Model Systems

Porphyrins in various configurations have traditionally served as the models of choice for *in vivo* chlorophyll. This is not at all surprising, considering the important role porphyrins and porphyrin derivatives play in respiration, electron transfer agents, and enzymes. The biosynthesis of chlorophyll proceeds along the same pathway as that of the porphyrins present in hemoglobin, cytochrome *c*, and peroxidase. As chlorophyll once extracted from photosynthetic organisms is rather fragile, the much sturdier porphyrins have been used to study optical and other spectroscopic properties, in the expectation that information acquired on porphyrin systems will be applicable to the chlorophylls.

The spectroscopy of monomeric porphyrins and metalloporphyrins has received much attention², and the results have made important contributions to the spectroscopy of the chlorophylls. However, the applicability of monomeric porphyrins as models for chlorophyll is open to serious question. Monomeric porphyrins have optical, redox, solubility, and aggregation properties markedly different from those of the chlorophylls, and thus have only limited utility. However, model systems based on porphyrins covalently linked to other porphyrins³ or to electron acceptors have played an important role in the study of electron transfer in photosynthesis. Particularly useful have been the models in which porphyrins have been linked to electron acceptors through rigid spacer molecules that position the donor and acceptor molecules at known fixed distances⁴. Several excellent reviews of these model systems are cited in Ref. 4.

There are good reasons to suppose that the photosynthetic apparatus, both in green plants and bacteria, contains very little monomeric chlorophyll, and that aggregated chlorophyll is implicated in photoreaction center function⁵. The aggregation properties of porphyrins are very different from those of the chlorophylls, and therefore

porphyrin models are at best rough approximations. Consequently, models in which covalently linked chlorophyll macrocycles are used have been developed, which more closely mimic the *in vivo* photoreaction center. These models consist of two pyrochlorophyllide, or better, chlorophyllide macrocycles, covalently linked through the hydroxyl groups of ethylene glycol (or longer chain diol) through the two propionic acid side chains of the macrocycles^{6,7}. The basic factors involved in the self-assembly process have been identified from IR and NMR spectroscopic studies on chlorophyll by Closs, Katz, and co-workers⁸.

We have considered model systems for photosynthesis research elsewhere⁹, and will not discuss these further here. For our present purposes, we have used model systems that are self-assembled, that is, we have used Chl a under conditions where self-assembly occurs to mimic both the primary electron donor in photosynthesis and the light harvesting antenna. For the antenna, we have used a chlorophyll a (Chl a) oligomer, (Chl a) $_n$, which is formed at ambient temperatures by a keto carbonyl interaction of one macrocycle and the central magnesium atom of another, i.e., keto C=O $\cdots$ Mg. In the absence of other nucleophiles, as in a nonpolar solvent such as *n*-octane, or methyl cyclohexane, aggregates containing twenty or more chlorophyll macrocycles are formed. This oligomer absorbs maximally at 680nm. For organisms that contain Chl b as well as Chl a , such as *Chlorella vulgaris*, an antenna model containing only Chl a is obviously deficient. We have therefore also chosen for study two photosynthetic organisms that contain only Chl b , but which nevertheless evolve oxygen in photosynthesis. The modest red shift relative to monomeric Chl b is indicative of only small π - π interactions in the oligomer, despite its large size. A reasonable presumption is that the chlorophyll macrocycles in (Chl b) $_n$ are orthogonal to each other^{9(c)}. This chlorophyll species appears to have a strongly diminished, if, in fact, any capacity at all, for fluorescence at room temperature.

To mimic the P700 of PSI we use in this paper a self-assembled Chl b -ethanol/methyl cyclohexane¹⁰ system contains significant amounts of 700 nm-absorbing species at low temperatures. Self-assembled systems can be formed that contain monomeric Chl a ($\lambda_{\text{max}} \sim 665$ nm), oligomeric (Chl a) $_n$ ($\lambda_{\text{max}} \sim 678$ nm), and species very similar to those formed by linked pairs in the folded configuration ($\lambda_{\text{max}} 698$ nm), depending on the temperature and the presence or absence of extraneous nucleophiles. These model systems, by virtue of the differences in the optical maxima, provide an excellent opportunity to study energy transfer by selective photoexcitation under well-defined conditions.

