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Photoacoustic Spectra and Fluorescence Lifetimes of Chlorophyll *a* and Chlorophyll *b* in Nematic Liquid Crystal

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With an aim to evaluate the yield of excitation energy transfer between ordered chlorophyll *a* and chlorophyll *b* molecules, the nematic liquid crystal (LC) mixture MBBA (p-methoxybenzylidene p'-butylaniline) and EBBA (p-ethoxybenzylidene p'-butylaniline) is used. The LC is oriented by deposition of the sample between stretched polyvinylalcohol films or between silicon oxide orienting layers; chlorophyll molecules are oriented similarly due to their strong interaction with LC molecules. Chlorophylls (chls) in LC are monomeric at concentrations lower than 10^{-2} M. The pigment fluorescence yields (η) were established from measurements of fluorescence lifetimes (τ) of chl *a* and chl *b* in LC and in ethyl ether. η of chl *a* is about twice that of chl *b*; therefore the yield of excitation energy transfer between pigments was obtained from photoacoustic spectra (PAS). In PAS measurements, natural and polarized light were used for sample illumination, in order to study the orientation of different species. Photoacoustic spectra and analysis of τ of pigment mixtures suggest that part of the energy absorbed in the Soret band of chl *a* is transferred to chl *b*. In fluorescence spectra, a new peak at 695 nm is observed, probably related to mixed chl *a*–chl *b*–LC "aggregates" which are differently oriented than the monomeric pigment. The energy absorbed by these aggregates is dissipated more efficiently than that absorbed by chl *a* alone. The formation of some mixed aggregates can explain why the τ and PAS values of pigment mixtures are different than the values calculated by assuming that chl *a* and chl *b* are contributing to fluorescence and deactivation effects independently of each other.

INTRODUCTION

Excitation energy transfer between chl *a* and chl *b* plays an important role in photosynthesis. In photosynthetic organisms, the pigments are located in a lamellar system which is oriented and fluid. The nemantic liquid crystals (LC) because of their fluid and easily orientable character appear to be a good medium to simulate the fluid and anisotropic lamellar system of a photosynthetic membrane.

It has been shown that from photoacoustic spectra (PAS) of the mixture of pigments with different yields of fluorescence, information regarding the efficiency of excitation energy transfer (ET) between the pigments can be drawn[1]. The fluorescence yield of chlorophyll *a* (chl *a*) is more than twice as high as that of chlorophyll *b* (chl *b*); therefore the PAS method for evaluation of the energy transfer between these pigments can be used. Specially convenient is the PAS method in the investigation of the "back transfer" from chl *a* to chl *b* because the contribution to PAS from chl *b* is higher than that from chl *a*, whereas in fluorescence excitation spectra the situation is opposite. Bauer, Szalay and Tombacz[2] have shown that excitation energy transfer from sensitization of chl *a* fluorescence by chl *b* is substantially smaller than that calculated from quenching of chl *b* fluorescence by chl *a*. The authors[2] tentatively explained this effect as superposition of fast ET (taking place before the Boltzmann distribution of vibrational energy had been reached) upon "slow" ET occurring after reaching vibrational equilibrium.

In a liquid crystal (LC) the orientations of chl *a* and chl *b* are different[3] although both pigments are oriented almost uniaxially[4]. Mutual pigment orientations influence the yield of excitation energy transfer. A similar situation has been found to exist *in vivo*, because the various pigments in the photosynthetic apparatus are differently oriented[5]. Thus, with a view to understanding the excitation energy transfer between oriented chl *a* and chl *b*, we have carried out polarized photoacoustic spectroscopy of chlorophylls in nematic liquid crystals located between stretched PVA films or in glass plates with SiO_x orienting layers. Yield of excitation energy transfer has also been calculated from lifetime measurements using the method proposed by Knox[6].

