

efficiency, and/or possibly a large S_1 - T_1 gap, thus placing phosphorescence in an experimentally inaccessible region. Thus, the position and role of triplet states in the photophysics of **3** must await further studies.

Conclusion

The high symmetry and planar structure of **3** give rise to a low-lying one-photon-forbidden electronic transition having an origin at ca. $2.10 \mu\text{m}^{-1}$. This transition represents the hypsochromically shifted $^1A_2' \leftarrow ^1A_1'$ transition observed in **2**, origin at $0.784 \mu\text{m}^{-1}$. If we presume that this transition is vibronically induced, a vibrational mode having a frequency of ca. 1400 cm^{-1} is implicated. Nonradiative decay from the (lowest) excited state appears to involve two different pathways, one possibly being intersystem crossing.

Experimental Section

All studies of **3** were carried out in N_2 -deaerated acetonitrile solution (Eastman Spectro). Lifetime measurements were performed with a time-correlated single-photon apparatus; an air-filled flashlamp (0.5 atm) running at 60 kHz was used as the excitation source. The 357.7-nm line was isolated with a 0.5-m Ebert-mounted Bausch and Lomb monochromator. Emission was viewed at 510 nm through a similar monochromator to which an RCA C-31000M photomultiplier tube was coupled. Pulses from the tube (which was at ambient temperature and kept at +2500 V, photocathode grounded) were processed with an Ortec 583 dis-

criminator (set at 60 mV). Decay curves were analyzed via a reiterative reconvolution approach based on software developed in our laboratory. Analysis was performed on a dedicated LSI 11/03 microcomputer. As an indication of quality of fit, χ^2 values of about 1.3 for decay curves spanning 3-4 decades of intensity were typical. Fluorescence spectra were obtained with a d.c. fluorimeter which incorporated a 200-W Hg(Xe) lamp and an EMI 9558 photomultiplier tube. Absorption spectra were obtained with a Cary 14 spectrophotometer. Temperature control was achieved with a home-made thermoelectric heater/cooler module attached to a fluorescence/absorption cell holder. A bridge-amplifier feedback arrangement allowed temperature control within ca. 0.2°C . The fluorescence quantum efficiency measurement was based on a value of 0.97 for $1.0 \times 10^{-5} \text{ M}$ solution of fluorescein (Kodak) in 0.01 M KOH in 95% ethanol; absorption and fluorescence characteristics agreed closely with those reported by Seybold et al.¹⁶

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Optical and Electron Spin Resonance Study of Cation and Cation-Crown Ether Induced Dimerization of Tetrakis(4-sulfonatophenyl)porphyrin

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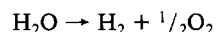
The effect of dimerization on the optical spectra of TPPS and the ESR spectra of its photoexcited triplet state were investigated. It is found that dimerization can be promoted by addition of cations and cation-crown ether complexes. Two distinct dimer species could be identified with ESR. Dimerization produces red shifts of the optical absorption (Q) bands and fluorescence peaks. In addition, the fluorescence intensity is strongly quenched. These results parallel findings reported for a variety of cofacial covalently linked chlorophylls and porphyrins. However, there is a striking difference between the triplet characteristics of the TPPS dimers on the one hand and covalently linked dimers on the other. The former exhibit a pronounced dimerization-induced reduction in zero-field splitting values. The values of the latter are very similar to those of their monomer precursors. In this respect, the TPPS system mimics changes found in the triplet ESR spectra associated with the transition from chlorophyll monomers (in vitro) to chlorophyll dimers in reaction centers of photosynthetic bacteria. Triplet ESR measurements focused on dimerization effects on the zero-field-splitting parameters, kinetics of triplet-state population and decay, and magnetophotoselection characteristics. It is found that the triplet-state properties cannot be interpreted with a simple exciton model. A satisfactory theoretical interpretation probably has to take charge-transfer contributions into account.