Photosynthetic Organisms

We have chosen three photosynthetic organisms for our comparative fluorescence study. *Chlorella vulgaris* may be taken as the exemplar of higher green plants; its photosynthetic pigments consist of Chl a and Chl b , and carotenoids. *Tribonema aequale* is a yellow-green alga (*Xanthophyceae*) that contains Chl a and carotenoids. This organism evolves oxygen during photosynthesis; although it contains no Chl b , and no phycobilins. *Anacystis nidulans* is a cyanobacterium (blue-green alga) that contains Chl a , the phycobilins phycocyanin and phycoerythrin, and carotenoids. Photosensitive excitation permits the preferential excitation of particular pigments in specific absorption bands, and the various pigment mixes in these three organisms provide good opportunities for the application of photosensitive excitation. The general techniques for recording the fluorescence spectra are described in detail elsewhere^{10,11}. Excitation was provided by a Molelectron UV1000 nitrogen laser at 337 nm or by the output of a dye laser pumped by the Molelectron.

Results

Figure 1A shows composite room temperature absorption spectra of the various Chl species present in the self-assembled systems, and also spectra of β -carotene and the phycobilins, phycocyanin and phycoerythrin. Figure 1B shows the absorption spectrum of *Anacystis nidulans*. Indicated by Roman numerals are (approximate) regions for light absorption by different pigment systems. The selection of excitation wavelengths was partially based on the wavelength regions where the different pigments absorb, but primarily on the wavelengths of absorption of specific chlorophyll entities *in vitro*^{10,12}. Reference 10 describes the parameters for selective excitation in detail. As indicated in Figure 1A, excitation in the 430-440 nm and 650-670 nm regions preferentially excites monomer chlorophyll. Excitation near 450 and 690-700 nm can be used to preferentially excite chlorophyll species having the spectral properties of special pair chlorophyll (P700). In addition, if the *in vitro* systems contain species with the properties of chlorophyll oligomers, these can be excited by 678-681 nm light².

Figure 2 shows the fluorescence spectra of the different pigment systems. Indicated are the emission wavelength maxima assigned to components of the *in vivo* photosystems PSI and PSII¹³⁻¹⁸. As can be seen in this figure, of the auxiliary pigments only phycocyanin shows significant emission in the PSI and PSII regions.

Obviously, under some conditions emission from this (and perhaps related pigments) could complicate interpretation of *in vivo* fluorescence observations in cyanobacteria. The most important aspect of the data in Figure 2 is the significant emission in the PSI and PSII regions from a Chl α -ethanol/methylcyclohexane self-assembled system both at room temperature and at 150 K. For example, the band head near 683-685 nm is in the self-assembled system at the wavelength that has been assigned to the light harvesting Chl a/b protein complex (LHC) in PSII. We also note the red shift of the Chl a emission in the PSI region that occurs with decreasing temperature. We have previously suggested that this phenomenon may reflect temperature dependent configurational changes in the self-assembled special pair type molecules that emit in this region⁹.

Figure 3 illustrates the effect of temperature and selective excitation on the fluorescence excited in the photosynthetic organisms we have used. In Table 1 we summarize in more detail the experimental observations, and in Table 2 we list the absorption and emission bands that have been assigned to components of the photosynthetic unit by various authors. These data, then, provide a basis for a discussion of possible relationships between *in vitro* and *in vivo* systems.

Discussion

Room temperature *in vivo* fluorescence emissions are generally very broad and ill-defined as can be judged from Figure 2. If we were to deconvolute these spectral bands into Gaussian components, the bands would clearly appear to be compound. This has been noted previously (cf. Litvin and Sineshchekov, ref. 19). What is important about this observation is the strong implication that there may be a large number of different species or different configurations of the same species that contribute to the emission in a particular wavelength region. It is, therefore, an oversimplification to talk about a limited number of *in vivo* states (i.e., PSI, PSII, etc.) as implied in the breakdown compiled from the literature in Table 2. Lowering the temperature does not necessarily result in the appearance of sharply defined fluorescence spectra that can be associated with a limited number of states, although Rijgersberg and Ames²⁰ show clearly defined 685 and 695 nm bands in the 77 K fluorescence spectrum of *Anacystis nidulans* excited with either 442 or 562 nm light. On the other hand, Satoh²¹ has also pointed out that it is often very difficult to detect a distinct F695 in the 77 K emission from the chloroplasts of higher plants and algae. It is clear

