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SPECTRAL PROPERTIES OF CHLOROPHYLL a IN LIQUID CRYSTAL

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Solution of chlorophyll a in liquid crystals mixture (MBBA + EBBA) was investigated. Chl molecules are in LC in low electric field oriented. They can be divided into two groups: one strongly interacting with LC and subjected to reorientation by the electric field, and another weakly interacting with the solvent and insensitive to the voltage applied. The emission spectrum of the first type of chlorophyll is strongly perturbed. At higher voltages, the pigment molecules orientation in the plane of the electrode is another. Pigment absorption and emission anisotropy provides information about the reorientation of LC molecules. Even at high (10^{-3}M) Chl concentration and regular pigment array, the interaction between the pigment and solvent exceeds pigment-pigment interaction because the solvent appears to have a stronger influence on the Chl spectrum.

1. Introduction

Various types of model systems simulating the porphyrin pigments orientation in lamellar structures of photosynthetic organism have been investigated: monolayers [1,2], anisotropic films [3–8], liquid crystals (LC) [7,9] etc. The liquid crystal matrix appears to be one of the most interesting models of lamellar systems because of its fluid oriented structure.

Anisotropic models provide information on the orientation of transition moments with respect to the skeleton of the molecule, as well as on the influence of pigment molecules orientation on intermolecular interactions.

Both these types of information are of value in studies of excitation energy migration in photosynthetic apparatus. For example the yield of excitation energy trapping in photoreaction centers depends among others, on the mutual orientation of "antenna" and "trap" molecules [10].

2. Material and methods

A solution of chromatographically purified chlorophyll a (Chl a) in MBBA + EBBA (p-methoxybenzylidene *p*′-butylaniline; *p*-ethoxybenzylidene *p*′-butylaniline) was located in an especially constructed cell with windows of conducting glass. The thickness of the pigmented liquid crystal layer was 2.2×10^{-5} m. (Chl a concentration about 10^{-3} M/ℓ). The reference cell was of equivalent construction.

By initial rubbing the inner surfaces of the windows in both the measuring and reference cell, a homogeneous orientation along the rubbing direction parallel to the window is achieved even without applying an electric field [11]. The investigated LC samples behave as uniaxial crystals with optical axis parallel to the direction of rubbing. Various potentials ranging from 0 V to 20 V were used, it means that electric field till 2×10^5/V/m was applied. Scheme of orientation at low voltage is presented in fig. 1c.

Absorption spectra were measured with a Carry 118 or UV-VIS Zeiss spectrophotometer equipped with two polaroid sheets and holders for cells. Polarisations were horizontal in both measuring and reference beams. The orientation axes of LC in both the measuring and reference cell were always parallel to each other. $A_\parallel$ and $A_\perp$, absorptions referring to electric vector of light at parallel and perpendicular appropriate rotation of the LC sample. Only the anisotropy of pigment absorption was recorded because the rotation of two uncolored samples located parallel in both beams practically cause not attenuation of light.

