

Spectral Properties of Phthalocyanines Oriented in Stretched Polymer Films

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Four various phthalocyanines dyes were oriented in uniaxially stretched polymer films. Polarized absorption, fluorescence, and photoacoustic spectra were measured. From a stepwise reduction procedure, the orientation of molecules with respect to the film stretching direction as well as the orientation of absorption transition moments vectors with respect to molecular skeleton of dye were evaluated. The complexation with various metals and the attachment of side groups to the phthalocyanine ring change the orientations and interactions of the dye molecules with polymer chains. Two bands, B1 and B2, with different orientations of their absorption transition moments were found in the short wavelength spectral region. The obtained results were discussed on the ground of literature data and compared with our previously gathered results concerning the possible application of investigated dyes in photodynamic therapy.

1. Introduction

The phthalocyanines (Pcs) are promising candidates for several practical applications because of their semiconductivity, photoconductivity, and chemical activity.^{1,2} They can be applied for artificial solar to electric energy conversion, chemical sensors, and also, they can be used as efficient sensitizers in photodynamic therapy (PDT) of cancer.^{2–5}

They exhibit rather high efficiency of generation by inter-system (singlet→triplet) crossing the very active triplet states.^{1,4} The destruction of neoplastic cells undergoes through the triplet state of sensitizer directly or by the generation of very photochemically active singlet oxygen. The sensitizer, which can be useful in PDT, also has to exhibit several other properties: it must be much more efficiently incorporated into malignant than into healthy cells, it has to be possibly not toxic for normal cells, etc.⁵ We have established previously⁶ that various Pcs are incorporated with different selectivity into healthy and stimulated human peripheral blood cells.⁶ It is important to find the correlation between Pcs properties such as complexation with various metals and attachment of different side groups with their interactions with cell membranes and proteins in the cells. In the present study, the interactions of Pc dyes with macromolecules are investigated on a simple model system—polymer film. Such a model system is much simpler than blood cells. It enables us to investigate the dye interactions with polymer chains and gives partial uniaxial orientation of dye molecules. In anisotropic matrix, the directions of various absorption and emission transition moments (TMs) with respect to the skeleton of the molecule and with respect to the chain of the polymer film, on the basis of the stepwise reduction procedure elaborated by Thulstrup and Michl,^{7–10} can be evaluated. The applied analysis of spectra requires at least partially oriented assembly of molecules, which can be reached using several anisotropic matrix, for example, by dissolving dyes

in oriented liquid crystal^{11,12} or, as in the present work, by embedding molecules in stretched polymer film.^{7–9} Such analysis can be applied not only to planar molecules of C_{2v} or D_{2h} symmetry but also to molecules exhibiting in good approximation D_{4h} symmetry as investigated by us.¹⁰

The four orbital model proposed by Gouterman and co-workers¹³ is usually a basis of assignments of Pcs optical spectra to various types of transitions. This model for metal complexes of Pcs predicts five $\pi-\pi^*$ bands, but only two of them (Q and B) are located in a spectral region investigated in this work (330–800 nm). The Gouterman's model was modified by Stillman and co-workers^{14–16} by showing, on the basis of spectral bands deconvolution, MCD spectroscopy, and calculations, that in the spectra of metal complexes of Pcs two overlapping bands, B1 and B2, are present. The spectral properties of Pcs depend on the complexation with metal and on the attachment of side groups. These properties, which are not yet known in detail, change the interactions of Pcs with neighboring molecules,^{16–19} also with proteins¹⁹ and with biological membranes;⁵ therefore, they are important for the application of investigated dyes as sensitizers in PDT. Two complexes of Pc with Al with different side groups, one complex with Mg, and one free-base Solar Pc were investigated (Figure 1). Various Pcs were already previously investigated.^{1,2,4–6} It seems that they are promising candidates for PDT sensitizers.

2. Material and Methods

The molecular structures of dyes investigated are presented in Figure 1. The MgPc and Solar Pc were prepared in a two stage procedure starting with $H_2Pc(SO_3H)_4$ and diethanol-amine according to the method described by Ion.²⁰ Pcs substituted by Al were purchased from Sigma-Aldrich and used without further purification. The method of poly(vinyl alcohol) (PVA) films preparation and stretching was described previously.²¹ The steady state photoacoustic spectra (PAS) were measured with a single beam photo acoustic spectrometer.⁵

Absorption spectra were measured using a Shimadzu UV-1601 UV–visible spectrophotometer, and fluorescence spectra were measured with a Hitachi F4500. Both arrangements were