from an examination of Table I and Figure 3 that the nature of the observed emissions depends strongly on both temperature and excitation wavelength. Although we do see emission band heads at 685 and 695 nm under specific excitation conditions, generally our emission curves are broad, which indicates that there are a number of emission bands in this wavelength region.

A very important question arises in connection with the observed emissions: how specifically can the emissions in a wavelength region be assigned to a particular species? For example, as indicated in Table 2, there is a widely held view that the 685 nm fluorescence emanates from the light-harvesting *Chl**a/b* protein complex (LHC or CP II) of PSII. Satoh²¹ challenges this assignment with the observation that a prominent emission near this wavelength is observed in *Tribonema* and *Anacystis* under a variety of excitation conditions. Neither of these algae contains *Chl**b*. Further, as indicated earlier and illustrated in Table 2, the emission wavelength for isolated light-harvesting *Chl* *a/b* protein complexes (LHC) tends to be closer to 681-682 nm than to 685 nm (see also reference 21). Moreover, the isolated LHC's have absorption maxima near 671-672 nm and not at 680 nm as is characteristically observed for *in vivo* absorption (Table 2, note both PSI and PSII fractions). Although such small differences in absorption maxima are not necessarily highly significant, they must be taken into account in arriving at an assignment of the 685 nm emission to an emitting species of specific composition. Finally, we note that fluorescence maxima in the 680-690 nm spectral region can be observed under a number of conditions. For example, as indicated in Figure 2, fluorescence maxima near 685 nm can be obtained from *Chl**a* in a methylcyclohexane/ethanol solution under appropriate conditions of excitation wavelength and temperature. It has been suggested that in this case, the emitting species may be a (*Chl**a*)_n oligomer coordinated to ethanol¹⁰. We have also seen weak emissions at 668 and 685 nm in Nujol mulls of H₂O-saturated octane. We observe a red shift of the emission wavelength for monomeric *Chl**a* in pyridine as the *Chl**a* concentration increases¹¹, a phenomenon that can be related to self-absorption in concentrated solutions. These various observations suggest that it is, at present, not possible to make a definitive attribution to the source of the *in vivo* 680-690 nm fluorescence.

Questions also arise about the origins of both the 695 nm and 710-730 nm fluorescence. One view is that these arise from antenna chlorophylls in PSI and PSII, respectively^{3,14}. It has been suggested¹⁵ that F695 arises from a species of chlorophyll in PSII, which forms on cooling to temperatures below 113 K and that the 710-730 nm

fluorescence also arises from a species formed at low temperature in PSI. The latter species is designated by Satoh and Butler as C705¹⁵. These authors consider that this species competes with P700 for the excitation energy in PSI. This interpretation is based on the assumption that there is no significant temperature effect on any of the fundamental rate constants for deexcitation by any pathway including nonradiative decay. The factor responsible for the large increase in fluorescence with decreasing temperature is presumed to be an increase in the concentration of C705 traps^{15,16}. Butler et al.¹⁷ suggested that this species may be present at all temperatures but becomes more fluorescent at low temperatures. It would appear equally reasonable to assume that the increase in the fluorescence quantum yield could be associated with the formation of concentrations of P700 species in excess of those required to carry out the photochemistry. Thus, it appears unnecessary to assume that C705 is qualitatively different from P700. Both the increase in fluorescence yield and the increase in fluorescence lifetime^{8,22} of PSI emitting fractions at low temperature are in accord with this view. We note that the in vitro experiments on self-assembly suggest the formation of a number of species or configurations that have P700 or special pair-like properties¹⁰.