Introduction

The study of porphyrins and metalloporphyrins has been an active field of research for several decades because of their involvement in many reactions of chemical and biological interest. Among the properties that have received much attention in recent years has been the ability of porphyrins to participate in photoinitiated electron-transfer reactions. This has suggested the possibility of their application as photocatalysts in systems capable of photochemical conversion and storage of solar energy.¹

Water-soluble porphyrins may be particularly suited for such an application.²⁻⁴ Illumination of these systems produces pho-

toexcited triplets with high efficiency. The long-lived triplet-state molecules then can participate in electron-transfer reactions that, for instance, can be utilized to initiate the water-splitting reaction



These porphyrins may be present as dimers or higher aggregates in aqueous solution.⁵ Since the formation of aggregates may have

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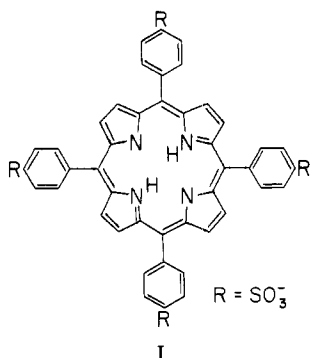
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a strong effect on their physicochemical properties, a thorough understanding of the conditions that promote aggregation is of importance. This consideration prompted us to initiate a study of the aggregation of water-soluble porphyrins and metalloporphyrins with the aid of optical spectroscopy and electron spin resonance (ESR) spectra of their photoexcited triplets. In this paper we report the results obtained in the study of tetrakis(4-sulfonatophenyl)porphyrin (I, TPPS).



Previous studies of aggregation of water-soluble porphyrins focused on the effects of concentration and pH. Mention is made as well of the effect of ionic strength on the absorption spectra.^{6,7} This phenomenon has been attributed to cation-induced aggregation. In the present study the role of the cations in the aggregation of TPPS has been investigated in some detail. Of particular interest is the profound effect of introduction of cation-crown ether complexes on TPPS aggregation. This observation has been reported earlier in a brief communication.⁸

The spectroscopic data establish the presence of a monomer-dimer equilibrium in aqueous solutions of TPPS. With the addition of cations or cation-crown ether the equilibrium can be shifted toward the dimer side. This makes it possible to investigate the changes in spectral parameters associated with porphyrin dimerization. A correlation of these parameters with published data⁹⁻¹⁵ on covalently linked chlorophylls and porphyrins allows us to draw some conclusions regarding the dimer structure. As far as the optical spectra are concerned, TPPS dimerization effects are very similar to those found for cofacial dimers of porphyrins and in vitro chlorophylls. On the other hand, previously reported triplet ESR spectra of porphyrin and in vitro chlorophyll dimers have been found^{16,17} to be very similar to those of their monomer precursors, whereas dimerization of TPPS is found to produce profound changes. Interestingly, in this respect the TPPS system mimics the changes found upon going from in vitro monomer chlorophylls to in vivo chlorophyll aggregates found in photosynthetic reaction centers of green plants and photosynthetic bacteria.¹⁷

Experimental Section

TPPS (sodium salt, Strem) and 18-crown-6 (Aldrich) were used as received. ESR spectra were recorded with a Varian E9 X-band

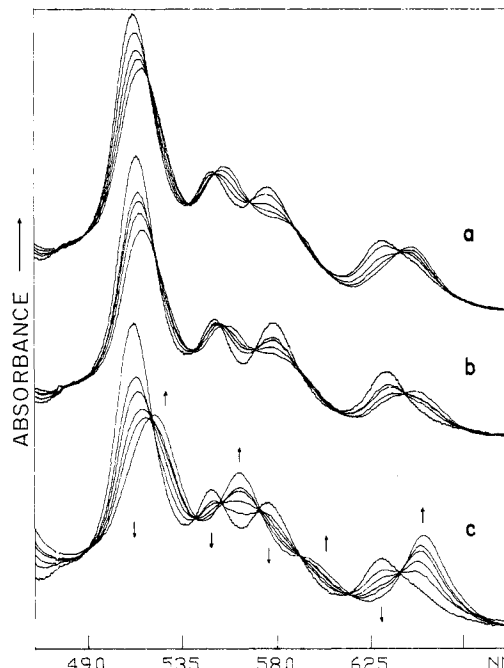


Figure 1. Optical absorption spectra of TPPS in aqueous solution: (a) effect of TPPS concentration in the presence of 0.1 M KCl (TPPS concentrations: 7.0×10^{-6} , 1.4×10^{-5} , 3.5×10^{-5} , 7.0×10^{-5} , 1.4×10^{-4} M; ratio of [TPPS] over cell path length constant); (b) effect of addition of KCl to a solution of TPPS (6.0×10^{-5} M) (KCl concentrations: 0, 0.02, 0.03, 0.05, 0.1 M); (c) effect of addition of 18-crown-6 to a solution of TPPS (6.0×10^{-5} M) in 10^{-2} M KCl solution (crown ether concentrations: 0, 5.0×10^{-4} , 1.0×10^{-3} , 2.0×10^{-3} , 3.0×10^{-3} , 1.0×10^{-2} M).

