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Fluorescence and Time-Resolved Delayed Luminescence of Porphyrins in Organic Solvents and Polymer Matrices

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Porphyrin dyes fulfill an essential function in photosynthesis and are important in photodynamic therapy and in a range of electronic devices. Their spectroscopic characteristics may play a crucial role in these processes. The spectral properties of two porphyrin dyes: tetraphenylporphyrin and tetraphenysulfporphyrin in organic solvents (acetone, chloroform, methyl alcohol, and dimethylsulfoxide) and in polyvinyl alcohol and poly(methylmethacrylate) films have been investigated. Absorption, fluorescence, and microsecond time-resolved delayed luminescence spectra have been measured at room temperature. The existence of different aggregated dye forms in the ground and excited states has been demonstrated. The manifold of dye species depends on the solvent/polymer. In the case of the polymers, it also depends on the solvent used to coat the polymer film. Delayed luminescence spectra and decay times of the two porphyrins in the different solutions and in polymeric matrices suggest that different mechanisms of deexcitation of the singlet excited states may be responsible for their generation in these and other porphyrin dyes.

KEY WORDS: Absorption; organic solvent; polymer matrix; porphyrin; fluorescence; time-resolved delayed luminescence.

INTRODUCTION

In the past 10 years or so, porphyrin dyes have become of great interest to physicists, chemists, and biologists because of their essential functions in some processes occurring in nature, in particular, in photosynthesis [1], and of interest to these and medical scientists in view of their use as photosensitizers in photodynamic therapy (PDT) [2]. Porphyrin dyes are also used in technical equipments for the detection and measurement of radiation [3] and in electronic devices ("solar batteries") in which light energy is converted into electric energy [4].

The processes of charge separation and electron transfer in photosynthesis [5] have inspired the investigation of this phenomenon in artificial model system in which conversion of light energy into electric energy can be observed to take place. Chlorophyll and its aggregated forms, which fulfill an essential role in these processes, can serve as an excellent representative example of the use of chlorin and porphyrin dyes for light to electrical energy conversion phenomena. Electrochemical devices with porphyrins embedded in sandwich-like cells are the subject of many publications, and such investigations are ongoing in our [6,7] and other [8–11] laboratories.

Porphyrins can also act as photosensitizers for singlet dioxygen production and, for that reason, are finding application in the photodynamic therapy (PDT) of cancer [2].

Thus, it is of some importance to determine the photophysical properties of porphyrins and of their ag-

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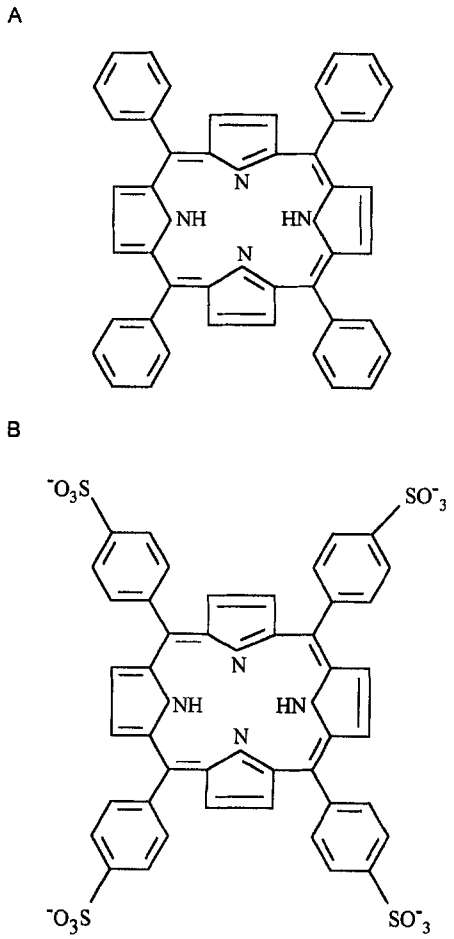

Fig. 1. Chemical structures of TPP (A) and $TPPS_4$ (B).