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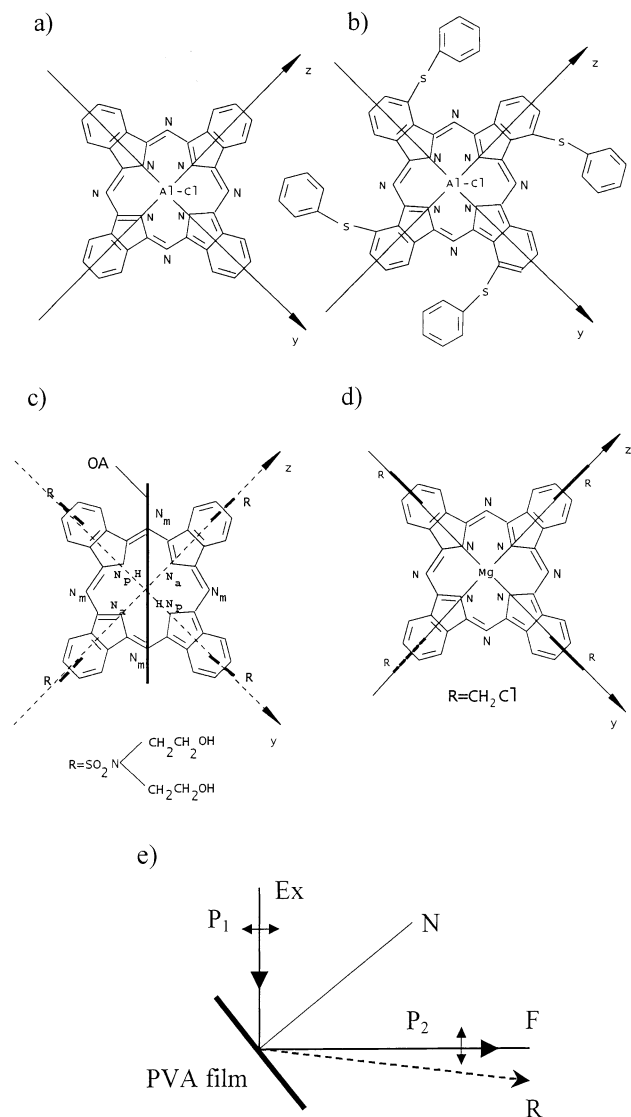


Figure 1. Structure of investigated Pcs (a–d) and fluorescence arrangement (e). (a) AlPcCl I, (b) AlPcCl II, (c) Solar Pc, (d) MgPc. In panel c, N_p denotes a pyrrole nitrogen and N_a and N_m denote pyrrole aza and mesobridging aza nitrogens, respectively. OA film stretching direction. In panel e, P₁, P₂, polarizers; Ex, excitation light beam; F, fluorescence beam; N, normal to PVA film plane; R, eventual reflection of light.

equipped with polarizers and film holders. The geometry of arrangement used in fluorescence measurements is shown in Figure 1e.

The measurements of polarized absorption carried out in the laboratory system delivered us the information about the absorption of light with the electric vector parallel (A_{par}) or perpendicular (A_{per}) to the direction of film stretching axis. From such results, the degree of dye molecule orientation (S) can be formally calculated from the formula:

$$S = (A_{\text{par}} - A_{\text{per}}) / (A_{\text{par}} + 2A_{\text{per}}) \quad (1)$$

Such calculation delivered results easy for the interpretation only in a case of elongated molecules with absorption TM directed parallel to the long axis of the dye. For Pcs, the interesting thing was the evaluation of the orientation of various absorption TMs in molecular frames measured with respect to symmetry axes of molecules. The locations and notations of these axes in a plane of molecule ring (z and y) are shown in Figure 1. The

x -axis is perpendicular to the Pc ring. The spectral regions of absorption of various TMs of Pcs are approximations known from theoretical predictions.^{13–17} To obtain polarized absorption spectra, the stepwise reduction procedure developed by Thulstrup, Michl, and Eggers^{7–10} was applied. The two sets of spectral reduction curves, $A_{\text{per}} - d_{\text{per}}A_{\text{par}}$ and $A_{\text{par}} - d_{\text{par}}A_{\text{per}}$ with the d_{per} and d_{par} ranging in steps from 0 to 0.1, were drawn.

The so-called “reduction factors” d_z^o and d_y^o were obtained from disappearing, at some wavelength, in the first linear combinations of two polarized components of absorption, the spectral features of polarization along the z -axis and for the second combinations, at different wavelength, the y -polarized features. The obtained reduction factors and the measured absorption components polarized parallel to the film stretching direction (A_{par}) and perpendicularly to this direction (A_{per}) were inserted in the equations:

$$A_z = A_{\text{par}} - d_z^o A_{\text{per}} \text{ and } A_y = A_{\text{per}} - d_y^o A_{\text{par}} \quad (2)$$

where A_z and A_y are reduced components of absorption spectra polarized in the molecular frame along the z and y directions.^{7–10,22–25}