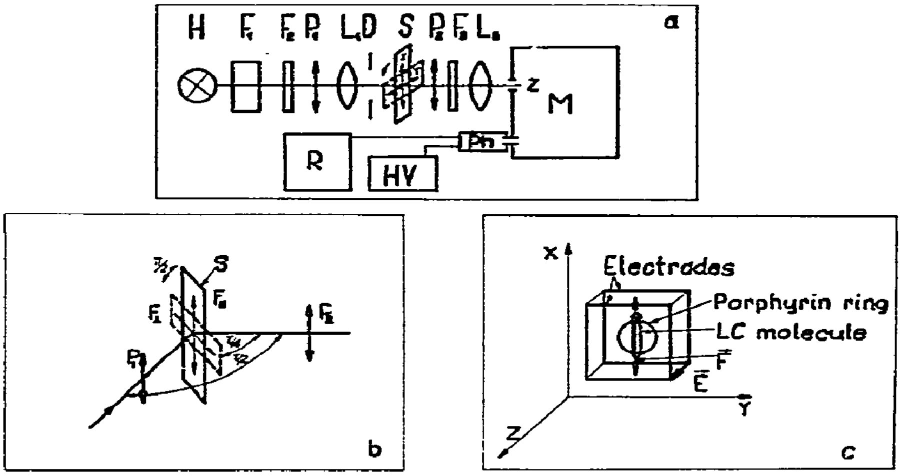

Fig. 1. Arrangement for measuring fluorescence spectra (a) and lifetime (b). S sample; H lamp; F_1 water filter; F_2, F_3 filters; P_1, P_2 polarizers; L_1, L_2 lenses, M double monochromator, Ph photomultiplier, H.V. power supply, R recorder, C proposed orientation of Chl and LC molecules at low voltage, E electric field, x rubbing direction, F orientation of red band Chl transition moment.

Absorption of the uncolored sample referred to air in both positions ($A_{0\parallel}$ and $A_{0\perp}$) were identical throughout the region from 14 to 23 × 1000 cm^{-1}; in the region from 23 to 25 × 1000 cm^{-1} $A_{0\parallel}$ was higher than $A_{0\perp}$ because of dichroism of the LC itself, but in the spectra reported this effect was compensated by the reference dichroism.

The two components of fluorescence were measured at excitation by unpolarized and by polarized light. The arrangement used for fluorescence spectra measurements is shown schematically in fig. 1a, and consists of double grating GDM 1000 Zeiss monochromator and photomultiplier Centronic type Q 4283 BX. Unpolarized excitation was used to obtain the spontaneous polarization [12,13]. The $F_{\parallel}$ and $F_{\perp}$ components of fluorescence, excited with polarized light, were obtained by two cell positions (fig. 1a) between parallel polarizers. Comparison $F_{\parallel}$ and $F_{\perp}$ provides information about the anisotropy in Chl molecular arrangement as well as about the emission spectra of Chl molecules differently located with respect to LC. It was suspected that differently ordered Chl molecules may interact to various degrees with the LC matrix.

Fluorescence lifetime τ was measured with a phase-shift fluorometer [14] in the setup shown in fig. 1b. Because of diverging literature values of τ for Chl a the lifetime of Chl a in ethyl ether was measured [8,9,15].

3. Results

Absorption spectra of Chl a in LC and in ethyl ether are shown in fig. 2. The spectrum of Chl a in LC is shifted towards longer wavelength with respect to the spectrum in ether. Observables from both spectra are listed in table 1. The shift in absorption maxima of Chl a in LC compared to the maxima in ether amounts to about 10 nm and is practically independent of the voltage applied (table 1). The ratios of various absorption peaks in the same spectrum vary with the electric po-

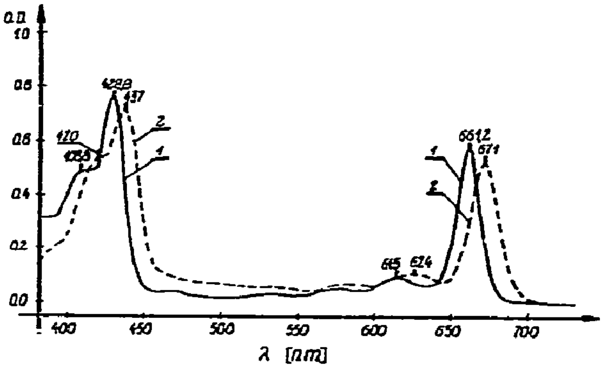

Fig. 2. Absorption spectra of Chl a in ethyl ether (1) and LC (2).