EXPERIMENTAL

Chl *a* and chl *b* were purified chromatographically and dissolved in nematic liquid crystal mixture: p-methoxybenzylidene p'-butylaniline

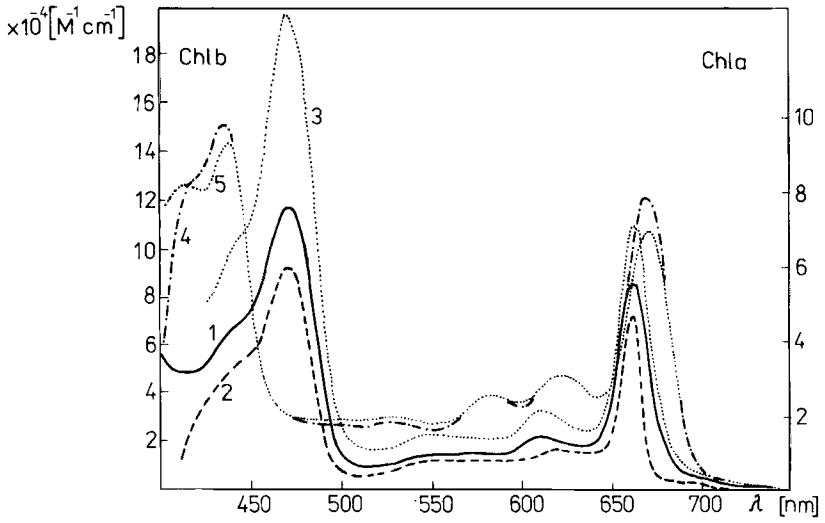

FIGURE 1 Absorption spectra of chl *b* (left scale; curves 1–3) and chl *a* (right scale; curves 4–5) in LC between PVA films, 1: natural light; 2, 5: $A_{\perp}$; 3, 4: $A_{\parallel}$. Concentrations as in Fig. 2 and 3.

(MBBA) and p-ethoxybenzylidene p'-butylaniline (EBBA). Concentrations of pigments vary from 2×10^{-4} M to 2×10^{-2} M. Only at highest concentration (2×10^{-2} M) do the aggregated forms of chlorophylls appear, as shown by our fluorescence spectra. For lower concentration (8×10^{-3} M) practically only monomeric forms of chlorophylls occur, as seen from absorption spectra Fig. 1, and from our previous results[4,7].

The orientation of chlorophyll molecules was achieved by injecting the solution of chlorophyll (in liquid crystal) in the empty space between the two 300% stretched PVA films[8], or between two glass plates with SiO_x orienting layers[3,4]. The PVA films or the glass plates were separated by Teflon spacers of the 30 μm and 20 μm thickness, respectively. These were then sealed by Epoxy glue. The stretched PVA films or the SiO_x layers help orient the liquid crystal molecules and hence the chlorophyll molecules as a result of the "host-guest" effect. The direction of stretching for both PVA films was parallel. These thin stretched PVA films have been found to facilitate the PAS measurements compared to the glass plates with SiO_x orienting layers which disturb strongly the photoacoustic signal. However, these glass plates were used for lifetime measurements and excitation spectra because of their durability. The PVA films or glass plates containing chlorophyll solution will be referred to as samples. It should be mentioned that it is not the subject of this paper to discuss the

orientation of LC molecules by stretched polymers. We have, therefore, taken the parallel component of absorption ($A_{\parallel}$) as the one with highest intensity of absorption whereas $A_{\perp}$, the perpendicular component, is the one for which the sample orientation is perpendicular to that for $A_{\parallel}$. The polarized components of emission and PAS were taken with the same experimental arrangement as the one used in absorption experiments.

Absorption spectra were recorded on Cary 17D spectrophotometer equipped with two polaroid sheets and holders for samples. Polarized spectra were measured for two orientations of each sample. The axes of reference (without pigment) and the sample were always parallel to each other.

Lifetimes of fluorescence were measured with a phase-shift fluorometer constructed in Poznan Technical University. Photoacoustic spectra were measured on a single beam photoacoustic spectrophotometer constructed in Centre de recherche en photobiophysique in Trois-Rivières[9].