spectrometer using field (100 kHz) and light (83 Hz) modulation with phase-sensitive detection at the modulation frequencies. This detection method takes advantage of the signal enhancement provided by spin polarization.¹⁸ ESR spectra of the TPPS triplets in glassy H_2O -glycerol (1:1) were recorded at a temperature of about 100 K, with a field modulation amplitude of 40 G and 0.5-mW microwave power. Typically, spectra were recorded in 10 min or less. A 1000-W Xe source powered by a Photochemical Research Associates supply with electronic modulation capability or Spectra Physics krypton laser (647.1 nm, 300 mW) was used for photoexcitation. Optical absorption spectra were recorded with a Cary 14 spectrometer and fluorescence spectra with a Perkin-Elmer 650-40 spectrometer. A Nicolet 1180E computer interfaced to the Varian and Cary spectrometers was used for data acquisition and analysis. The kinetics of formation and decay of the triplet ESR signals was recorded by exciting with square-wave modulated (13 or 26 Hz) Xe or laser light. The computer, used in the time-averaging mode, was triggered at the light-on edge, and the ESR vs. time profile was stored in a 1K memory block. The kinetic curves presented here represent the average of about 1000 light on-off periods. Magnetophotoselection experiments¹⁹ were carried out using the polarized light of the Spectra Physics laser.

Results

Optical Spectra. Aqueous solutions of TPPS exhibit a series of well-defined absorption bands in the visible region of the spectrum. Figure 1a shows the Q-band region of the spectra from TPPS in a 0.1 M KCl solution. The path lengths of the cells used were inversely proportional to the TPPS concentration to highlight the deviations from Beer's law. It is observed that, with increasing concentration, the spectra exhibit (a) a decrease in absorbance and (b) a red shift accompanied by broadening of the bands. As shown in Figure 1b, similar effects can be produced by addition of increasing amounts of cation. Finally, Figure 1c illustrates the pronounced effect of 18-crown-6 in the presence of cation on the

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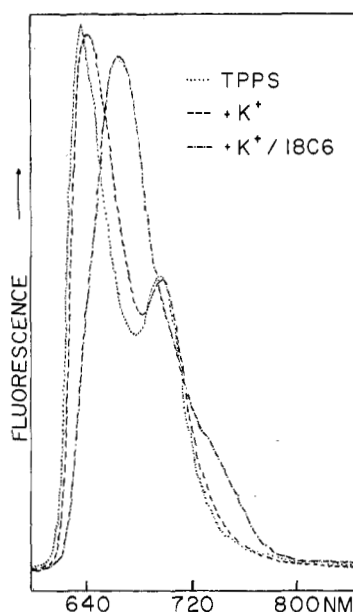


Figure 2. Fluorescence emission spectra of TPPS (5.0×10^{-5} M): no addition (---), with 0.1 M KCl (---), with 10^{-2} M KCl and 10^{-2} M 18-crown-6 (---). Excitation wavelength 420 nm.

TPPS spectrum. In this case all Q bands show a considerable reduction in absorbance as well as red shifts. Addition of 18-crown-6 alone does not produce these changes. Cations and cation-crown cause a slight broadening of the Soret band but do not shift the band.

Figure 2 shows the emission spectra of aqueous solutions of TPPS. The spectrum of TPPS alone shows two well-defined bands centered at 643 and 702 nm. Addition of cations results in a 8-nm red shift of the 643-nm band. In the presence of K^+ -18-crown-6, a broad emission band is found at 669 nm and a shoulder at about 750 nm. The addition reduces the emission intensity by about a factor of 2. The fluorescence excitation spectra mirror the cation and cation-crown effects on the absorption spectra. Crown ether alone does not affect the fluorescence spectrum of TPPS.