The orientation factor for a given f transition at uniaxial orientation with respect to the z -axis enabled us to calculate the angle between TM of this transition and orientation axis z :

$$k_{fz} = \langle \cos^2 f, z \rangle \quad (3)$$

On the basis of reduction factors d_z^o and d_y^o , the orientation factors k_z and k_y can be obtained according to¹⁰

$$k_z = d_z^o / (d_z^o + 2) \text{ and } k_y = d_y^o / (d_y^o + 2) \quad (4)$$

where d_z^o and d_y^o are reduction factors from eq 2. The orientation factor k_x for the transitions perpendicular to the Pc ring was obtained from the dependence:

$$k_x = 1 - k_z - k_y \quad (5)$$

The stepwise reduction procedure^{7–10} enabled us to obtain the reduced components of absorption polarized along the axis in the molecular frame and the angles between the directions of various TMs and the locations of TMs with respect to the dye ring. It can also deliver information about “hidden” transitions and $n-\pi^*$ transitions with TMs located out of Pc ring, especially when polarized absorption is applied together with polarized fluorescence spectroscopy and magnetic circular dichroism (MCD) spectroscopy.^{14,15,22–24} The type of applied anisotropic matrix depends on the solubility of investigated molecules. The PVA film was a suitable matrix for our Pcs.

The obtained reduced components A_z and A_y usually represent the total sum of absorption polarized along the given axis of the investigated Pc molecule. The directions of the main axes of the molecule with respect to the film stretching direction can be easily predicted for molecules with elongated shape whereas for Pcs, having almost D_{4h} symmetry, several other spectral experimental and theoretical results have to be taken into account.^{13–18,24}

In a case of stretched films, the following four polarized components of fluorescence were measured, VVV, VH V, VHH, and VVH (H, horizontal; V, vertical). The first and the last letters refer to the direction of electric vector of the excitation and fluorescence light, respectively, and the middle letter refers to the position of the film stretching axis.²⁵

The components with identical polarization of excitation and fluorescence beams (they differ only in the positions of the sample axes) can be compared without additional corrections. Two pairs of components, (VVV; VHV) and (VVH; VHH), are not equivalent. For the first pair, we measure the emission of molecules that have their emission TMs oriented in the same direction as the absorption TMs of the molecules directly excited by the light absorption. In the second case, we measure the emission depolarization by several acts of the excitation energy transfer in a chain of differently oriented molecules or the emission of the molecules with different directions of absorption and emission TMs.

The calculated anisotropy coefficients from these components, $r_a = (VVV - VVH/VVH + 2VVH)$ and $r_b = (VHV - VHH/VHV + 2VHH)$, deliver also different information. The r_a value is high for the TMs of absorption and fluorescence forming a low angle with the direction of film stretching. The interactions with anisotropic surroundings can have a strong influence on this coefficient. The r_b can be high when absorption and emission TMs form the large angle. The next fluorescence anisotropy coefficient $r_c = (VVV - VHV/VVH + 2VHV)$ has to be large when a fraction of the "well-oriented" molecules contributes strongly to the measured emission, whereas $r_d = (VVH - VHH/VVH + 2VHH)$ became negative when the number of molecules oriented under a large angle to film axis is higher than the number of well-oriented.

To check the influence of TMs orientation on observed polarization of fluorescence and also coefficients:

$$r_a^* = \frac{(VVV/VOV) - (VVH/VOH)}{(VVV/VOV) + 2(VVH/VOH)} \text{ and } r_b^* = \frac{(VHV/VOV) - (VHH/VOH)}{(VHV/VOV) + 2(VHH/VOH)} \quad (6)$$

where O concerns nonstretched isotropic film, where measured. These coefficients are low when the orientation of TMs along the film axis is low, and observed r_a and r_b values are predominantly related to the effect of the photoselection by polarized light.

As it follows from these remarks from the set of fluorescence anisotropy coefficients, some information about orientation of dye molecules in film as well as about mutual orientation of the TMs of emission and absorption can be obtained. Additional information follows from the comparison of absorption and fluorescence anisotropy as well as from the calculation from r_a and r_b coefficients, the Legendre's polynomials:

$$\langle P_2 \rangle = \frac{2 + 7r_a - 14r_b + 5r_ar_b}{23 - 14r_a + r_b - 10r_ar_b} \text{ and } \langle P_4 \rangle = \frac{-12 + 21r_a + 21r_b - 30r_ar_b}{23 - 14r_a + r_b - 10r_ar_b} \quad (7)$$

The $\langle P_2 \rangle$ should be compared with the absorption orientation parameter (S); it could be different than S in a case when differently oriented molecules exhibit various yields of fluorescence.

The value of $\langle P_4 \rangle$ is very sensitive to molecular movements. It could be negative at a strong rotational depolarization or at a wide distribution function of the molecular axis around the orientation axis of anisotropic matrix.¹² In a rigid PVA matrix, the second possibility is more important.