Implicit in the preceding discussion is the presumption that the low temperature PSI fluorescence arises from special pair type molecules, i.e. nucleophile-containing chlorophyll species. We know of no experimental observations indicating significant fluorescence from any chlorophyll species that are not monomeric or oriented by bifunctional nucleophiles. If, therefore, the antennae are oligomeric chlorophyll species, as is suggested by the absorption spectra^{9,10,12} then no antenna fluorescence should be observed. Thus, the observed fluorescence associated with PSII, F685 and F695, would appear to also involve chlorophyll molecules coordinated to a ligand.

As indicated in Table 1, excitation of intact *Tribonema* at 337 nm suspended in their growth medium at room temperature results in a broad fluorescence emission with maxima at 690 nm and 740 nm. Cooling to 77 K narrows the fluorescence emission band and shifts the principal emission band to approximately 720 nm, with a distinct shoulder in the 690 nm region. Warming the solutions to room temperature results in reversion to the original fluorescence band shapes and maxima.

When 450 nm radiation is used for excitation at room temperature the primary emission band from *Tribonema* is at 686 nm with a broad tail to the red. The primary band has a shoulder at approximately 673 nm, near the wavelength expected for monomer Chl *a* fluorescence. This is also the case for *Anacystis* (see Figure 3A).

As indicated earlier, this emission cannot originate from a *Chl**a/b* protein complex since these algae contain no *Chl b*. Cooling to 77 K results in spectral changes similar to those observed with 337 nm excitation, and the red maximum is near 715 nm.

The results obtained with 672 or 681 nm radiation on *Tribonema* are particularly interesting. At room temperature the primary emission band is now observed at 693 nm (Figure 3D). The only other condition under which we see a band at this wavelength is at low temperature. When the excitation wavelength is 672 nm, there is evidence for a shoulder in the 685 nm region. The primary emission band (695 nm) is relatively narrow, suggesting that the species responsible for the emission may be well defined in a structural sense. On cooling, the fluorescence emission is red shifted and broadened and at 148 K, the primary emission is observed near 705 nm. Obviously, the observations in this case are not consistent with the assumption that the F695 forms on cooling or that F695 is present, but nonfluorescent at room temperature (see prior discussion).

An important aspect of the present observations is that both the emission wavelengths and the shape of the emission bands depend on the excitation wavelength as well as on temperature. For example, in Figure 3A and 3C we show room temperature fluorescence spectra for *Anacystis* and *Chlorella* excited by 450 nm radiation. At room temperature, the principal emission for both algae is at 685 nm. The major difference is the shoulder near 650 nm in *Anacystis* resulting from phycocyanin emission. We contrast these results with those of Figure 3B, where *Anacystis* is excited by 627 nm radiation, i.e., in the absorption region of phycocyanin. In this case, at room temperature the principal emission is at 651 nm with a secondary maximum at 708 nm. This suggests that the fluorescence is dominated by emission from phycocyanin. Such an assignment agrees with the observations of Dale and Teale²³ who found that c-phycocyanin isolated from *Anacystis* has a fluorescence maximum at 651 nm with a secondary maximum near 710 nm. The fact that we see such a strong phycocyanin emission at 651 nm but not the *Chl a* maximum at 682-685 nm suggests that energy transfer from phycocyanin to *Chl a* may be slow. If the pigment composition were homogeneous and the energy transfer fast, no dependence of the fluorescence on the excitation wavelength would be observed.

The fluorescence intensity of phycocyanin at wavelengths longer than 670 nm is much less than that of *Chl*

when the pure pigments are excited at their respective absorption maxima (Figure 2A). A comparison of these spectra with the room temperature spectra of Figure 3A and 3B shows that there must be a significant contribution by Chl_a to the *Anacystis* fluorescence at wavelengths longer than 670 nm. At low temperature this comparison strongly suggests that the fluorescence maxima at 682 and 715 nm as well as the shoulder in the 690-700 nm region (Figure 3B) are contributed by Chl_b species. The marked difference in the fluorescence spectra of *Anacystis* obtained with different excitation wavelengths suggests that in addition to possibly slow energy transfer steps there may be a significant heterogeneity in the pigment distribution. Such a heterogeneity, coupled with a slow rate of excitation energy transfer between the different structures would be consistent with the observed dependence of the fluorescence wavelengths on excitation frequency. This interpretation is the same as that advanced to explain a similar phenomenon in *vitro* chlorophyll solutions containing a mixture of species¹⁰.