Table I. Solubility of TPP and $TPPS_4$ in Solvents

Solvent	TPP	$TPPS_4$	ε
Chloroform	+	−	4.81
Acetone	+	−	20.70
Methyl alcohol	−	+	32.70
DMSO	−	+	46.68

[a] +, high solubility; −, low solubility; ε, dielectric constant.

gregated forms. In the work reported here, we describe the spectral properties of two porphyrin dyes: uncharged tetraphenylporphyrin (TPP) and negatively charged tetraphenylsulfporphyrin ($TPPS_4$) dissolved in fluid organic solvents [chloroform, acetone, methyl alcohol, dimethylsulfoxide (DMSO)] and immobilized by embedding them in polyvinyl alcohol (PVA) and poly(methylmethacrylate) (PMMA). The solvents and polymers are characterized by different polarities. Absorption, fluorescence, and delayed luminescence spectra are presented. As far as we are aware, time-resolved delayed luminescence in the microsecond time range and the investigation of the influence of various media on this process have not been investigated previously for TPP and $TPPS_4$, so particular attention is paid here to this aspect.

MATERIALS AND METHODS

Porphyrins

The chemical structures of the porphyrin dyes used in the experiments are shown in Fig. 1. Negatively charged $TPPS_4$ is substituted with sulfonate (SO_3^-) groups attached to the pyrrole rings. The porphyrins used were synthesized from pyrrole and benzaldehyde in propionic acid as a reaction medium [12]. The purification was effected by reaction of the crude products with 2,3-dichloro-5,6-dicyanoquinone [12]. For $TPPS_4$ synthesis, the method described in Ref. 13 was used.

Porphyrins in Solution

The solubilities of the neutral and charged porphyrins investigated vary considerably between the solvents used (Table I). In view of this, we have confined our measurements of the dyes in solution to TPP in chloroform and acetone and $TPPS_4$ in methanol and DMSO. These solutions were prepared at a concentration of 2.5×10^{-5} *M*.

Porphyrins in Polymer Films

We have used two different polymeric matrices: highly polar PVA and PMMA, which has a low polarity. Powdered PVA was dissolved into solutions of TPP in chloroform and in acetone and of $TPPS_4$ in methanol and in DMSO. After spreading the PVA/dye solution in a thin layer, the solvent was evaporated and PVA film cast according to a previously described method [14,15]. Due to the low solubility of PMMA in the other solvents, only TPP-containing PMMA films were prepared, in a manner similar way to that for the PVA films.

Spectroscopic Measurements

Absorption spectra in the wavelength range of 350–700 nm were measured with a Specord M40 spectrophotometer (Carl Zeiss, Jena) controlled by a personal computer. The appropriate solvents or PVA or PMMA

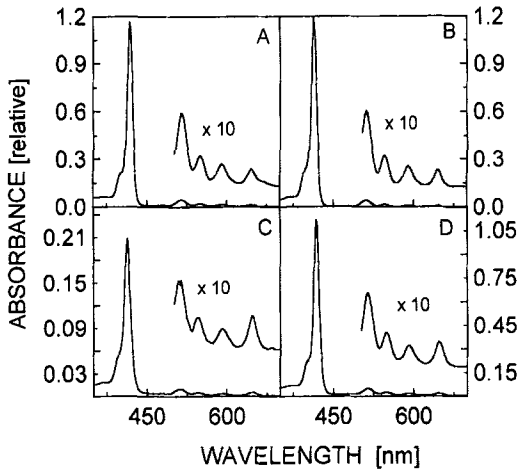

Fig. 2. Absorption spectra of porphyrins: (A) TPP in chloroform; (B) TPP in acetone; (C) $TPPS_4$ in methyl alcohol; (D) $TPPS_4$ in DMSO. The spectra are magnified 10 times in the range from 500 to 700 nm.

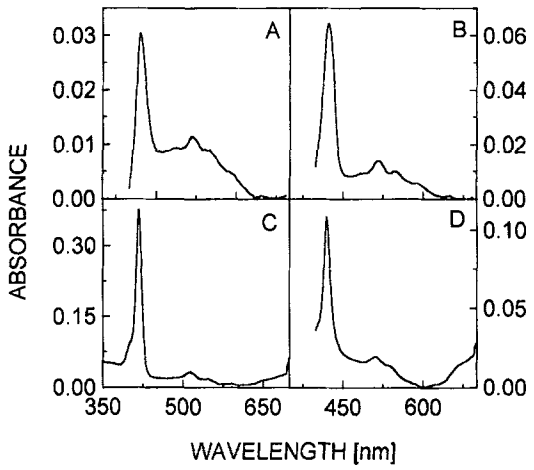

Fig. 3. Absorption spectra of porphyrins: (A) TPP in PVA/chloroform; (B) TPP in PVA/acetone; (C) TPP in PMMA/chloroform; (D) $TPPS_4$ in PVA/DMSO.