The fluorescence excitation spectra, using for the excitation the light polarized parallel (V) and for observed emission

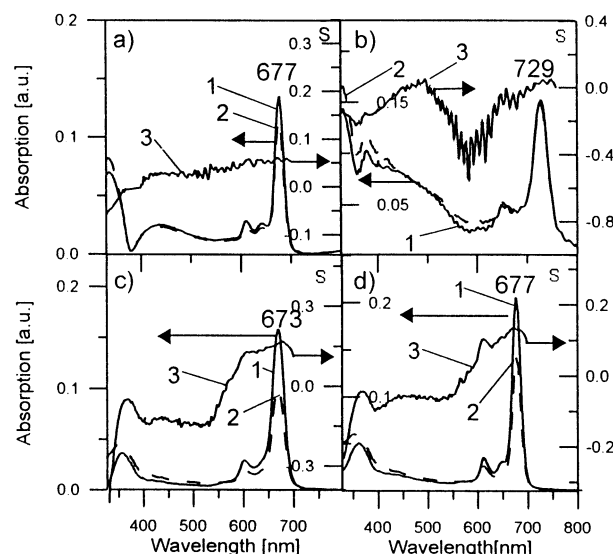


Figure 2. Polarized absorption spectra of Pcs in uniaxially stretched PVA film. Parallel component A_{par} (curve 1); perpendicular component A_{per} (curve 2). Anisotropy of absorption S (curve 3). (a) AlPcCl I, (b) AlPcCl II, (c) Solar Pc, and (d) MgPc.

TABLE 1: Absorption and Fluorescence Properties of Main Q Band of Investigated Pcs in Stretched Film^a

dye	λ_A (nm)	S	ϕ (deg)	λ_F (nm)	r_a	r_b	r_c	r_d	$\langle P_2 \rangle$	$\langle P_4 \rangle$
AlPcCl I	677	0.06	52	682	0.34	0.22	0.09	0.03	0.05	-0.10
AlPcCl II	729	0.01	54	733	0.43	0.39	0.05	0.03	0.05	0.01
MgPc	677	0.13	50	680	0.50	0.33	0.21	0.04	0.12	0.04
Solar Pc	673	0.16	48	679	0.42	0.30	0.09	-0.03	0.08	-0.04

^a S , anisotropy of absorption (eq 1, ϕ , angle between TM of Q-band film stretching axis); r_a , r_b , r_c , r_d , r_a^* , r_b^* , $\langle P_2 \rangle$, and $\langle P_4 \rangle$ equations given in text.

polarized parallel or perpendicular (V or H) to the film stretching axis, were also measured.

3. Results and Discussion

Polarized absorption spectra of investigated Pcs in 300% stretched PVA are shown in Figure 2. The absorption was measured in a region from 330 to 800 nm. The anisotropy of absorption S is also shown in Figure 2 and in Table 1.

The S value is rather low, which shows that investigated dyes have almost D_{4h} symmetry or/and that the film stretching axis is not parallel to any one of the TMs. Anisotropy is usually positive in a region of Q band (which is located at about 670 nm) and in a region of vibrational transitions of this band (605–640 nm) and negative in absorption in the B band region (330–360 nm). It shows that the TM of the Q band forms a smaller angle with the film stretching direction than the TM of the B band. Comparison of absorption anisotropy S values in the Q region (Figure 2 and Table 1) shows that MgPc and Solar are oriented to a higher degree than AlPcCl I and that the AlPcCl II exhibits the lowest orientation.

It shows that the degree of orientation depends not only on the side groups attached to the Pc ring but also on the complexation with metal. The Q and B bands have π – π^* character, and their TM are deposited almost in the plane of the Pc ring.^{13–16}

From theoretical predictions and experimental results for other Pcs and porphyrins,^{13–18,24,26–28} it is known that for free-base Pcs the TM of the main Q band is almost parallel to the z direction in Figure 1 and that there are two (B1 and B2) bands

TABLE 2: Orientation Factors of Pcs in PVA Stretched Film (k_z , k_y , k_x , eqs 4 and 5)

dye	k_z	k_y	k_x
AlPcCl I	0.37	0.31	0.32
AlPcCl II	0.34	0.29	0.37
MgPc	0.42	0.29	0.29
Solar	0.44	0.23	0.33

in short wavelengths region. The TM of the B1 band is close to the y direction, whereas $n-\pi^*$ bands TMs are perpendicular to the ring plane; this means that they are directed along the x -axis. Results from Table 1 suggest that all investigated Pcs exhibit similar axis of orientation in PVA.