Table 1
Spectral parameters of absorption of Chl a. ϵ_S, ϵ, ϵ'_S extinction coefficients of Soret, red and Soret satellite bands

Solvent	ether ethyl			LC								
				natural light			polarized light					
				0 V			0 V		5 V		20 V	
							$A_\parallel$	$A_\perp$	$A_\parallel$	$A_\perp$	$A_\parallel$	$A_\perp$
position of maximum (nm)	409	429	661	420	437	671	as for natural light					
band half width (nm)	39		17	42		22	as for natural light					
ϵ_S/ϵ	1.32			1.33			1.16	1.57	1.18	1.62	1.37	1.27
ϵ_S/ϵ'_S	1.53			1.36			1.22	1.36	1.13	1.30	1.20	1.20

tential applied to the measuring and reference cells. Table 1 gives ratios of Soret and red bands intensities ϵ_S/ϵ as well as Soret main band and Soret satellite ϵ_S/ϵ'_S for various potentials. In fig. 3 shows absorption spectra of the two polarized components of light for Chl a in LC. Three types of effects are presented in fig. 3: at 0 V–Chl array due to electrodes rubbing; at 5 V–maximal degree of Chl orientation; at 20 V–influence of "dynamic scattering" [11] effects on Chl a absorption.

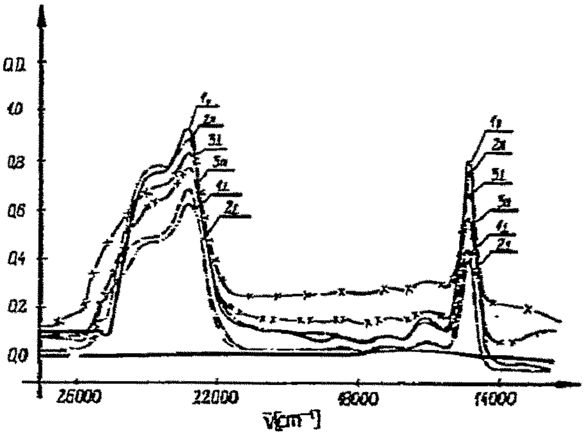

Fig. 3. Absorptions parallel (∥) and perpendicular (⊥) components of polarized light of Chl a in LC (curve 1: 0 V; 2: 5 V; 3: 20 V).

Fig. 4 shows linear dichroism (LD) spectra calculated using formula [16];

$$\frac{\mathrm{LD}}{A}=\frac{A_\parallel - A_\perp}{\frac{1}{2}(A_\parallel + A_\perp)}=\frac{A_x - A_y}{\frac{1}{2}(A_x + A_y)}, \qquad (1)$$

where A is the absorption of unpolarized light.

In our case $A = \frac{1}{2}(A_\parallel + A_\perp)$ is valid only under two conditions: (1) The Chl rings are oriented parallel to the xy electrode surfaces, or when x direction is the sym-

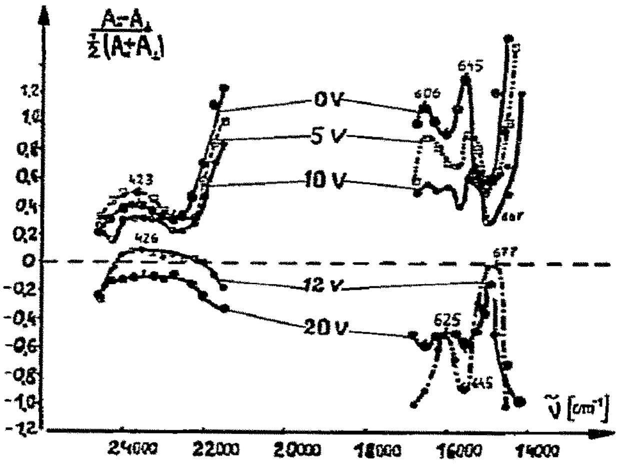

Fig. 4. Dichroism spectra of Chl a in LC for various voltages.

Table 2
$\epsilon_x f_x + \epsilon_y f_y$ (arbitrary units)

Band	0 V	5 V	20 V
Soret	158	148	157
red	120	111	120
Soret satellite	123	123	130

metry axis of Chl alignment (fig. 1) and (2) all transition moments of Chl lie in the plane of the phorphyrin ring.