Table II. Absorption and Fluorescence Band Positions for TPP and $TPPS_4$ in Solutions and Polymers

	Absorption (λ_{max})					
Dye	Solvent	Soret band	Red band	Polymer	Soret band	Red band
TPP	Chloroform	419	515	PVA	420	515
				PMMA	418	515
	Acetone	413	512	PVA	423	515
$TPPS_4$	Methanol	413	512	PVA	420	515
	DMSO	419	515	PVA	419	510
	Fluorescence					
	Solvent	λ_{max}		Polymer	λ_{max}	
TPP	Chloroform	650	713	PVA	650	720
				PMMA	650	710–720
	Acetone	650	710	PVA	630	720
$TPPS_4$	Methanol	650	710	PVA	650	715
	DMSO	650	716	PVA	650	716

films prepared in the same way as the samples, but without the porphyrin, were used as the reference samples for these determinations and as blanks for the emission spectral measurements. In the latter, the absorbance of all samples was sufficiently low to avoid significant reabsorption and secondary fluorescence effects.

Fluorescence and time-resolved delayed luminescence spectra (DL) were determined with a laboratory-built apparatus described elsewhere [16,17]. In the DL experiment, a nitrogen-laser-pumped dye laser was employed as the excitation light source. Fluorescence and DL spectra were monitored in the wavelength region of 600–800 nm and the samples were excited at 413 or 419 and at 512 or 515 nm. The spectra were corrected for variation in the response of the detector system to light of different wavelengths. All measurements were carried out at room temperature.

RESULTS

Absorption Spectra

Absorption spectra of TPP in chloroform and acetone, and of $TPPS_4$ in methanol and DMSO, are shown in Fig. 2. The general character of these spectra is similar and they are in accordance with previous data in the literature [18]. Each spectrum is characterized by an intense Soret band in the range of 400–430 nm and a number of less intense bands in the region from 500 to 700 nm. The location of the Soret maximum varies slightly with solvent. The Soret bands for TPP in acetone and $TPPS_4$ in methanol peak at 413 nm, while those for TPP in chloroform and $TPPS_4$ in DMSO are bathochromically shifted, to about 419 nm. The red shifts may arise from differences in electric fields local to the dye molecules [19] due to the differing solvent polarities and/or to the creation of aggregated dye forms [5]. Absorption band maxima for all samples are presented in Table II.

The measured absorption spectra of the dyes in the polymeric films are shown in Fig. 3 (see also Table II). The shapes of the spectra are not drastically changed in the film compared with those in solution, but smaller or larger (from 1- to 10-nm) red shifts of the main band

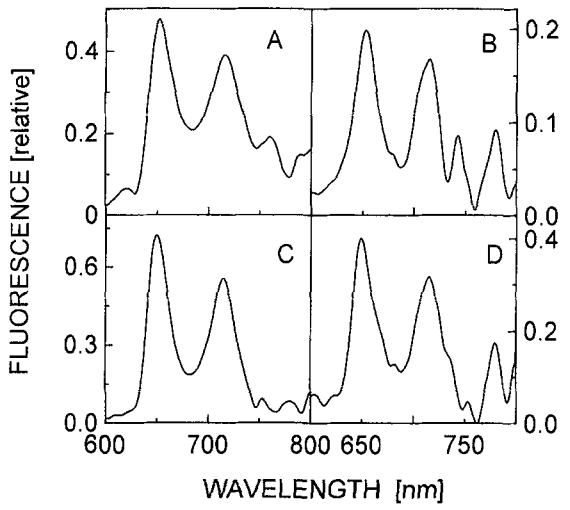

Fig. 4. Fluorescence spectra of porphyrins. TPP in chloroform; (A) λ_{ex} = 419 nm; (B) λ_{ex} = 515 nm. TPP in acetone; (C) λ_{ex} = 413 nm; (D) λ_{ex} = 512 nm.