On the basis of reduction factors, the orientation factors k_z and k_y of bands Q and B were calculated according to eq 4, whereas the orientation factor k_x for the transitions perpendicular to Pc ring was obtained from eq 5.¹⁰ Obtained values are gathered in Table 2. For all investigated Pcs, $k_z > k_y$. For AlPcCl I and MgPc, k_x is similar to k_y , but for AlPcCl II and Solar Pc, $k_x > k_y$. It seems that the film stretching axis is in all cases located between the TM of Q (z) and the TM of B (y) bands (Figure 1). Out of plane TMs, perpendicular to both z and y directions, have different values of k_x for different Pcs (Table 2). After the reduction procedure, the z direction, which is near to the Q band TM, is included in the A_z component, and TMs located along both other directions y and x contribute predominantly to the A_y component. It is under approximated supposition that after reduction almost uniaxial orientation of molecules along axis z (Figure 1) occurs. The MgPc exhibits rather high uniaxial orientation along the z -axis ($k_z = 0.42$ and k_y is similar to k_x). The AlPcCl I exhibits low k_z , but values of two other orientation factors are similar. It suggests low but uniaxial orientation. Table 2 shows that orientations of various Pcs are different.

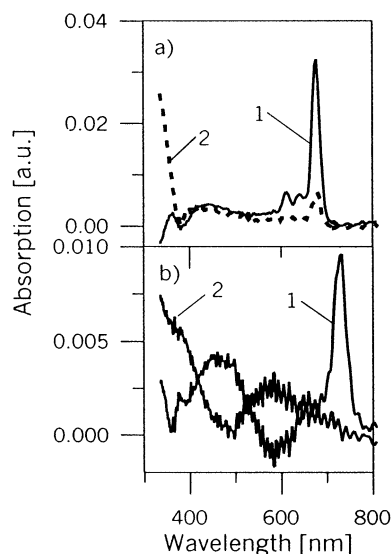
Low anisotropy of absorption in a region of Q band (Table 1) obtained on the ground of the Thulstrup and Michl procedure^{7–10} and the angle ϕ between Q TM and film stretching axis (equal to about 50° (Table 1) and about 57–58° for B1 band) confirm the suggestion that the stretching axis is located between almost mutually perpendicular TMs of Q band (at about 670 nm) and B1 bands (in 300–330 nm region).^{15,18} Better oriented molecules exhibit lower angles ϕ . The TMs of the B band are forming different angle ϕ in various spectral regions (not shown).

At a low degree of orientation, the anisotropy of absorption in the region 450–550 nm characteristic to $n-\pi^*$ transitions is very low (Figure 2). Therefore, to establish the directions of TMs with respect to molecular frame, the reduced polarized absorption spectra obtained by the stepwise procedure proposed by Thulstrup and Michl^{7–10,22,23} were used.

The examples of the reduced polarized spectra are presented in Figure 3. The presented reduced spectra are not normalized. On the basis of such reduced spectra, the averaged angles Θ between TMs of various transitions and the direction z (marked in Figure 1) were calculated^{10,12} from the formula

$$\cos \Theta = [(2S + 1)/3]^{1/2} \quad (8)$$

where S is anisotropy of absorption obtained on the basis of such spectra as in Figure 3 for A_z and A_y components. Results are shown in Table 3. As usual in metal complexes of Pcs, an intense Q band located at about 670 nm is followed by a series of vibrational components $Q(0,1)$, $Q(0,2)$, etc. As it follows from Table 3, these vibrational components exhibit, as it is pre-

**Figure 3.** Reduced polarized absorption components: A_z , curve 1; A_y , curve 2 (directions z and y as in Figure 1). (a) AlPcCl I and (b) AlPcCl II (polarized components are not normalized).**TABLE 3: Angles Θ between Various TMs and Direction z (Figure 1) Calculated on the Basis Reduced Polarized Absorption Spectra (Figure 3) of Pcs in Stretched PVA Film and Eq 8**

dye		type of transition						
		$Q(0,0)$	$Q(0,1)$	$Q(0,2)$	$n-\pi^*$	$n-\pi^*$	B2	B1
AlPc Cl I	λ (nm)	676	645	610	450	442	363	330
	Θ (deg)	31	37	33	50	50	47	90
AlPc Cl II	λ (nm)	728			593	460	380	330
	Θ (deg)	19			90	23	32	32
MgPc	λ (nm)	676	648	610	450		365	330
	Θ (deg)	24	33	36	36		61	90
Solar Pc	λ (nm)	673		605	450		360	330
	Θ (deg)	10		28	23		46	90

dicted,^{16,26,27} similar orientation to the main $Q(0,0)$ band only in the cases of better oriented dyes (AlPcCl I and MgPc). For other dyes, the situation is not so clear. At uniaxial orientation of dye molecules, TMs directed perpendicularly to the molecular frame contribute to the A_y component. The negative anisotropy of absorption ($A_y > A_z$) is observed, in a region of $n-\pi^*$ absorption, for AlPcCl I (Figure 3) as well as for MgPc, and Solar Pc (not shown) is due to TM directed perpendicularly to the ring.