RESULTS AND DISCUSSION

Photoacoustic spectra

Fig. 2–4 show photoacoustic spectra of chl *a*, chl *b* and pigment mixture excited with natural and polarized light. The spectral bandwidth of incident light is 6 nm, therefore the red bands of chl *a* and chl *b* in pigment mixtures are not well resolved. Using 2 nm spectral bandwidth, it is possible to resolve these bands but at such low intensity of incident light the signal to noise ratio is much smaller than those for the spectra presented in Fig. 2–4. Fig. 5 compares the experimentally measured PAS of a pigment mixture with theoretical PAS of the mixture calculated from spectra of the separated pigments. Both spectra are normalized at 670 nm (almost at the chl *a* red absorption maximum). The choice of normalization at this wavelength is due to the fact that there is some overlapping of chlorophyll absorption with that of liquid crystals at the Soret band wavelengths. Calculations were done supposing that in mixture, excitation energy is not transferred between chl *b* and chl *a* molecules and that pigments are separated by LC. Therefore, it was taken into account that the contribution of each pigment of a mixture to PAS is proportional to $\epsilon \cdot c \cdot (1 - \eta)$, where ϵ is the molar extinction coefficient, c, molar concentration of pigment in mixture and η, the yield of fluorescence of pigment calculated from measured fluorescence lifetimes in LC and the reference values for τ and η in ethyl ether[10].

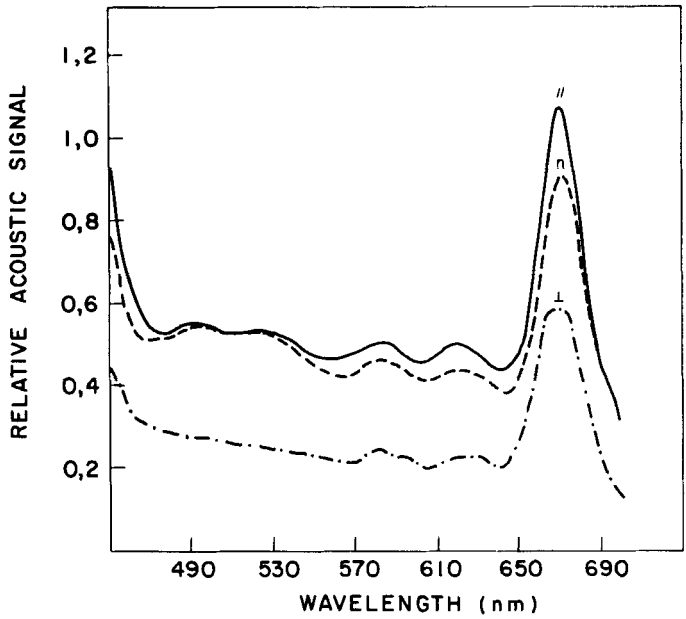

FIGURE 2 Photoacoustic spectra of chl *a* in LC ($C_a = 7 \cdot 10^{-3}$ M). Illumination by natural (n) and polarized light (||, ⊥).

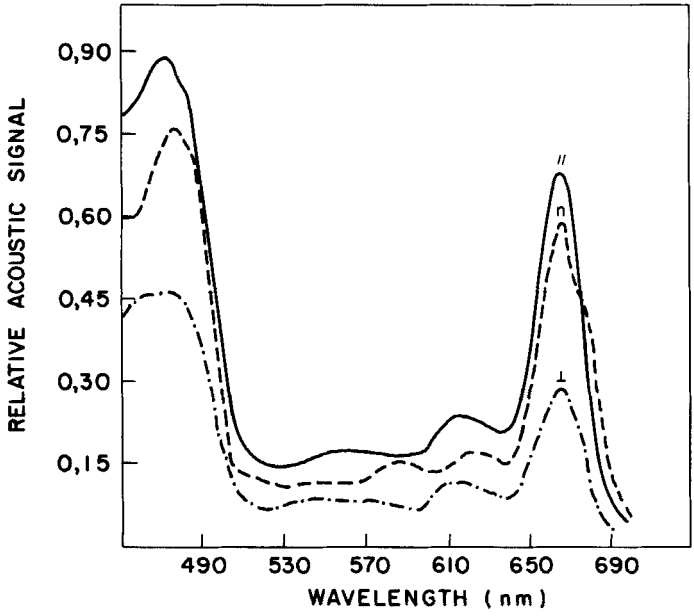

FIGURE 3 Photoacoustic spectra of chl *b* in LC ($C_b = 4 \cdot 10^{-3}$ M). Illumination by natural (n) and polarized light (||, ⊥).