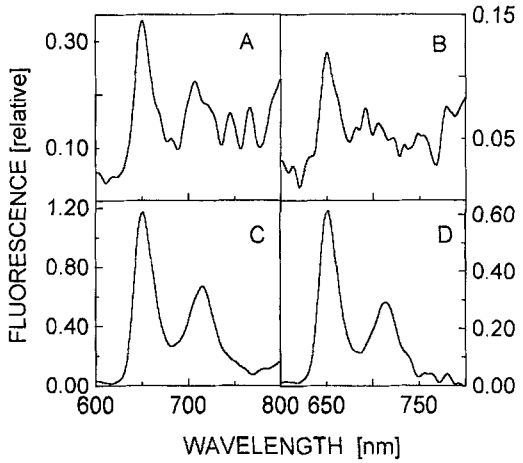

Fig. 5. Fluorescence spectra of porphyrins. $TPPS_4$ in methyl alcohol; (A) λ_{ex} = 413 nm; (B) λ_{ex} = 512 nm. $TPPS_4$ in DMSO; (C) λ_{ex} = 419 nm; (D) λ_{ex} = 515 nm.

are apparent. The Soret bands are quite strongly bathochromically shifted, from 413 nm in solution to 423 nm for TPP in the acetone-cast PVA film, and from 413 nm in solution to 420 nm for $TPPS_4$ in the methanol-cast PVA film. No changes in the band position for TAP in chloroform-cast PMMA or for $TPPS_4$ in DMSO-cast PVA compared with the solution values were detected (Table II). The data suggest not only that does the polymer itself influence the absorption spectral features of these dyes, but also that the solvent used for casting the films can affect them. Chloroform and PMMA are media of low polarity, while DMSO is the most highly polar solvent used here. When a low-polarity film is cast from a low-polarity solvent (chloroform-cast PMMA) or a high-polarity film cast from a polar solvent (DMSO-cast PVA), no particular changes are observed compared with the solvent spectra. Other combinations of low- or high-polarity films cast from low- or high-polarity solvents elicit changes in the film spectra compared with the appropriate solvent spectra, which may be due to the effect of either the solvent or the polymer.

Fluorescence Spectra

Both TPP and $TPPS_4$ show intense fluorescence at 650 and 710–716 nm when excited either in the "blue" (Soret band) region at 413 or 419 or at 512 or 515 nm (Figs. 4 and 5). In all samples, the intensity of the band peaking at 650 nm is always higher than of that peaking at 710–716 nm.

However, fluorescence spectra monitored for two excitation wavelengths show shape changes. In almost all cases, though, no changes in the 650-nm band position were observed, but specific differences were noted in the emission region of 660–800 nm. In some of the spectra, a shoulder at about 660–670 nm can been seen, and the 710- to 716-nm band has various shapes, with a small hump on its short-wavelength side. The smallest differences are observed for $TPPS_4$ in DMSO (Figs. 5C and D), while the most drastic variations in spectral shape are manifested by $TPPS_4$ in methyl alcohol (Figs. 5A and B). In the latter spectra, new well-resolved bands are clearly identified. These differences in emission spectra with excitation wavelength evidently indicate the existence of more than one absorption spectral form of the dye in the samples. Moreover, the much larger differences between the fluorescence spectra of TPP and $TPPS_4$ in various solvents (compared with those for absorption spectra) suggest that the mutual interaction of dye molecules and/or of dye molecules with the solvent is stronger when the dye is in its excited state than when in its ground state, so that the existence of excited-state dimers (excimers) cannot be excluded from contributing to the observed effects.