In a case of AlPcCl II (Figure 3b) in the 450–550 nm region, two mutually shifted maxima exhibiting respectively positive and negative anisotropy are observed. For this dye, accuracy of calculated anisotropy is low, because of a very low degree of molecule orientation. The reduced polarized absorption spectra can include in the same spectral region the contributions from various differently oriented TMs belonging to different bands. In literature,²⁶ there are the suggestions that metal Pc complexes can exhibit in the Q region mixed (z and y) polarization and also that some contributions from perpendicular components can be generated by interactions with matrix.¹⁸ It was found²⁷ that also for molecules with D_{4h} symmetry some perpendicular to ring plane $\pi-\pi^*$ transition in the 600 nm region can occur. In a case of porphyrins, the complexation with metal generates a component orthogonal to the ring plane.²⁸ Similar effects can occur for Pcs. Several other effects can have also influence on the value of the angle Θ shown in Table 3. In a case of our Pcs, it is also not easy to decide how the main axis of orientation is directed. A much easier situation is for

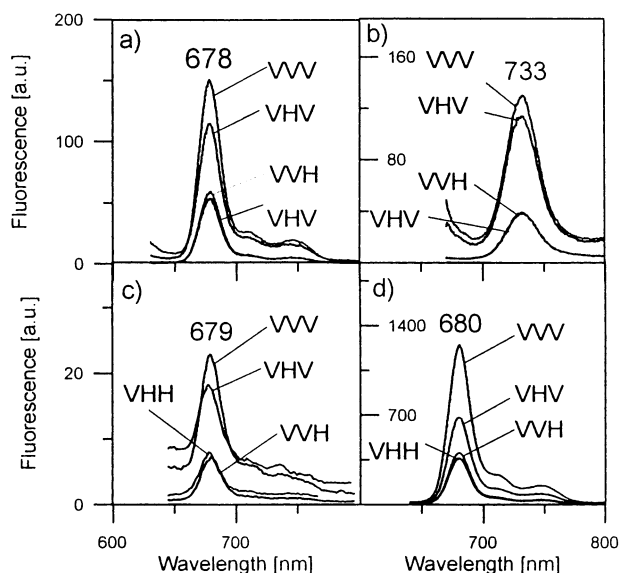


Figure 4. Polarized fluorescence spectra. V, vertical; H, horizontal. The first and the last letters refer to the direction of the electric vector of the excitation and fluorescence light, respectively, and the middle letter refers to the position of the orientation axis of the PVA film. (a) AlPcCl I, $\lambda_{\text{ex}} = 610$ nm; (b) AlPcCl II, $\lambda_{\text{ex}} = 650$ nm; (c) Solar Pc, $\lambda_{\text{ex}} = 605$ nm; and (d) MgPc, $\lambda_{\text{ex}} = 610$ nm.

molecules with C_{2v} symmetry because in this case every one TM has to be directed along one of the axis of symmetry and out of plane transitions can be neglected.²⁹

The orientation coefficients k_z , k_y , and k_x (Table 2) show that for some Pcs the orientation is not exactly uniaxial¹⁰ and it is different from the various investigated Pcs. It was shown (ref 10, pp 418–419) that for molecules having similar shape (tetraphenylporphyrin), a high degree of orientation ($k_z = k_y = 0.4$) was observed and that for molecules with similar shapes the orientations can be strongly different. It seems (from Tables 2 and 3) that in a case of AlPcCl II and Solar Pc the contributions from out of plane of ring transitions can be higher than for AlPcCl I and MgPc.

The data obtained for the short wavelength region confirm results obtained by Stillman and co-workers^{14–16} because two bands, B1 and B2, are observed. In most cases, these bands exhibit quite different orientations of their TMs (Table 3). The differences between S values at 360 nm and for $\lambda < 330$ nm are clearly seen for AlPcCl I, Solar Pc, and MgPc (Figure 2a,c,d).

Figure 4 shows the polarized fluorescence spectra of the same samples. The anisotropy of fluorescence coefficient r_a (Figure 5) depends not only on dye orientation but also on the effect of the photoselection by polarized light. It follows from the similar values of r_b and r_a coefficients, especially for dyes exhibiting low anisotropy of absorption, for example, for AlPcCl II. A similar conclusion follows from the almost zero values of r_a^* and r_b^* (eq 6) calculated for the ratios of polarized fluorescence intensities for stretched and unstretched samples (e.g., VVV/VOV and VVH/VOH) for dye exhibiting a low degree of orientation (Figure 5). The differences between r_a and r_b values are of course larger for better oriented MgPc and SolarPc than for AlPcCl II (Table 1). Rather high anisotropy r_a of emitted fluorescence is partially due to strong polarized photoselection effects and low, in rigid matrix, depolarization of emission. The depolarization can occur predominantly by excitation energy transfer between absorbing molecules and other slightly differently oriented fluorescent molecules. Values of fluorescence