The first of these assumptions can not be exactly fulfilled because as it follows from table 2 the value of

$$\epsilon_x f_x + \epsilon_y f_y$$

(where f_x, f_y, f_z and ϵ_x, ϵ_y, ϵ_z are elements of orientation and absorption tensors, respectively [7,9]) is voltage dependent. Nor is the validity of the second assumption generally accepted [6,7]. None the less, the function $(A_\parallel - A_\perp)/\frac{1}{2}(A_\parallel + A_\perp)$ provides information about the arrangement of the Chl molecules, because scattering on LC is compensated by the reference sample being in the same conditions. Fig. 5 shows LD/A versus electric field, for various absorption maxima. In

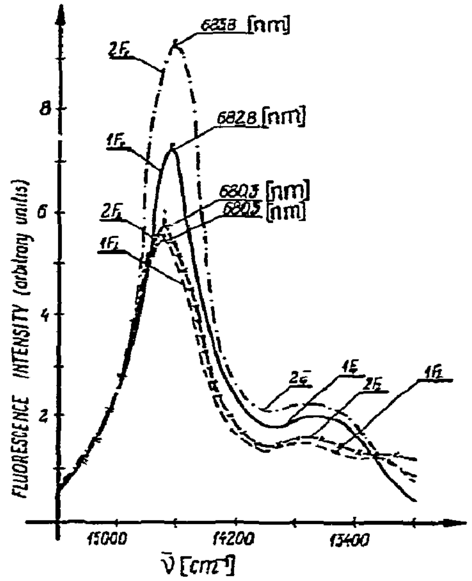

Fig. 6. Spectra of polarized components of fluorescence excited with natural light (1) 0 V; (2) 4 V; $\lambda_{exc} = 437$ nm.

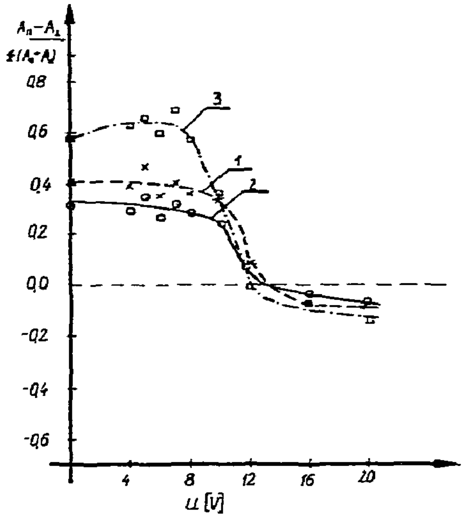

Fig. 5. Dichroism as a function of voltage applied for various absorption maxima; (1) 420 nm; (2) 437 nm; (3) 671 nm.

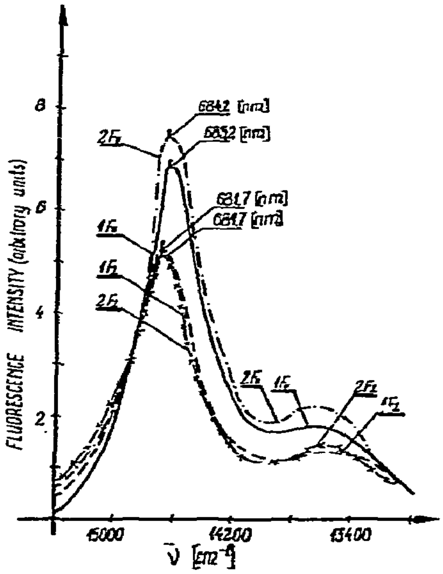

Fig. 7. Spectra of polarized components of fluorescence excited with polarized light (1) 0 V; (2) 4 V; $\lambda_{exc} = 437$ nm.

the region 0–8 V, the change in dichroism is small than, LD/*A* decreases and changes the sign. The highest anisotropy is exhibited by the red band, the lowest by the main Soret band (at 437 nm). This means that at 0 V and at low voltages the red band transition moment is oriented at low angle with respect to the orientation direction of the LC molecules.