Fluorescence spectra for two excitation wavelengths (419 and 515 nm) for TPP are shown in PVA (Figs. 6A and B, respectively) and in PMMA (Figs. 6C and D, respectively). Comparing the fluorescence of TPP in solution with that in films, particularly large changes in shape are observed in the region of the 650-nm band for chloroform-cast PVA and solution samples excited in the Soret region (Figs. 6A and 4A, respectively) and for acetone-cast and solution samples excited at 515 nm

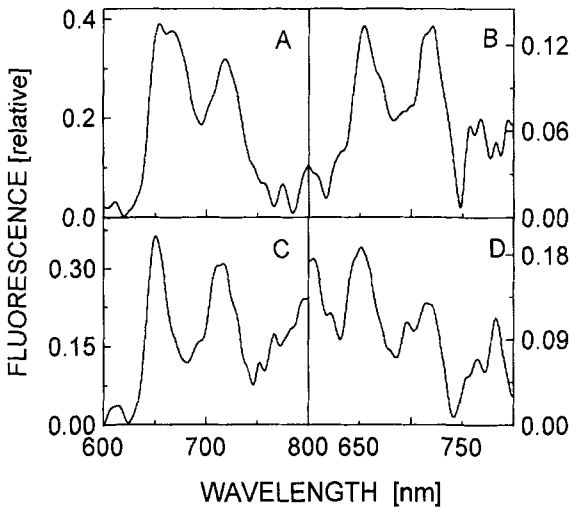

Fig. 6. Fluorescence spectra of porphyrins. TPP in PVA/chloroform; (A) λ_{ex} = 419 nm; (B) λ_{ex} = 515 nm. TPP in PMMA/chloroform; (C) λ_{ex} = 418 nm; (D) λ_{ex} = 515 nm.

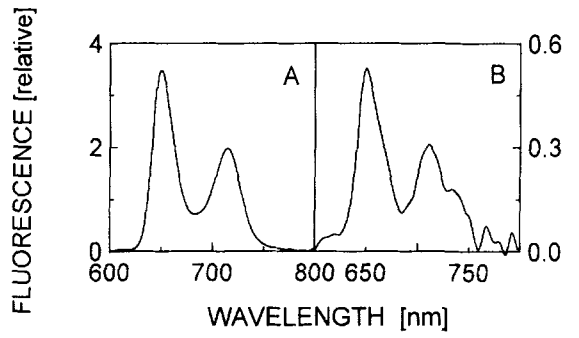

Fig. 7. Fluorescence spectra of porphyrins. $TPPS_4$ in PVA/DMSO; (A) λ_{ex} = 419 nm; (B) λ_{ex} = 512 nm.

(spectra not shown). This variation of the fluorescence spectral shapes indicates the coexistence of a manifold of forms of the dyes in polymeric films cast from chloroform or acetone solutions. The fluorescence data also suggest that for TPP in chloroform-cast PMMA film, the existence of more than one spectroscopic form of the dye cannot be excluded, even though no changes in absorption spectra between TPP in chloroform solution and in PMMA film were evident.

Similar observations were made for $TPPS_4$ in methyl alcohol-cast PVA film. The drastic differences observed there on excitation at 419 nm compared with 515 nm were similar to those observed for the methyl alcohol solution (Figs. 5A and B). The smallest changes in fluorescence spectra were seen for $TPPS_4$ when incorporated into DMSO-cast PVA film with excitation at

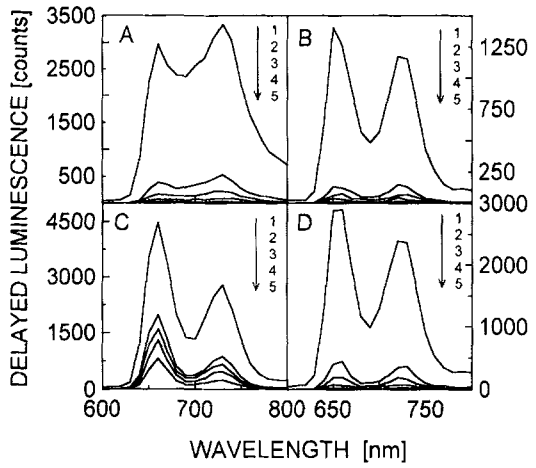

Fig. 8. Delayed luminescence spectra. TPP in chloroform; (A) λ_{ex} = 419 nm; (B) λ_{ex} = 515 nm. $TPPS_4$ in DMSO; (C) λ_{ex} = 419 nm; (D) λ_{ex} = 515 nm. Time windows: 1, 0.2–5 μs; 2, 5–10 μs; 3, 10–15 μs; 4, 20–25 μs; 5, 45–50 μs.