ESR Data. The ESR spectrum of the photoexcited triplets of TPPS randomly oriented in a H_2O -glycerol matrix at about 100 K is shown in Figure 3a. With the addition of increasing amounts of cation (NH_4^+ , Na^+ , K^+ , Ba^{2+}), a new triplet signal grows in. However, as is illustrated in Figure 3b, even in the presence of 10^{-1} M counterion, the original triplet signal has not been completely replaced. A spectrum of the new species alone can be obtained by spectrum subtraction or by laser (647.1 nm) excitation. In the latter case use is made of the fact that the species formed by cation addition is excited preferentially. The triplet ESR spectrum of TPPS in the presence of 10^{-1} M K^+ obtained with laser excitation is displayed in Figure 3c. Figure 3d shows the spectrum of TPPS in the presence of K^+ -18-crown-6. From a comparison of the spectra reproduced in Figure 3b,d, it is evident that, in the presence of crown ether, the cation concentration required to produce the new triplet species is reduced by orders of magnitude.

The ESR spectra show a pair of peaks for each of the three orientations for which the magnetic field (H) is parallel to a principal axis (x , y , z) of the zero-field-splitting (zfs) tensor.²⁰ The peak positions give the values of the zfs parameters D and E presented in Table I. It is noteworthy that there are three sets of zfs values, namely for TPPS alone, for TPPS with added cation, and for TPPS with cation-crown. The values of D and E for the species generated by the addition of cation or cation-crown do not depend on the cation used. Also, changes in the anion (Cl^- , ClO_4^- , CNS^- , OH^-) accompanying the cation do not affect these values.

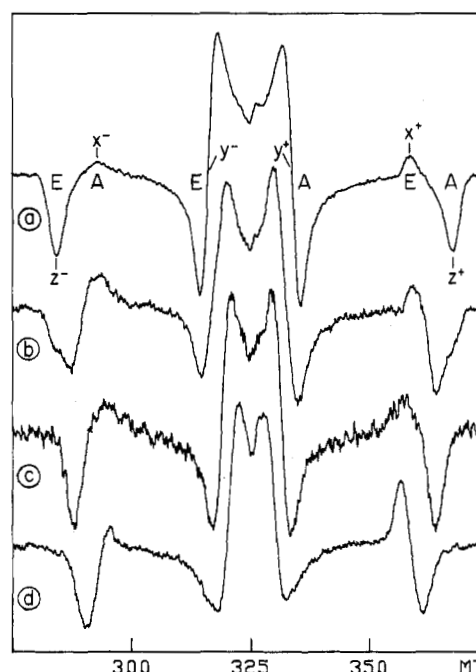


Figure 3. ESR spectra of the photoexcited triplets of TPPS (6.0×10^{-4} M) in H_2O -glycerol (1:1) at about 100 K: (a) no addition, (b) with 10^{-1} M KCl, (c) as (b) excited with krypton laser, (d) with 10^{-2} M KCl and 10^{-2} M 18-crown-6. Absorption (A) and emission (E) peaks have been labeled.

TABLE I: TPPS Zero-Field-Splitting Parameters (10^{-4} cm $^{-1}$)^a

	monomer	dimer I	dimer II
D	(+) 391	(+) 359	(+) 334
E	(-) 75	(-) 78	(-) 80
X	(+) 205	(+) 198	(+) 191
Y	(+) 55	(+) 42	(+) 31
Z	(-) 261	(-) 239	(-) 223

^a It has been assumed that the out-of-plane zfs parameter $D > 0$,¹⁷ and the in-plane axes are chosen so that $X > Y$ (estimated uncertainty $\pm 5.0 \times 10^{-4}$ cm $^{-1}$). Dimer I is TPPS-cation and dimer II TPPS-cation-18-crown-6.

As is shown in Figure 4, excitation with light polarized along the field direction ($\vec{E} \parallel \vec{H}$) strongly attenuates the outer peaks (z^- , z^+) in the three triplet spectra. With $\vec{E} \perp \vec{H}$, the z peaks gain in intensity relative to the y peaks. The magnetoselection characteristics of TPPS alone and TPPS with added cations (or cation-crown) show a subtle difference. Difference spectra (cf. Figure 4) establish that in the former case the relative intensities of the x and y peaks remain unchanged. In the other triplet spectra the relative intensities of the x and z peaks are unaffected by the change in light polarization direction. The optical transition moment of the $Q_x(0,0)$ transition excited with the laser light lies in the porphyrin plane.²³ For porphyrin triplets one predicts that the z peaks correspond to an orientation for which H is perpendicular to the molecular plane.^{17,21} The data presented are in agreement with this prediction.