Concluding Remarks

Fluorescence emission from the algae *Tribonema aequale*, *Anacystis nidulans*, and *Chlorella vulgaris* have been recorded as a function of excitation wavelength and temperature. Light emission from the algae are found to depend on both wavelength and temperature. The fluorescence data suggest that there are slow steps in energy transfer between pigment systems in these algae. We observe considerable similarity in the effects of excitation frequency and temperature on the fluorescence of intact algae and that of suitably chosen *in vitro* chlorophyll systems. The parallelism in behavior between *in vivo* and *in vitro* systems suggest that self-assembly processes result in the formation of new chlorophyll species not present at room temperature in photosynthetic organisms as a result of lowering the temperature, and that as a consequence, interpretation of low temperature observations in terms of the photosynthetic species present at ordinary temperatures may be open to question.

Acknowledgement

Work performed under the auspices of the Office of Basic Energy Sciences, Division of Chemical Sciences, U.S. Department of Energy under contract W-31-109-ENG-38.

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Figure Legends

Figure 1. Absorption spectra.

A. Pigments

--- Chl *a* in ethanol-methylcyclohexane at 298 K. Chl *a* in ethanol-methylcyclohexane at 150 K. (Self assembled special pair.)

Chl *a* = 2.25×10^{-3} M.

Ethanol = 3.6×10^{-2} M.

x—x β -carotene in octane (Absn. scale not comparable with Chl *a*).

— Phycoerythrin in 0.1 M phosphate buffer.

pH = 5.9 (Absorption scale not comparable with Chl *a*).

.... Phycocyanin in 0.1 M Na phosphate buffer.

pH = 5.9 (Absorption scale not comparable with Chl *a*).

B. *Anacystis nidulans*

— *Anacystis* (H₂O), suspended in glycerol, 298 K.

↓ Wavelengths for selective excitation.

450, 696 nm, "self-assembled" special pairs.

620 nm, phycocyanin.

660 nm, monomer Chl *a*.

670, 680 nm, oligomer (antenna) Chl *a*.

I. Chlorophyll *a* Soret.

II,III. Auxiliary pigments.

IV. Chlorophyll *a*, Q_y region.

Figure 2. Fluorescence spectra of pigments.

A. 298 K, fluorescence scales for different pigments not comparable.

.... Phycoerythrin in 0.1 M Na phosphate buffer.

pH = 5.9, $\lambda_{\text{exc}} = 337$ nm.

— Phycocyanin in 0.1 M Na phosphate buffer.

pH = 5.9, $\lambda_{\text{exc}} = 627$ nm (Note Figure 1B).

x—x Chlorophyll *a* in ethanol/methylcyclohexane.

$\lambda_{\text{exc}} = 672$ nm, similar spectra obtained with 681 nm excitation.

PSII, PSI, ↓ Fluorescence regions assigned to Photosystems I and II in vivo, see text.

B. — Phycocyanin in 0.1 M Na phosphate buffer.

pH = 5.9, 130 K, $\lambda_{\text{exc}} = 627$ nm.

x—x Chlorophyll *a* in ethanol/methylcyclohexane, 150 K, $\lambda_{\text{exc}} = 672$ nm. Similar spectrum obtained with 681 nm excitation.

Figure 3. Fluorescence spectra of algae. S indicates a shoulder.

A. *Anacystis* (H_2O) suspended in growth medium.

$\lambda_{\text{exc}} = 448\text{-}451$ nm.

— 290 K.

.... 77 K.

B. *Anacystis* (H_2O), growth medium.

$\lambda_{\text{exc}} = 627$ nm.

— 298 K.

.... 77 K.

C. *Chlorella* (H_2O), glycerol suspension.

$\lambda_{\text{exc}} = 450$ nm.

— 298 K.

.... 77 K.