419 and at 512 nm (Figs. 7A and B), which are very similar to those observed for the DMSO solution (Figs. 5C, D). The $TPPS_4$–DMSO data are the only case in this study where there is practically no difference between either absorption spectra or fluorescence spectra in solution compared with film cast from the same solvent.

Time-Resolved Delayed Luminescence Spectra

Delayed luminescence (DL) spectra were observed in the region of fluorescence (600–800 nm), but on the microsecond time scale. Representative DL spectra for TPP in chloroform and $TPPS_4$ in DMSO for excitation at 419 and 515 nm are shown in Fig. 8. These spectra exhibit two main bands, with maxima at 660 and 730 nm. For both dyes, the DL spectra observed for the different excitation wavelengths are very different. The intensity ratios of the 660 to the 710 to 720-nm bands change and are different from those observed in the fluorescence spectra. When TPP in chloroform is excited at 419 nm, the 730-nm band is more intense than the shorter-wavelength one band (Fig. 8A). In the remaining spectra (Figs. 8B–D), the relationship between the 650- and the 730-nm bands is inverted. The DL decay times for TPP in chloroform and for $TPPS_4$ in DMSO are also different. From Fig. 8 it is evident that the delayed luminescence of $TPPS_4$ in DMSO decays much more slowly than that of TPP in chloroform, particularly when excited in the Soret region. These drastically different decay kinetics reflect differences in the kinetics of the

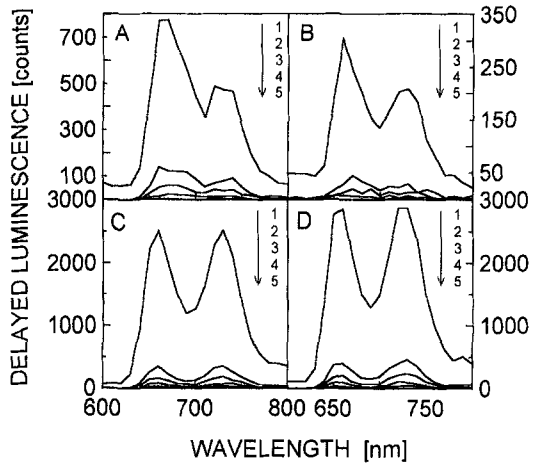

Fig. 9. Delayed luminescence spectra. TPP in PVA/chloroform; (A) λ_{ex} = 419 nm; (B) λ_{ex} = 515 nm. TPP in PMMA/chloroform; (C) λ_{ex} = 419 nm; (D) λ_{ex} = 515 nm. Time windows as in the legend to Fig. 8.

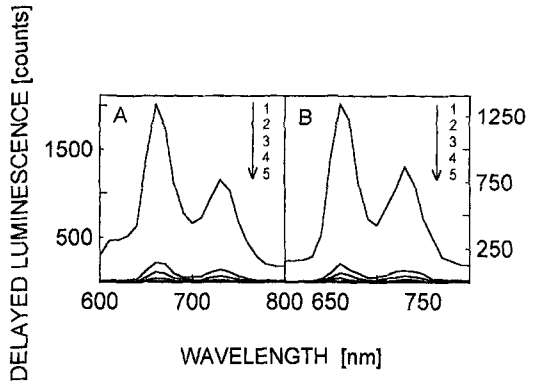

Fig. 10. Delayed luminescence spectra of $TPPS_4$ in PVA/DMSO; (A) λ_{ex} = 419 nm; (B) λ_{ex} = 512 nm. Time windows as in the legend to Fig. 8.

excited states responsible for the delayed process in the two dyes.

Marked alterations in its DL spectrum are also elicited by the inclusion of TPP in PVA and PMMA matrices (Fig. 9). Particularly large changes are observed in PVA (film cast from TPP–chloroform solution), and smaller changes in PMMA. In general, for TPP in PVA, the band peaking at 660 nm becomes dominant over that at 730 nm (Figs. 9A and B), while for TPP in PMMA the effect is the opposite (Fig. A. 9C and D).