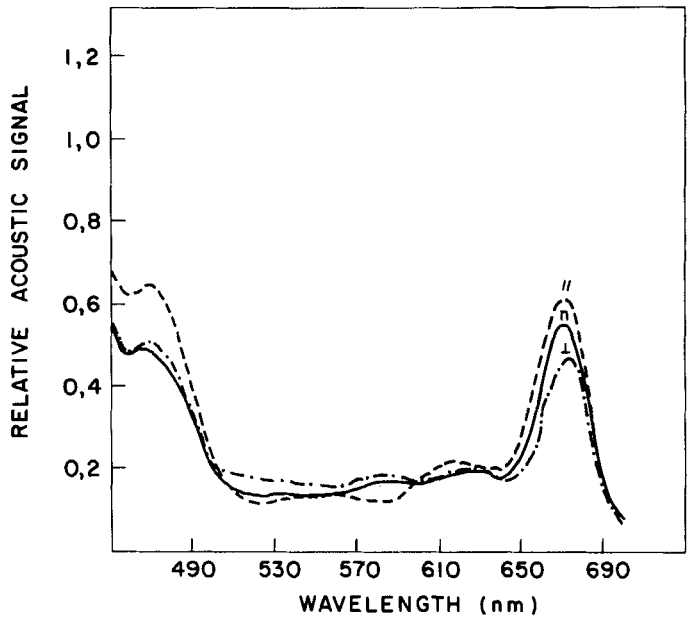

FIGURE 4 Photoacoustic spectra of chl *a* and chl *b* mixture in LC ($C_a = 1,8 \cdot 10^{-3}$ M and $C_b = 0,5 \cdot 10^{-3}$ M). Illumination by natural (n) and polarized light (||, ⊥).

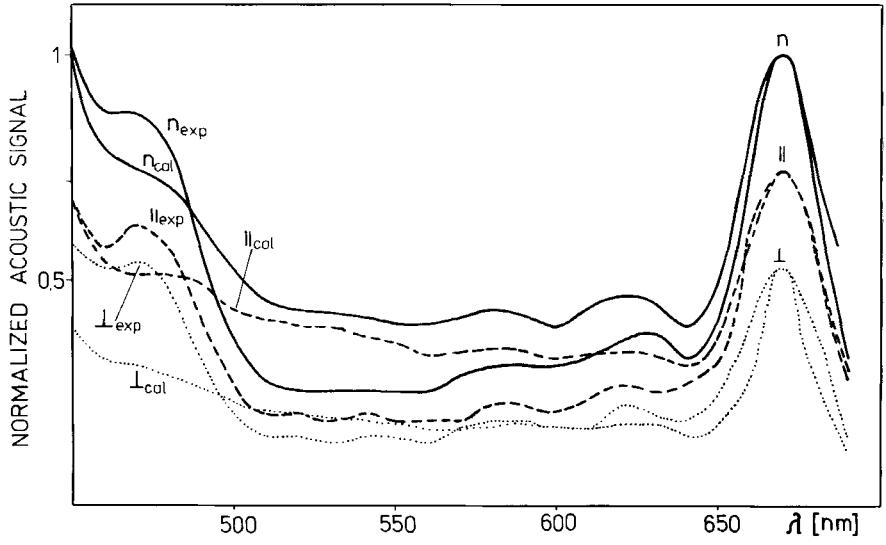

FIGURE 5 Experimental (exp) and calculated (cal) (explanation in text) photoacoustic spectra of pigment mixture. See Fig. 2 and 3 for the definitions of the abbreviations. Every pair of exp and cal spectra are normalized at 670 nm.

From Fig. 5, it is seen that the measured PAS exceeds the calculated PAS in the region of predominant chl *b* absorption (470 nm and 660 nm). Chl *b* gives higher contribution to PAS than chl *a* because of its lower yield of fluorescence. Both PAS and absorption spectra are normalized at the red maximum of chl *a*. The results obtained suggest efficient excitation energy transfer from chl *a* to chl *b* ("back transfer"). From the difference between both curves at 470 nm divided by the "calculated" value of signal at the same wavelength, the yield of excitation energy transfer from chl *a* to chl *b* is obtained as $\phi_{\text{chl } a \rightarrow \text{chl } b} = 0.16$. From the comparison of PAS obtained with illumination of sample with two polarized components of light, it follows that this ET effect is more pronounced for the perpendicular component (Fig. 5). It is evident that the efficiency of energy transfer is different for differently oriented fractions of molecules. On the basis of this observation it seems most probable that some new species is formed from chl *a* and chl *b* dissolved in LC. It has to be oriented differently from either chl *a* or chl *b*. It has strong absorption in the neighborhood of 470 and 660 nm and has a higher thermal dissipation rate than chl *a*.