Spectra of the polarized components of fluorescence, excited with polarized light, are shown in fig. 7. The meaning of the polarized components measured is explained in fig. 1a: $F_{\parallel}$ is contributed predominantly by the emission of molecules with, at 437 nm, transition moments provalently oriented parallel to the LC orientation axis, whereas $F_{\perp}$ by molecules with absorption oscillator oriented perpendicularly to the LC orientation axis. Similar fluorescence components albeit excited with unpolarized light, are shown in fig. 6.

The positions and halfwidths of the maxima occurring in parallel ($F_{\parallel}$) and perpendicular ($F_{\perp}$) components are different and change with the voltage (fig. 7 and table 3). All parallel components are shifted towards longer wavelengths the largest shift is observed at 4 V.

The positions of the perpendicular components do not vary with the potential applied; this means that they are independent of the degree of Chl orientation.

Fig. 8 shows the degree of fluorescence polarization, defined as $(F_{\parallel} - F_{\perp})/(F_{\parallel} + F_{\perp})$, versus the electric potential. As it follows from fig. 8, the curves for the main fluorescence maximum (at 685 nm) and those for the satellite maximum (at 735 nm) are different, but in all cases the maximum of fluorescence polarization occurs at 4 V. In the case of the main maximum, the value of the polarization of emission is higher at excitation with unpolarized light than at excitation

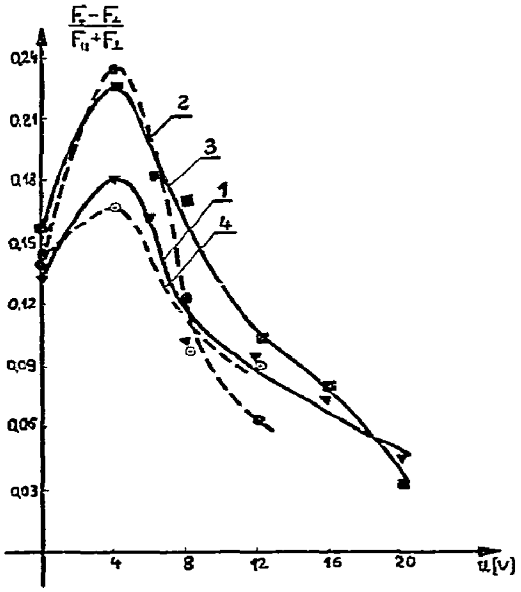

Fig. 8. The dependence of fluorescence polarization degree on voltage applied. (1;2) at 683 nm (main band), (3;4) at 735 nm (satellite band), (1;3) excitation with polarized light, (2;4) excitation with natural light.

Table 3
Spectral parameters of emission maxima of Chl a in LC

Voltage (V)	Excitation with natural light				Excitation with polarized light			
	Position of maximum λ (nm)		Halfwidth δ (cm^{-1})		λ (nm)		δ (cm^{-1})	
	$F_{\parallel}$	$F_{\perp}$	$F_{\parallel}$	$F_{\perp}$	$F_{\parallel}$	$F_{\perp}$	$F_{\parallel}$	$F_{\perp}$
0	682.8	680.3	569.2	607.7	683.2	681.7	569.7	569.2
4	683.8	680.3	561.5	638.5	684.2	681.7	538.5	576.9
6	–	–	–	–	684.2	681.7	546.1	576.9
8	682.1	680.3	584.6	630.8	683.4	682.5	561.5	576.9
12	682.5	680.3	592.3	630.8	683.4	681.7	561.5	584.6
16	–	–	–	–	683.2	681.7	569.2	584.6
20	–	–	–	–	684.2	681.7	584.6	584.6

Table 4

Voltage (V)	Spontaneous polarization degree	Degree of orientation in %
0	0.14	11
4	0.24	20
8	0.12	9
12	0.06	5

with polarized light, whereas for the satellite the situation is the opposite.

f, the degree of orientation of Chl a molecules was calculated from the spontaneous polarization degree using formula [13]:

$$f = \frac{2P}{3\,1-P}\,100\,\%, \tag{2}$$

where $P = \dfrac{F_x - F_y}{F_x + F_y}$, ($x,y$ as in fig. 1).