Analysis of the DL decay times of TPP in the films shows that incorporation of the dye into PVA changes the decay kinetics. On the other hand, practically no differences in decay times are observed for TPP embedded in the PMMA matrix at any of the excitation or emission wavelengths examined.

DL spectra for $TPPS_4$ in PVA films are shown in Fig. 10. These spectra also have two main bands peaking at the same wavelengths as those observed for TPP (660 and 730 nm). The DL spectra for $TPPS_4$ in PVA are similar in shape to those of $TPPS_4$ in DMSO solution and are similar to those of fluorescence, which is not the case for TPP. This indicates that the DL of $TPPS_4$ is due predominantly to a single spectral form of the dye. The most marked difference between the delayed luminescence of $TPPS_4$ in DMSO solution and that in PVA film cast from the dye–DMSO solution is in its decay. As shown in Figs. 8 and 10, DL decays over a period several times longer in DMSO solution than in PVA film, indicating a marked rigid polymer matrix effect on the mechamism of deactivation of the long-lived excited state.

DISCUSSION

In interpreting the data presented, we have to take a number of particular points into consideration: the difference in chemical structure of the two dyes, especially with respect to the presence or absence of charged groups, the influence of solvent, and the effect of rigidity of the polymeric matrices.

The porphyrins used in these studies were metal-free species with different substituents. TPP is an electrically neutral dye without additional functional groups attached to the macro ring, whereas $TPPS_4$ is an anionic dye with SO_3^- ring substituents. The presence of different (charged or uncharged) substituents can lead to differences in the electronic energy levels of the dyes due to the different distributions of their electron clouds, reflected in the spectral properties of the dyes. The existence of the dye in monomeric and/or aggregated forms depends strongly on the solvent as well as the concentration of the dye.

The dyes examined in the present studies are metal-free porphyrins for which creation of dimers and/or other aggregated forms depends on plane-to-plane π–π electronic interaction between the porphyrin rings, as we have observed for pheophytin, a metal-free chlorophyll derivative [14,15]. In solution or in a polymer matrix, porphyrins can occur in the form of monomers or aggregates, the latter being either covalently-linked or self-associated dimers [20]. The configuration of these dimers (tail-to-tail or face-to-face) drastically affects their absorption and/or emission properties [21,22].

The experiments reported here were designed to establish whether or not charged substituents and/or various solvent and polymer environments can lead to large differences in the spectral properties of these dyes. Some differences in the absorption spectra for the two dyes in the various media were observed. Nevertheless, no particular relationship between absorption (or fluorescence) band positions and solvent polarity was observed for TPP in chloroform and $TPPS_4$ in DMSO, or in polymer matrices, even though the two species—TPP and $TPPS_4$—are chemically very different and are dissolved in very different solvents. DMSO is the most polar solvent used here (ε=46.68), whereas the polarity of chloroforms is low (ε=4.81), but the Soret band maxima of both these dyes in both solvents are located at 419 nm. It seems, however, that there are at least two effects which can affect the absorption spectra to some appreciable extent. In previous work [13,23], we reported some studies of $TPPS_4$ in aqueous solutions of a high polarity ($\varepsilon \approx 80$). For this porphyrin, the free monomeric form was observed to have its Soret peak at 413–414 nm. Essentially the same was observed for TPP and $TPPS_4$ in acetone and methanol, respectively, in the present work, i.e., peak absorption at 413 nm. On the other hand, a red shift of this band from 413 to 420 nm has been observed in complexes of positively charged tetraaminoporphyrin (TAP) with the biopolymer melanin [23–25]. Again, according to Uehara and co-workers [27], several differently aggregated species of chlorophyll can be formed, depending on the kind of solvent used. In light of the present results, as well as those reported elsewhere [24–27], our absorption measurements exclude the possibility that the influence of the local electric field is the only effect altering the electronic energy levels of the dyes investigated. On the other hand, it is well known that the ability of porphyrin to aggregate is strongly affected by solvent. As shown by Katz and co-workers [28], porphyrins form strongly interacting dimers without weak solvent participation, and this is probably what we are observing here for TPP in chloroform. The coexistence of monomeric and aggregated forms in TPP–chloroform solutions is also confirmed by the fluorescence spectra. In the polar medium of DMSO, strong interaction between the dye ($TPPS_4$) and solvent molecules cannot, a priori, be excluded. Thus, our absorption data indicate the contribution of two effects: that of the local (solvent) electric field and that of aggregation. The alterations in absorption and, particularly, fluorescence spectra of the dyes in polymer films confirm that both the polymer itself and the solvent used in preparing the films can influence the composition of dye species in such samples.