It is well-known that the intersystem crossing (isc) process generating the triplets, as well as the triplet decay process, is spin selective.²¹ For TPPS in H_2O -glycerol at 100 K the relative magnitudes of the triplet lifetime and electron spin relaxation time (T_1) are such that, even under steady-state illumination, thermal equilibrium is not established. With light modulation coupled with synchronous detection using a lock-in amplifier, the spin-polarization effect is enhanced strongly.¹⁸ This accounts for the observation of absorption (A) as well as emission (E) signals in the ESR spectra (cf. Figures 3 and 4). The spin-polarization

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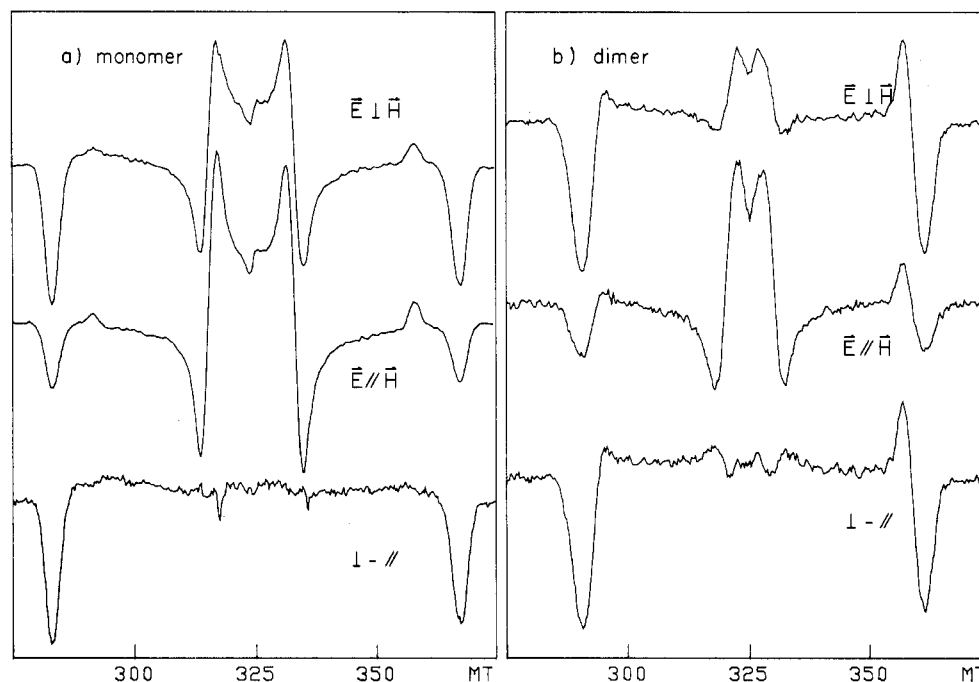


Figure 4. Triplet ESR spectra of TPPS (6.0×10^{-4} M) excited with polarized light of a krypton laser: (a) TPPS alone, (b) with 10^{-2} M KCl and 10^{-2} M 18-crown-6. From top to bottom: light polarized perpendicular to field, light polarized parallel to field, and difference spectrum.

pattern observed in the spectra of the three triplet species, EAEAEA, corresponds to that found in the spectrum from free base tetraphenylporphyrin (TPP).²² It signifies that the population and depopulation rates of the zero-field T_y spin state are larger than those of the other two states (following convention, the order of the energy levels is chosen as $T_x > T_y > T_z$). Even though the spin-polarization patterns are similar, the lock-in amplifier phase settings required to optimize the signals from TPPS and TPPS in the presence of cation-crown differ by about 90° . This points to a difference in spin kinetics. To explore this in more detail, the time dependence of the triplet signals was recorded. Indeed, differences are found in the growth and decay of the resonance peaks in the three triplet spectra. For instance, going from TPPS to TPPS-cation to TPPS-cation-crown, the average triplet decay rate (k_{av}) increases from 190 to 470 to 510 s^{-1} . In the Discussion section an analysis of the time dependence will be presented.