The results are given in table 4.

From table 4 it follows that the highest degree of orientation of the Chl molecules occurs at 4 V. When using these results, one should keep in mind that formula (2) is fulfilled for cylindrically symmetric alignment only [13], whereas the samples investigated may exhibit some differences in fluorescence intensities in the directions z and y/xy being the plane of the windows (fig. 1a) as a result of preferention of Chl rings orientation in the xy plane of the electrodes (fig. 1a). Therefore, the data of table 4 can be dealt with only qualitatively, as indicators of the changes in degree of Chl orientation.

At both positions of the cell (fig. 1b), the lifetime of fluorescence was equal to 5.7 ± 0.2 ns. The same value of τ was obtained for Chl a in ethyl ether solution.

From the absorption of the red band of Chl a in LC, the oscillator strength, F [23] was obtained to 0.245, whereas for Chl a in isotropic solvent $F = 0.23$ [17] theoretically predicted F for the Q_y transition is even higher [17]. This similarity in values of the oscillator strengths is consistent with the identical values of τ obtained in both solvents as well as for two fractions of diffently aligned molecules in LC.

3. Discussion

From the results some preferred directions of Chl molecules alignment appear. It is possible that planes of the Chl porphyrin rings are oriented almost parallel in the xy plane of the electrodes (fig. 1a), albeit with some tilt angle [11] as it follows from table 2. The tilt angle α between the Chl a ring and electrode plane is largest at 4 V, and according to our estimate, does not exceed 15°. The estimate is based on the assumption that $\alpha = 0°$ at 0 V and that only the alignment, but not intensity of the absorption transition moment is influenced by the voltage. As follows from table 2, the Soret satellite behaves differently from the red and Soret main bands. The Soret satellite transition moment may probably be out-of-plane, polarized as suggested by Norden and Davidsson [7].

The tilt angle should be more accurately defined by solving the equations giving the orientation matrix elements f_x, f_y, f_z [7]. This will be the purpose of further study, after more exact measurements of LD/A by Norden's [16] technique. The observed spectral anisotropies of the sample depend on π-electron system symmetry of the Chl molecule, as well as on the Chl molecular "shape" (which, from simple geometrical considerations, affects the orientation). The π-system of the Chl a molecule possesses rather D_{2h} than D_{4h} symmetry [18]; therefore at a definite orientation of the ring anisotropy of absorption and emission occurs [8,3].

From Norden [16] approximate formula, on the basis of measured LD/A, the degree of orientation f was evaluated assuming a simple model in which the molecules are oriented according to their shapes.

On assuming D_{4h} symmetry for the Chl a molecules and $\beta = 0$ (where β is the angle between the plane of orientation and the transition moment) one obtains $f = 0.6$. On assuming D_{2h} symmetry and a parallel configuration of the red band transition moment and direction of LD molecule orientation one comes to a lower value of $f = 0.3$.

Both calculations were carried out for 0 V potential, but LD varies only slightly from 0—to 8 V (fig. 5).

Comparison of these values and those obtained from spontaneous fluorescence polarization (table 4) suggest that Chl a in LC matrix behaves rather as a prolate than an oblate spheroid. This conclusion is by no means unexpected since on excentric phytol group attached to the circular porphyrin ring may strongly favor some orientation of the molecule.

Absorption spectra: The shift in absorption spectrum of Chl a in LC with respect to that in ethyl ether can be explained in two ways: (1) as due to interaction between the pigment and LC molecules, or (2) as due to an increase in pigment-pigment interactions as a result of the regular arrangement of Chl molecules.