From PAS of chl *a* and chl *b* (normalized to the unit of absorbed natural light and recorded under identical conditions), a ratio of photoacoustic signal of chl *b* to chl *a*, i.e. PAS(*b*)/PAS(*a*), equal to 1.48 is obtained. Taking yields of fluorescence obtained from our lifetime measurements, i.e. $\eta_{\text{chl } b} = 0.15$ and $\eta_{\text{chl } a} = 0.32$, a ratio of thermal deactivation of excitation of chl *b* to chl *a*, i.e., $(1 - \eta_{\text{chl } b})/(1 - \eta_{\text{chl } a})$, equal to 1.25 is calculated. This is reasonably close to the value obtained from PAS ratio (1.48) taking into account that PAS ratio was obtained for two different samples with PVA windows, which never are quite identical.

Fluorescence spectra

Fig. 6 shows a set of fluorescence spectra of investigated samples at very high concentrations ($10^{-3} - 10^{-2}$ M). Such high concentrations have to be used because of the difficulties related to the observation of eventual chl *b* fluorescence sensitization by chl *a* (strong overlapping of the bands of the pigments and low yield of chl *b* fluorescence). At high concentrations chl *a* occurs in aggregated form (emission at about 725 nm) and in monomeric form (band at about 680 nm) due to the strong interaction with LC. Using the 470 nm excitation wavelength, the aggregated form of chl *a* is predominantly excited (Fig. 6). Shape of chl *b* emission band at both excitation, i.e. $\lambda_{\text{exc}} = 430$ nm and 470 nm, is similar. In pigment mixture at short and long wavelengths excitation, an additional maximum located between

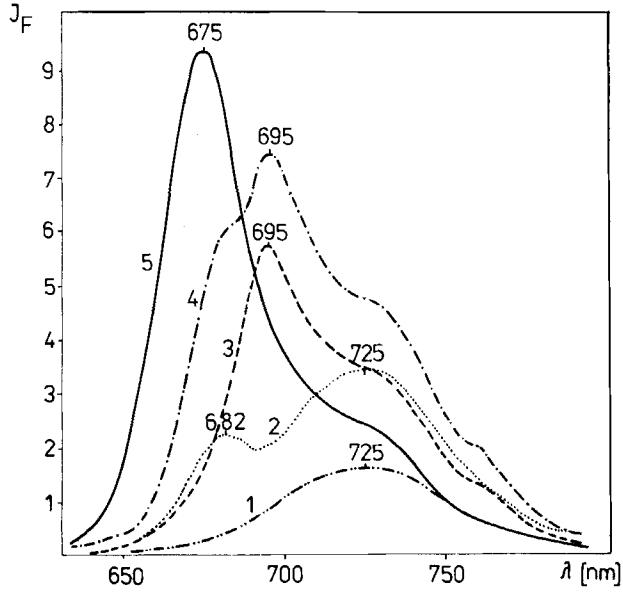

FIGURE 6 Fluorescence spectra of chl *a* ($C_a = 2,3 \cdot 10^{-2}$ M), $\lambda_{exc} = 470$ nm (curve 1); $\lambda_{exc} = 430$ nm (curve 2); chl *b* ($C_b = 5,2 \cdot 10^{-3}$ M), $\lambda_{exc} = 470$ nm (curve 5); chl *a* + chl *b* mixture ($C_a = 1,7 \cdot 10^{-2}$ M; $C_b = 3,6 \cdot 10^{-3}$ M), $\lambda_{exc} = 430$ nm (curve 3); $\lambda_{exc} = 480$ nm (curve 4).