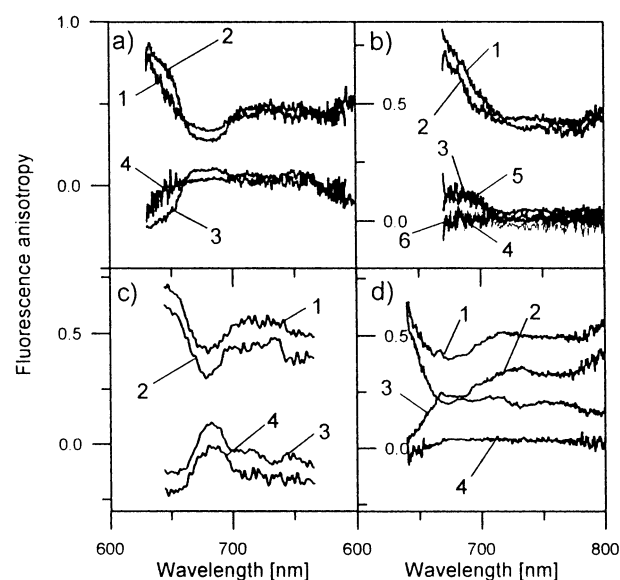


Figure 5. Anisotropy of fluorescence coefficients. Curves: 1, r_a ; 2, r_b ; 3, r_c ; 4, r_d ; 5, r_a^* ; and 6, r_b^* (given in text and eq 6). (a) AlPcCl I, (b) AlPcCl II, (c) Solar Pc, and (d) MgPc.

anisotropy r_c (Table 1) deliver information about the influence of dye orientation on anisotropy of observed emission. As one can expect, this coefficient is low for AlPcCl II and AlPcCl I and higher for MgPc. An unexpected low value of r_c is observed for Solar Pc exhibiting rather high anisotropy of absorption. From r_a and r_b values, the Legendre polynomials $\langle P_2 \rangle$ and $\langle P_4 \rangle$ (eq 7) were calculated (Table 1). The $\langle P_2 \rangle$ can be compared with anisotropy of absorption S (Table 1). For AlPcCl I and MgPc, these values are comparable; for AlPcCl II and Solar Pc, these values are different, which suggests a strong dependence of the yields of fluorescence on orientation of these dye molecules. The value of $\langle P_4 \rangle$ delivers information about wideness of the distribution of the TM around the orientation axis.¹² From comparison of $\langle P_4 \rangle$ values for investigated Pcs, it follows that AlPcCl I and Solar Pc exhibit negative values of this coefficient but the absolute value of it is highest for AlPcCl I. Results from Table 1 show that larger AlPcCl II molecules are more strictly distributed around their average direction of orientation than smaller AlPcCl I. The orientations of these two Pcs can be compared because of the complexation with the same metal.

Figure 6 shows polarized fluorescence excitation spectra measured for AlPcCl I and AlPcCl II. For a better oriented sample (AlPcCl I), the excitation spectra are strongly polarized, in a higher degree than for badly oriented dye (AlPcCl II). At observation in the main fluorescence band, the anisotropy of excitation spectra is positive in the long wavelength (Q) region. The fluorescence observed in the long wavelength region (for AlPcCl I at 712 and 748 nm) probably gives the aggregates emission. Similar aggregates emission was previously observed for porphyrins.³⁰ At long wavelength fluorescence observation, the fluorescence excitation anisotropy is negative for the whole measured region, but the highest negative values are observed in the 400–550 nm range. This differently polarized emission can be also due to dye molecules differently attached to polymer chain. The intensities of such untypical emission are much lower than those observed for main emission at the Q band. It shows that the orientation of dye aggregates or dye–PVA complexes is different than that of monomeric forms. From absorption and fluorescence spectra (Figures 2 and 4), it follows that the investigated Pcs in PVA are not strongly dimerized. It was found in a case of porphyrin type dyes³¹ that ring to ring dimerization

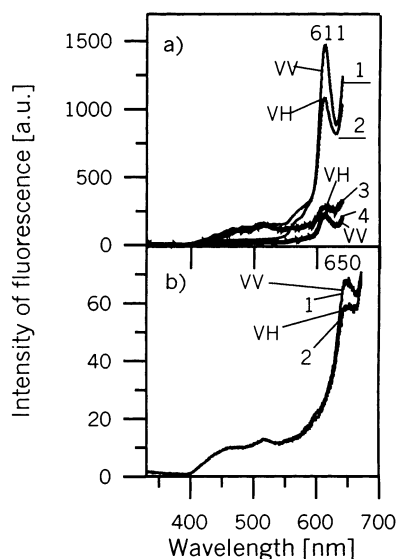


Figure 6. Polarized fluorescence excitation spectra. The first letters refer to the direction of the electric vector of exciting light, and the second refers to the position of the orientation axis of the stretched film (V, vertical; H, horizontal). (a) AlPcCl I; curves 1 and 2 for $\lambda_F = 682$; curves 3 and 4 for $\lambda_F = 712$. (b) AlPcCl II for $\lambda_F = 733$ nm (curves 1 and 2).