The first of these two possibilities seems the more plausible one, because the observed shift is independent of the degree of pigment orientation.

Taking into account the second possibility it is possible to assess whether the observed shift can be explained on the exciton model [19,22], for which a red shift appears if

$$0 \leqslant \alpha < 54.7°,$$

where α is the angle subtended by the transition dipoles and the line connecting the molecular centers [19,20,22]. In order to establish whether the exciton shift can be responsible for the effect observed, we calculate the distances *r* between interacting molecules on the basis of the Hochstrasser and Kasha [19] formula.

From [19], the shift in wave numbers is equal to:

$$\Delta\tilde{\nu} = 4\frac{N-1}{N}\frac{\mu^2}{r^3}(1-\cos^2\alpha) \tag{3}$$

and was taken from the experimental shift between absorption maxima in LC and ether; *N* is the number of molecules in the aggregate; for large aggregates: $N \to \infty$; and for dimers $N = 2$;

The transition moment μ was obtained from the absorption spectrum applying the following formula [23]:

$$\mu^2 = \frac{6909}{\mathfrak{N} 8\pi^3}\frac{1}{XC}\int\frac{E(\tilde{\nu})}{\tilde{\nu}}\,d\tilde{\nu}, \tag{4}$$

with: *n* refractive index of the medium, *x* sample thickness, *c* concentration of Chl a, $\mathfrak{N}$ Avogardo's number.

The results given in thable 5 refer to the two limiting values of α. Exciton shifts of the order of 1 nm, was also considered because such changes in position, of the emission maxima were observed as a result of the increase in degree of Chl ordering (table 1).

As follows from table 5, for α = 54.7° reasonable distances between molecular centers are obtained, such at which resonance interaction can occur. Exciton shift of the order of 10 nm was found in thin film of porphyrin [21]. Moreover it seems that the positions of Chl a absorption maxima can be more naturally explained by LC-pigment interaction. The observed shift, as well as the changes in shape of the absorption spectrum, are comparable with those due to interaction with isotropic solvents, as it follows from the results of Seely and Jensen [24]. The position of the red absorption maximum in LC can be expressed [24] as:

Table 5
(explanation in text)

α^0	Δλ (nm)	*r* (nm)	
		$N = 2$	$N \to \infty$
54.7	10	1.8	2.2
54.7	1	3.9	4.8
0	10	11	13
0	1	23	29

$$\lambda = 6429 + 1092\frac{n^2-1}{2n^2+1} = 6691\ \text{Å} \tag{5}$$

since the refractive index of the LC used was $n = 1.542$. This λ value is close to the observed position of the red band. Because of experimental difficulties in direct determinations, the molecular extinction coefficient of the red band of Chl a in LC, was obtained from the relation [24]:

$\epsilon\delta$ = const. for various solvents,

where ϵ extinction coefficient, δ halfwidth; ϵ_{eth} and δ_{eth} were taken from literature [9], δ_{LC} from our absorption spectra. $\epsilon_{\text{LC}} = 6.58\ 10^4$ ℓ/mol cm was obtained.

The magnitude of the changes in ϵ_s/ϵ and ϵ_s/ϵ'_s, is also similar to that observed between some isotropic solvents [23]. This discussion shows that it would be risky to draw final conclusions from the shift in absorption spectrum only.