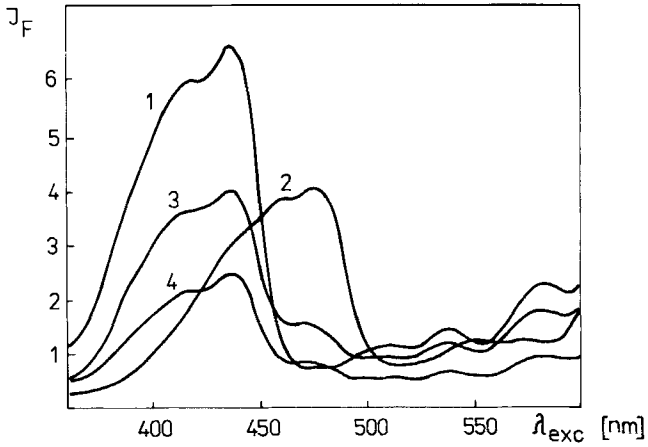

FIGURE 7 Fluorescence excitation spectra of chl *a* (fluorescence measured at $F_m = 680$ nm, curve 1); chl *b* ($F_m = 670$ nm, curve 2); chl *a* + chl *b* ($F_m = 680$ nm, curve 3); chl *a* + chl *b* ($F_m = 670$ nm, curve 4); concentrations as in Fig. 6.

chl *a* monomer and aggregate peaks appears (Fig. 6). As in pure chl *a* solution the 430 nm excitation is more efficient in exciting chl *a* monomer than the 470 nm excitation wavelength. The decrease in chl *a* aggregation as a result of chl *b* addition could be due to two effects:

1. the dilution of solution of chl *a* by chl *b*;
2. the formation of "mixed aggregates" involving chl *a* and chl *b* competing with the process of chl *a* self-aggregation.

These mixed aggregates have an emission band hidden in a region of emission of both pigments which therefore can be seen only at high pigment concentrations. Because of a strong overlapping of emission bands of monomers, aggregates and mixed aggregates, it is not possible to show the existence chl *a*–chl *b*–LC aggregates by means of fluorescence excitation spectra (Fig. 7).

Fluorescence lifetimes

Table I presents the results of lifetimes measurements for chl *a*, chl *b* and their mixture in the same LC. Each value in Table I is obtained by averaging three or four independent measurements. As can be seen from Table I, τ for all chl *a* + chl *b* mixture is much closer to that for chl *b* than that for chl *a*. Measurements were done on two regions of fluorescence spectra by using filter transmitting wavelengths, 1) $\lambda > 620$ nm, e.g. for the entire chl *a* and chl *b* emission bands; 2) $\lambda > 695$ nm which transmits more fluorescence of chl *a* than for chl *b*. In case of partial aggregation of chl *a* (see Fig. 6), one can expect more emission of aggregated chl *a* than monomeric chl *a* in the region of wavelengths greater than 695 nm. As can be seen from Table I, the difference between τ of chl *a* alone in these two regions of emission is in the limit of experimental error. It seems that either emission bands of various chl *a* aggregates are overlapped to a high degree or that the emission of monomer predominates. The latter suggestion is less plausible because of the shape of the emission band (Fig. 6) and the dependence of chl *a* lifetime on wavelength of exciting light (Table I). For chl *b* and chl *a* + chl *b* mixture, τ for emission region greater than 695 nm is larger than τ obtained for the entire emission region greater than 620 nm. This effect is stronger in case of chl *b* than for the pigment mixture, therefore, it seems to be related to chl *b*.

It is known that chl *b* forms aggregates much easier than chl *a*,[2] and that the emission spectra of chl *b* monomers and aggregates are quite similar. Comparing all results presented in Table I, one concludes that because of strong overlapping of emission spectra of chl *a*,

TABLE I

Fluorescence lifetimes of chl *a*, chl *b* and chl *a* + chl *b* mixture in MBBA + EBBA ($C_a = 1,7 \cdot 10^{-2}$ M, $C_b = 3,6 \cdot 10^{-3}$ M).