Discussion

A detailed quantitative spectroscopic study of trisulfonated TPP (TPPS₃) has been reported by Pasternack and co-workers.⁶ They established the existence of a monomer-dimer equilibrium for this system. In solutions containing 0.1 M KNO₃ the equilibrium constant is given as $4.82 \times 10^4 \text{ M}^{-1}$. The equilibrium constant decreases with decreasing concentration of added electrolyte. In a 0.01 M Tris buffer, without added electrolyte, TPPS₃ solutions were found to obey Beer's law in the concentration range of 10^{-6} – 10^{-5} M. The important role cations play in dimerization equilibria of many water-soluble porphyrins, metalloporphyrins, and phthalocyanines has been well documented.⁵ In cases involving paramagnetic systems, the occurrence of cation-induced dimerization could be proven using ESR data.⁵ For the interpretation of the spectroscopic data presented here it is important to note that addition of alcohols has been found to drive the dimerization equilibrium to the monomer side.^{5,6} For instance, TPPS₃ in ethylene glycol-water (4:1) shows no evidence of dimerization.⁶

The experimental results presented here clearly support the conclusion that a dimerization equilibrium exists for TPPS as well. The effect of concentration on the absorption spectrum of TPPS, illustrated in Figure 1a, can only be accounted for by assuming the existence of some aggregation equilibrium. The observation of a series of isosbestic points in the spectra as the concentration

of TPPS is increased and cell path length reduced is compelling evidence for an equilibrium involving two species. The species predominant at low concentration has the same spectroscopic characteristics (optical and ESR; vide infra) as free base tetraphenylporphyrin (TPP) and must be the TPPS monomer. It is concluded that the species predominant at higher concentrations must be the dimer. This conclusion agrees with data from a temperature-jump kinetic study by Krishnamurthy et al.²⁴ These authors report a dimerization constant of $9.6 \times 10^4 \text{ M}^{-1}$ for TPPS in an aqueous solution containing 0.05 M NaNO₃.

Figure 1a depicts spectral changes associated with changes in TPPS concentration in a 0.1 M KCl solution. Spectral changes effected by TPPS concentration variation become smaller as the ionic strength of the solution is reduced. This establishes that addition of cations promotes dimerization, as is the case for TPPS₃⁶ and many other porphyrins.⁵ The effect of cation addition on the monomer-dimer equilibrium is illustrated in Figure 1b. It should be noted that the cation effect on TPPS aggregation was found previously by Nahor and co-workers.⁷ For some unexplained reason, Fleischer et al.²⁵ and Kalyanasundaram et al.²⁶ did not find evidence of TPPS aggregation (pH > 6).

Cations such as NH_4^+ , Na^+ , and K^+ readily form strong complexes with crown ethers.^{27,28} If these ions participate in the dimerization reaction, one predicts that the addition of a crown ether must affect the dimerization equilibrium. Indeed, as Figures 1–3 illustrate, addition of 18-crown-6 has a remarkably strong effect. By varying the TPPS concentration while maintaining a constant cation-crown concentration, it could be established that the cation-crown-induced spectral changes must be due to dimerization. Indirect evidence supporting this conclusion is provided by the finding that the absorption (cf. Figure 1c) and emission (cf. Figure 2) spectra of the new species strongly resemble the corresponding spectra from a covalently linked TPP dimer.¹³ Furthermore, rigid-matrix ESR spectra of VOTPPS and CuTPPS showed evidence of cation-crown-induced dimerization. Optical spectra establish that addition of alcohols (including glycerol)

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TABLE II: Dimerization-Induced Absorption Band Shifts (nm) in Free Base Porphyrins

system ^a	Q _y (0,1)	Q _y (0,0)	Q _x (0,1)	Q _x (0,0)	ref
TPPS dimer ^b	9	12	~15 sh	22	this work
Face to Face					
25a	5	13	10	9	14
25b	11	16	17	20	14
6	5	3	5	6	12a
7	7	5	6	7	12a
(TPP) ₂	3	~5	~-9	23	13
Side by Side					
13	0	0	0	0	12a
7	4	1	3	1	11
9	4	2	3	2	11

^aThe numbering system of the original publications has been retained. ^bData for the TPPS-cation-18-crown-6 are given.

drives the dimerization equilibrium to the monomer side. The presence of glycerol and absence of additional cations account for the fact that the triplet ESR spectrum displayed in Figure 3a is that of monomer TPPS.

It is concluded that the cation-crown complex strongly promotes dimerization. The cation effect has been attributed⁶ to a shielding of the sulfonate groups by the positively charged ions. This reduces the electrostatic repulsion between porphyrins which facilitates dimer formation through π - π interaction between the ring systems. The reason why the cation-crown complex is much more effective in promoting dimerization is not understood at this time. It should be noted that Thanabal and Krishnan¹⁵ recently reported on porphyrin dimerization induced by cation-crown complex formation. The systems studied by these authors involve crown ethers covalently linked to a porphyrin core. Their results do not appear to have a bearing on the cation-crown promoted dimerization discussed here. However, it would be of interest to investigate how the cation-induced dimerization affects the photoexcited triplet characteristics of their systems.