Finally, we focus particular attention on the importance of the DL measurements. The appearance of the DL spectra suggests that important photophysical processes occur in excited porphyrins on the microsecond time scale. The shapes of the spectra and the kinetics of their decays are different for various dye forms (monomers, aggregates), and they depend on the kind of media in which the dye molecules are embedded. The similar character of the DL spectra for TPP in chloroform and in PMMA film suggests that the forms of dye in solvents of low polarity are preserved in rigid PMMA, a conclusion also supported by the decay data for these systems. In the case of $TPPS_4$, however, the significant reduction in $TPPS_4$ decay times in polymer film compared with those of the dye in solution are probably due to particularly strong interaction of the dye with the polymer. These results indicate that some polymers can modify the deactivation processes of the long-lived states giving rise to the DL. A strong influence on these processes was also observed for TAP and $TPPS_4$ in the polymer melanin [23]. In previous works [29,30], as well as elsewhere [31], it has been shown by fluorescence lifetime and confocal microscopy that PVA film cast from DMSO solution exhibits pocket-like structures containing different chlorophyll species, even though, in that case, the absorption and steady-state fluorescence spectra were essentially characteristic of monomers. Thus it seems that we cannot exclude heterogeneity in the porphyrin–PVA/DMSO system in this work, which may result in a manifold of dye forms and changes in the spectral properties. The spectral differences which we observe for the two porphyrins in the absence and presence of the polymer suggest that the channels for thermal deactivation of differently aggregated forms are different in the two media. The competition between radiative and nonradiative processes in porphyrins depends strongly on the form of the porphyrin in the sample, as we have shown previously [23]. Vibrational interaction between the polymer matrix and the excited dye may shorten the lifetime by thermal quenching.

Although the DL spectra were measured in the same spectral region as fluorescence (600–800 nm) so that deactivation from the first singlet excited state to the ground state of the dye was observed, the kinetics of the long-lived excited state were nevertheless monitored. There are at least two mechanisms responsible for such delayed emission, which we have discussed previously [17,23,29]: reversible intersystem crossing from the triplet state to the first excited singlet state and/or ion recombination. These processes may differ in monomeric and aggregated dye forms. In almost all samples, the DL spectra, although similar to, are not identical with, the

fluorescence spectra. There are several reasons for this observation. Particularly large differences between the DL spectra and the fluorescence spectra were observed for TPP in chloroform (Fig. 8A) and TPP in PMMA (Figs. 9C and D). In the former, the band at 730 nm is more intense than that at 660 nm. The most similar fluorescence and DL spectra were noted for $TPPS_4$ in DMSO (Fig. 8C) and $TPPS_4$ in PVA/DMSO (Figs. 10A and B). The data indicate the dominance of monomeric forms of $TPPS_4$ in DMSO solution and also on incorporation into a PVA matrix. On the other hand, the existence of aggregated dye forms is not excluded and is, in fact, supported by the observed sensitivity of the fluorescence spectra to the excitation wavelength. Aggregated dye contributes strongly to the emission band at 730 nm. This band is usually assigned to vibrational modes of the monomer and to emission of excited dimers or other aggregated dye forms. However, if the process involves only one dye form, the fluorescence and DL spectra should be essentially identical. If, instead, the delayed emission arises from both monomeric molecules and aggregated forms, spectroscopic differences between fluorescence and delayed luminescence should be expected. The differences in decay kinetics of the DL at 650–660 and at 710–730 nm explains why the band ratios differ in DL and fluorescence. These data strongly support the existence of more than one form of porphyrin in the samples investigated.

Based on our absorption, fluorescence and delayed luminescence measurements, we have demonstrated a heterogeneity of porphyrin forms in some solvents and polymer matrices. The creation of spectroscopically different forms of the dyes in their ground and/or excited states depends strongly on the solvent and polymer in which the dye molecules are embedded.

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