Sample	Wavelength of excitation (nm)	Wavelength of fluorescence (nm)	Lifetime τ (ns)
Chl *a*	405	> 620	5.56 ± 0.03
	405	> 695	5.53 ± 0.02
	436	> 620	5.59 ± 0.02
	436	> 695	5.60 ± 0.02
	466	> 620	5.35 ± 0.02
	466	> 695	5.38 ± 0.01
	491	> 620	5.17 ± 0.02
	491	> 695	5.20 ± 0.02
Chl *b*	405	> 620	8.61 ± 0.03
	405	> 695	8.91 ± 0.03
	436	> 620	8.81 ± 0.03
	436	> 695	9.37 ± 0.01
	466	> 620	8.75 ± 0.03
	466	> 695	9.19 ± 0.04
	491	> 620	8.46 ± 0.03
	491	> 695	8.95 ± 0.04
Chl *a* + Chl *b*	405	> 620	7.82 ± 0.03
	405	> 695	8.01 ± 0.02
	436	> 620	7.99 ± 0.03
	436	> 695	8.13 ± 0.02
	466	> 620	7.65 ± 0.03
	466	> 695	7.72 ± 0.02
	491	> 620	7.49 ± 0.05
	491	> 695	7.70 ± 0.04

chl *b* and their aggregates, it is not possible to measure the τ belonging to each individual pigment in the pigment mixture.

The result for τ for pigment mixtures can be related to two effects:

1. the excitation of each pigment followed by the overlapping of their emissions which are characterized by different τ;
2. the change in the fractions of emitting pigments by the excitation energy transfer or by the formation of mixed aggregates.

The first effect is trivial. To check if the second effect plays an important role in our system, we have analyzed lifetimes of pigment mixtures using the Pearlstein, Tumerman and Sorokin formula[6] which does not take into account the excitation energy transfer between the pigments:

$$\tan\delta = \frac{(1 + \tan^2\delta_2) f_1 \phi_1 \tan\delta_1 + (1 + \tan^2\delta_1) f_2 \phi_2 \tan\delta_2}{(1 + \tan^2\delta_2) f_1 \phi_1 + (1 + \tan^2\delta_1) f_2 \phi_2} \qquad (1)$$

where δ is the observed phase shift for the pigment mixture, δ_1, δ_2 are the phase shifts for the individual pigments in separate samples; f_1 and f_2 are fractions of light absorbed by chl *a* and chl *b*, respectively, and ϕ_1 and ϕ_2 are the yields of fluorescence of chl *a* and chl *b*, respectively.

Furthermore, $\tan\delta = -\omega\tau$; $\omega = 7.36 \cdot 10^7\ s^{-1}$ where ω is the frequency of light modulation used in the phase fluorometer.

It was found that δ obtained from experiment is different from that calculated from formula (1). For example, at $\lambda_{exc} = 491$ nm, $\tan\delta_{cal} = -0.41$; whereas the experimental value found is $\tan\delta_{exp} = -0,56$.

It is evident that in our sample the emission is at least partially excited by ET or that mixed aggregates, with τ different from that of chl *a* and chl *b*, are formed.

In order to calculate the yield and the direction of excitation energy transfer between investigated pigments, the formula proposed by Knox[6] is used:

$$\delta_{f_1 f_2} = \arctan\left[\frac{\left(f_2 + \frac{A_1}{A_2} f_1\right)\omega}{F + f_2 k_1 + \frac{A_1}{A_2} f_1 k_2}\right] - \arctan\left(\frac{\omega}{k_2}\right) - \arctan\left(\frac{\omega}{k_1 + F}\right) \tag{2}$$

where A_1 and A_2 are natural radiative rates of chl *b* and chl *a*, respectively; k_1 and k_2 are the total decay constants for uncoupled systems; and F is the rate of excitation energy transfer. It is supposed in these calculations that energy is transferred from chl *b* to chl *a*. $\delta_{f_1 f_2}$ is phase shift predicted when the absorbed fractions are f_1 and f_2. Data used for the calculation of $\delta_{f_1 f_2}$ at two wavelengths of exciting light are presented in Table II.