Theoretical considerations and experimental data on other tetrapyrrole dimers show that the absorption band shifts associated with dimerization can be used to make a choice between the following two dimer models: (a) a side-by-side structure in which the cations or cation-crown complexes link the porphyrins by electrostatic interaction with the sulfonate groups and (b) a face-to-face structure with the cations or cation-crown complexes sandwiched between the sulfonate groups. Of course, these characterizations do not define unique dimer geometries. They merely serve to distinguish between a structure in which there is a relatively large distance between the porphyrin cores with no π - π interaction and a structure in which they form some kind of sandwich. A theoretical analysis of the effect of porphyrin dimerization on the optical absorption spectrum²⁹ predicts a negligible effect for the side-by-side dimer. This is because the exciton interaction between the chromophores is proportional to R^{-3} , where R is the separation between the ring centers. Indeed, literature data⁹⁻¹⁴ on observed dimerization-induced absorption band shifts demonstrate that the first structure cannot account for the observed changes in the optical spectra. Model b, on the other hand, accounts satisfactorily for the experimental data. With this structure, exciton coupling is enhanced so that the Q-band positions can be affected.²⁹ Experimentally, it is found that the formation of face-to-face (free base) tetrapyrrole dimers always is associated with red shifts of the Q bands similar to those found for TPPS. These shifts are found in spectra of the covalently linked porphyrins as well as the TPP dimer linked by cation-crown ether interactions.^{15,30} Table II shows the close correspondence between the absorption band shifts found in this study and those reported for covalently linked face-to-face porphyrins. Of course, the magnitudes of the shifts vary, reflecting differences in distance

and tilt angle of the porphyrin planes.²⁹

Additional information on the dimer structure can be derived from the ESR spectra. First of all, the ESR spectra show a *slight* shift of the equilibrium to the dimer side in the series NH_4^+ , Na^+ , K^+ , Ba^{2+} . This could be indicative of a role of the sulfonate-cation ion-pairing equilibrium on the dimerization reaction. However, as noted earlier, D and E values are not affected by changes in cation. One must conclude that, even though cations are involved in the dimerization reaction, they do not play an important role in determining the dimer structure. In the presence of cation-crown, the dimerization equilibrium is *strongly* affected by changes in cation. This effect can be related to variations in the formation constant of the cation-crown complex.^{27,28} Namely, an increase in formation constant correlates with an increase in dimer formation. Judging from the constant D and E values, in this case changes in cation do not affect the dimer structure either. However, the zfs parameters of the TPPS dimer involving 18-crown-6 differ from those of the other dimer (cf. Table I). The spectroscopic data indicate that the involvement of crown ether forces the dimer into a conformation which allows for increased porphyrin-porphyrin interaction.

Chlorophyll dimers are believed to be involved in the primary events of photosynthesis in green plants and photosynthetic bacteria.³¹⁻³⁴ Studies of in vitro chlorophyll dimers and porphyrin dimers have been stimulated by the consideration that these model systems can give an insight into the structure and properties of the in vivo chlorophyll aggregates.^{35,36} Many of the model systems have been found to mimic the absorption band shifts found upon going from chlorophyll monomers to reaction center chlorophyll dimers. However, so far there have been no reports in the literature of model systems that do exhibit the large reduction in zfs values associated with the formation of reaction center chlorophyll dimers.^{17,35,36} By contrast, TPPS dimerization strongly affects optical as well as triplet ESR spectra. The question is what information can be derived from the dimerization-induced changes in ESR parameters.