Linear dichroism spectra: In the case of a single type of absorbing molecule in anisotropic medium, the LD spectra depend on the anisotropy of the molecules and their degree of orientation [12]. In the samples investigated probably two kinds of absorbing and emitting centers are created by various Chl interactions with LC. Such a supposition is siggested by the fluorescence spectra. One type of centers is oriented in a higher degree than the other. Therefore, the shape of the LD/A spectra obtained cannot be treated quantitatively at this stage of our work, the more so as LD is obtained by subtraction of $A_{\parallel}$ and $A_{\perp}$, leading to low accuracy in regions of low absorbance. Such results are not shown in fig. 4. The ratio LD/R is in lower degree voltage dependent than polarizations of fluorescence but it is not constant within an absorption band. This fact reveals some kind of heterogeneity linked to orientation of absorption transition moments. The shape of the LD/A spectrum is not typical for chlorophyll in anisotropic media, as it follows from the comparison of fig. 4 with the literature [4,5]. This is explicable because the LD/A spectra represent the result of subtraction of two absorption spectra with slightly different band shapes and different intensities. At low voltages LD/$A > 0$ because absorption by molecules with strong transition moments directed at low angles to the LC axis of orientation (x in fig. 1a,c) is predominant. An increase in voltage causes a change in the regular LC arrangement because of the emergence of ionic current between the electrodes. As a result, so called "dynamic scattering" effects arise in the LC cell [11]. The, attenuation of light by scattering on LC molecules should be compensated by the reference cell, but it is possible that Chl can modify the dynamic scattering of LC. Secondary effects can diminish the dichroism of absorption with the increase in potential. However, the change in sign of LD/A as well as the fluorescence data strongly suggest that the average orientation of Chl molecules in the xy plane (fig. 1a) is radically changed.

Fluorescence spectra: Norden and Davidsson [7] measured LD of tetraphenyl porphyrin in various anisotropic media and found that the matrix could play an active role in perturbing the electronic spectrum by stimulating some vibronic transitions and attenuating others. The presence of a polymer chain oriented parallel to some direction in the plane of the porphyrin ring may cause a perturbation of the π-electron chain symmetry [7]. A similar effect can be predicted in the LC matrix. Since the tilt angles of the Chl ring and LC molecules are probably the same, the LC and Chl molecules are parallel to one other and can form some type of strongly interacting "aggregates". Chl being part of such an aggregate undergoes reorientation jointly with LC in electric field, whereas Chl not included in "aggregates" is not reoriented. The emission spectra are more strongly perturbed than absorption spectra; thus, it appears that excited Chl interacts with LC more strongly, than Chl in the normal state.

As a result of strong interaction between the excited pigment and the long LC molecule attached to it, the vibronic transition polarized parallel to the long axis of LC is enhanced, whereas that perpendicular thereto diminishes. As a result, the halfwidth of the band also decreases. The maximum of emission of such perturbed Chl is shifted towards longer wavelengths. A low electric field, by causing a more exact orientation of this part of the Chl molecules, increases their contribution to $F_{\parallel}$ and, as a result, enhances $(F_{\parallel} - F_{\perp})/(F_{\parallel} + F_{\perp})$.

The Soret band used for excitation possesses a transition moment, as it follows from the anisotropy of absorption (fig. 5), which is not paralleling that of the red band. The latter is almost parallel to the LC orientation axis (x in fig. 1a). Therefore excitation with light polarized parallel to the x axis is less efficient in $F_{\parallel}$ excitation than with natural light.

Spontaneous polarization of fluorescence of satellite band (at 735 nm) is lower than that for the main maximum. This means that, in this spectral region, contributions from nonoriented Chl predominate. In the case of excitation of unoriented molecules with polarized light, only some molecules are photoselected; therefore a higher fluorescence anisotropy is found than at natural light excitation. Results reported in literature diverge concerning the polarization of this part of Chl emission spectrum [8,17,18] e.g. contributions from only "plane oscillators" of symmetry D_{4h} has been [8].

The different shapes of dichroism and fluorescence anisotropy versus voltages can be related with larger changes in fluorescence than in absorption spectrum as a result of interaction. Reorientation of molecules with strongly anisotropic emission gives more marked changes in fluorescence spectrum, than reorientation of the same fraction of molecules in absorption. The similarity between $\tau_{\parallel}$ and $\tau_{\perp}$ indicates that the shape of the perturbed and unperturbed emission spectrum can be changed without changing the transition strength.

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