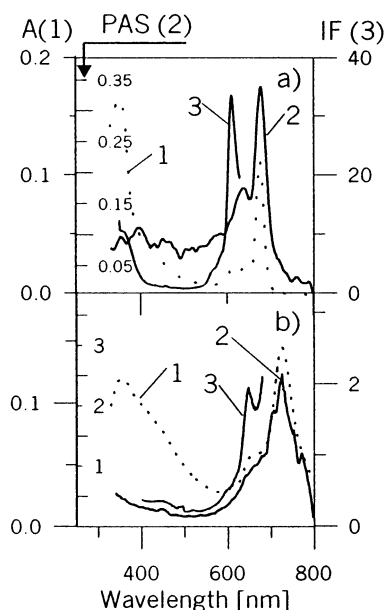


Figure 7. Absorption, A (curve 1); photoacoustic spectra, PAS (curve 2); and fluorescence excitation, IF (curve 3); $\lambda_F = 682$ (AlPcCl I) or $\lambda_F = 733$ nm (AlPcCl II). (a) AlPcCl I and (b) AlPcCl II.

causes the decrease in fluorescence yield and the increase in triplet state generation. Our previous⁴ and present results do not show such correlation between fluorescence yield and triplet state generation for Pcs.

At similar absorptions, the PAS amplitudes (Figure 7) are much higher for AlPcCl II than for AlPcCl I. The excitation of fluorescence is much more efficient for AlPcCl I than for AlPcCl II (Figure 7). It shows that the efficiency of thermal deactivation of excitation is higher for AlPcCl II and fluorescence yield is lower for this dye than for AlPcCl I. It was shown previously⁴ that AlPcCl I and MgPc exhibit a higher yield of triplet generation than AlPcCl II. It suggests that dyes better oriented in polymer film can be more efficient sensitizers in PDT treatment.

4. Conclusions

(i) All investigated Pcs exhibit a TM of Q(0,0) band located not exactly along the z direction. It can be a result of some admixture of contribution from $n-\pi^*$ bands located not exactly perpendicular to the dye ring but also the admixture of $\pi-\pi^*$ bands located in a region of Q band and polarized along y , as it was predicted for Pc metal complexes.²⁷ Such y -polarized admixture is also observed for free-base Solar Pc.

(ii) Most of the investigated Pcs exhibit two bands, B1 and B2, located, as it was predicted in the literature,^{14–16} in the short wavelengths region and characterized by different orientations of their TMs.

(iii) The stretching axis of PVA film is located between the averaged directions of the orientation of TMs of the Q and B band but closer to averaged direction of Q TM. The positions and intensities of $n-\pi^*$ bands in various Pcs are different. Because of molecular orientation, the contributions from such out of ring bands are included predominantly to reduced component of absorption A_y .

(iv) Different Pcs differently interact with biological macromolecules;^{19,31} therefore, their internal conversions from higher singlet states to the Q state are responsible for fluorescence, and the fluorescence and thermal deactivation yields are different. Various spectroscopic methods^{15,16,24,29,32} have to be applied in order to establish the influence of these interactions on the possibility of the dye applications in PDT. The efficiency of singlet oxygen formation is for differently substituted Pcs;³³ therefore, the knowledge of spectral properties of dyes can help to select Pcs suitable for PDT.

(v) The fluorescence polarization is a functional parameter in monitoring cellular stimulation, staining, and photochemistry;³⁴ therefore, our results concerning anisotropy of fluorescence of sensitizers in rigid medium can be helpful in finding proper conditions in PDT.

(vi) Previously,^{5,6} it was found that Solar Pc was selectively incorporated, much stronger in malignant than in healthy cells, but it exhibits low efficiency of triplet state generation;⁴ therefore, after illumination, it cannot efficiently destroy the cancerous cells. Much higher efficiencies of triplet generation are observed for MgPc and AlPcCl I. All of these properties have to be taken into account in order to choose proper sensitizers for PDT.

(vii) We have shown that spectral properties of various Pcs depend differently on the dye interaction with surroundings and on the polarization of light reaching incorporated in rigid matrix molecule. Similar effects can be predicted for dye incorporated into tissue and used in PDT. It seems that MgPc and AlPcCl I are promising candidates for the applications in PDT.

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