D. *Tribonema* (H₂O), culture medium.

$\lambda_{\text{exc}} = 672 \text{ nm}$ ($\lambda_{\text{exc}} = 680 \text{ nm}$, also shows 693.4 nm band)

_____ 298 K

.... 77 K

Table 1. Emission of Intact in vivo Systems obtained by Selective Excitation

Species (Pigments)	$\lambda_{ex}(nm)$	Temp K	Emission $\lambda(nm)$ (sh) designates shoulder
<i>Tribonema</i>	337	298	690,740
(Chl <i>a</i>)		77	720,690 (sh)
(carotenoids) ^a	450	298	686,673 (sh)
		77	715
	650,661	298	687,690-700,720
	672	298	695,685 (sh)
		77	705 (very broad)
<i>Anacystis nidulans</i>	337	298	653,700
(Chl <i>a</i>)		77	653,694,706 (red tail)
(carotenoids) ^a	450	298	685,651 (sh)
(xanthophylls) ^b		77	715
(phycobilins) ^c	500	298	651,684,580 (sh)
		77	715,650,586 (sh)
	629	298	651,708
		77	653,683,715
	640	298	700 (broad), 655 (sh)
		77	715,650 (sh), 755
	681 ^d	77	695,710 (tail to red)
	685 ^d	298	?
		77	705-715
	696 ^d	298	?
		77	Some fluorescence possible above 730 nm
<i>Chlorella vulgaris</i> ^e	337	298	685 (tail to red)
(Chl <i>a</i>)		77	722,684
(Chl <i>b</i>)	450	298	686,730
(carotenoids) ^a		77	684,695,713
(xanthophylls) ^b	500	298	685
		77	715,685 (sh)
	627	298	
		77	685,715
	660	298	685
		77	685,712
	685 ^d	298	tail from laser to 790 nm
		77	723
	696 ^d	298	some fluorescence with laser band
		77	723

Footnotes for Table 1

^a β -carotene absorption max 468 broad with S445, 496. No fluorescence when excited at 430-50.

^bXanthophylls (oxycarotenes), like carotenes, absorption 430-500 nm, weakly fluorescent.

^cAccording to Rijgersberg and Ames²⁰, the 650 nm emission in *Anacystis* involves two bands contributed by C-phyococyanin and allophyococyanin. Bands at 650 nm and 680 nm obtained from isolated phycobilisomes are ascribed to allophyococyanin and allophyococyanin B, respectively.

^dVery little room temperature fluorescence when pumped at 680-85 and 695 nm.

^eThe *Chlorella* used for the fluorescence studies were suspended in glycerol.

^fThe 694 and 706 nm emissions represent band heads in a very broad emission spectrum with a shallow minimum at 700 nm.

Table 2. Assignments of Absorption and Emission Bands for Photosynthetic Unit Components

	Temp K	Absorption λ (nm)	Emission λ (nm)
PSI Fraction Composite ^a	298 77	437,680	682(730-740) ^b 730,680 ^b
CPI chlorophyllin ^c	298 77	673-77,490 ^d	685,725,735(sh) ^e 685,695,705,720,735
PSI Fraction ^g	298 77	437,680	682(730-740) ^b 730,735
PSI, Antenna and Reaction Center ^g	77	681	730-5 ^{g,h}
PSII Fraction	298	436,471	682(730-740)
LHC, Chl <i>a/b</i> Protein ^a	77	653,680	683-4,695-6
Antenna, trap ^g	77	650,677 670(sh)	694-5 ^h
CPII chlorophyllin ⁱ Chl <i>a/b</i> chlorophyllin	298	652,672 475	681

^aSearle et al.¹⁸^bVery weak emission.^cThornber et al.²⁴^d β -carotene-chlorophyllin, Thornber et al.²⁴^eshoulder, sh^fEmission data from Brown²⁵, both 290 K and 77K. At 77 K, 685 nm band decreases relative to 695 nm band and amplitude bands 705, 720, 735 variable with different preparations.^gKitajima and Butler²⁶. Assignment of absorption wavelength based on excitation spectra.^hButler¹⁶.ⁱCPII chlorophyllin - light harvesting Chl *a/b* protein complex in PSII. May be complex mixture including oligomeric forms. See reference (6).

Figure 1

Figure 2

Figure 3