A_1 and A_2 are obtained from red absorption bands of chl *b* and chl *a*, respectively, by using the following formula:

$$A = \frac{1}{\tau_0} = 3.10^{-9}\tilde{\nu}^2 \cdot \Delta\tilde{\nu} \cdot \epsilon_{max} \tag{3}$$

where $\tilde{\nu}$ is the position of the band maximum in cm^{-1}, $\Delta\tilde{\nu}$ is the half-bandwidth in cm^{-1}, and $\cdot\epsilon_{max}$ is the extinction coefficient at maximum of absorption ($M^{-1}cm^{-1}$).

k_1 ($= 1/\tau_{chl\ b}$) and k_2 ($= 1/\tau_{chl\ a}$) are obtained from lifetimes of separated pigments.

TABLE II

Values of parameters used in the calculation of the efficiency of the excitation energy transfer on the basis of formula (2).

Wavelength of excitation (nm)	Pigment	A (s^{-1})	k (s^{-1})	f	τ (ns)	$\tan \delta_{f_1 f_2}$	$F_{\text{chl } b \to \text{chl } a}$	$\Phi_{\text{chl } a \to \text{chl } b}$
466	chl a(2)	$2,78 \times 10^7$	$18,7 \times 10^7$	0,57	5,35	− 0,5630	$-2,2 \times 10^7$	0,12
	chl b(1)	$2,83 \times 10^7$	$11,4 \times 10^7$	0,43	8,75			
491	chl a(2)	$2,78 \times 10^7$	$19,3 \times 10^7$	0,71	5,17	− 0,5513	$-5,0 \times 10^7$	0,26
	chl b(1)	$2,83 \times 10^7$	$11,8 \times 10^7$	0,29	8,46			

It is found that in all cases $F_{\text{chl } b \to \text{chl } a}$, the rate of ET from chl *b* to chl *a*, is negative. Supposing that no mixed chl *a* – chl *b* aggregates are formed, one can conclude that rate of ET from chl *a* to chl *b* predominates in the investigated system. Therefore, the yield of ET from chl *a* to chl *b* under such a supposition can be calculated as $\phi_{\text{chl } a \to \text{chl } b} = -F_{\text{chl } b \to \text{chl } a} \cdot \tau_{\text{chl } a}$.

All excitation wavelengths used are located in a region of chlorophyll Soret bands. The different values of $\phi_{\text{chl } a \to \text{chl } b}$ obtained for various λ_{exc} are related to different fractions of monomers and aggregates of pigments.

On the basis of fluorescence lifetimes of pigment mixtures, one concludes, in agreement with the PAS results, that there is migration of excitation energy from chl *a* to chl *b* or that mixed aggregates are formed which have τ different from the lifetimes of chl *a* and chl *b*.

CONCLUSION

Using a simple model system consisting of chl *a*, chl *b* and their mixtures in an oriented LC matrix, it is shown that PAS provides information concerning excitation energy transfer and formation of aggregates in addition to that provided by fluorescence measurements. Such information could be valuable especially in case of biological light scattering samples for which the fluorescence measurements are strongly perturbed. Using polarized light in photoacoustic spectroscopy it is possible to distinguish the contributions of differently oriented pigment fractions to the PAS signal. This is very useful in the investigation of biological samples because in biological membranes various forms of pigments oriented differently are known to exist[5,6].

Presented results strongly suggest that in the investigated model system at high pigment concentrations, aggregates including both pigments: chl *a* and chl *b* are formed, because the fluorescence spectra of chl *a* and chl *b* mixtures in LC show the appearance of an additional peak located between the emission peaks of the two substituant pigments. This peak is probably related to strongly interacting sets of chl *a*, chl *b* and LC molecules. Such an aggregate has to be treated as one big molecule rather than as a separated donor and acceptor of excitation energy. In such a system, the energy absorbed in the chl *a* or chl *b* Soret band is emitted as aggregate emission.

The lifetime of the aggregate is longer than that of chl *a* but closer

to τ of chl *b*. The thermal deactivation of excitation energy in the aggregate is higher than that of chl *a*. Orientation of the chl *a*–chl *b*–LC aggregate is different from that of the monomeric pigment, therefore the photoacoustic signal depends on exciting light polarization. The nature and the geometry of aggregates will be the subject of forthcoming investigations. On the ground of presented results, it seems that the mutual chl *a*–chl *b* interaction can also have some influence on pigment ordering in a photosynthetic lamellar system.

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