The observed reduction in zfs values can have a number of origins.^{17,21} First, it is possible that the triplet excitation remains localized on one porphyrin ring. In that case the changes must be attributed to a perturbation of the localized triplet state by the neighboring ground-state TPPS molecule. In order for the triplet excitation to be localized on the time scale of the ESR experiment, the exchange interaction between the dimer constituents has to be exceedingly small (of the order of the zfs or less). As noted earlier, to produce the observed absorption band shifts, the two porphyrin planes have to be closely spaced in some kind of face-to-face configuration. Such a geometry is associated with intermolecular π - π interaction which is expected to give rise to appreciable exchange coupling. In view of this, it is unlikely that we are dealing with a localized triplet. Second, the change in zfs values can be due to a charge-transfer mechanism. Complete charge transfer could produce the strong reduction in the absolute value of D observed experimentally. The sign of D would change from positive to negative and, for a parallel face-to-face structure, the z axis would remain perpendicular to the molecular planes. Without knowledge of the structure of the dimer the effect of dimerization on the E value is impossible to predict. Finally, the zfs values can be affected by rapid transfer of excitation energy between dimer constituents.^{37,38} If this triplet exciton mechanism applies, the dimerization effects on zfs parameters, triplet kinetics, and magnetophotoselection characteristics can be related to the dimer geometry. In fact, the exciton theory has been invoked to

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TABLE III: Kinetic Parameters Triplets^a

	p_x	p_y	p_z	k_x	k_y	k_z	W_x	W_y	W_z
TPP ^b	0.31	0.54	0.14	300	600	150			
TPPS monomer	0.30	0.53	0.17	170	340	90	1500	1000	1000
TPPS dimer ^c	0.31	0.42	0.27	400	800	200	3000	2000	2000

^a Decay rates (k) and relaxation rates (W) in s⁻¹; only the ratio of the population rates (p) has been determined. ^b TPP data from ref 39. ^c Dimer data are for the TPPS-K⁺-18-crown-6 system.

derive structural information on reaction center chlorophyll dimers from magnetic resonance data on the triplet state.³⁵ In view of this, it is of interest to explore whether or not the TPPS triplet data can be accounted for by using the exciton model.

For rapid exchange, the expression for the principal values of the zfs tensor (X^* , Y^* , Z^*) in the dimer in terms of the monomer values (X , Y , Z) has the general form^{35,37,38}

$$X^* = l^2 X + m^2 Y + n^2 Z$$

Here it has been assumed that there is incoherent exchange of energy and that the dimer system contains a 2-fold symmetry axis. The direction cosines between the principal axis in the dimer (x^*) and the monomer axes system are given by l , m , and n . Similar equations can be given for Y^* and Z^* . Evidently, if corresponding axes in the dimer constituents are collinear, the exciton mechanism does not produce changes in zfs values. Hence, to account for the observed dimer induced changes, the TPPS planes have to be rotated with respect to each other. The values of the principal components of the zfs tensor for the monomer and two dimer triplets are given in Table I. The table shows that the variation in the X component barely exceeds experimental uncertainty. According to the exciton theory, this means that the x axes of the dimer constituents are virtually collinear. The change in the other two components then must be accounted for by a rotation of one porphyrin plane by an angle β around the x axis, away from the other plane. A rotation angle of 28° gives 3.7×10^{-3} and -24.3×10^{-3} cm⁻¹ and an angle of 36° 2.5×10^{-3} and -23.1×10^{-3} cm⁻¹ for the values of Y^* and Z^* , respectively. These values agree reasonably well with the zfs values of the two dimers (cf. Table I), suggesting that the exciton theory may be a reasonable approximation. However, if that is the case, the geometry used to account for dimer-induced changes in zfs values should also be able to account for changes in the time dependence of the triplet signals. The theory analyzing the temporal behavior of the spin populations in the triplet sublevels of a system subjected to periodic light excitation has been discussed in a number of articles.³⁹⁻⁴¹ The analysis shows that the growth and decay of the ESR signals are governed by the population rate constants (p_i) of the zero-field spin levels, the decay rate constants (k_i), the spin-lattice relaxation times (W_i ; $i = x, y, \text{ or } z$), and the orientation of the magnetic field with respect to the zfs axes. If the exciton model applies, the rate constants in the dimer can be related to those in the monomer with equations similar to those given for the zfs parameters.^{35,42} Therefore, for the proposed dimer structure, p_x and k_x should be unaffected by dimerization. The other kinetic parameters can be derived from the monomer values by using the angles between the TPPS planes extracted from the zfs changes.

Figure 5 shows the experimentally observed time dependence of the six resonance peaks in the monomer and TPPS-cation-crown dimer spectra. Also shown are the calculated curves that, in a trial-and-error procedure, came closest to fitting the experimental observations. For the calculations the theoretical expressions derived by Winscom⁴⁰ were used. The values of the parameters utilized in the simulations are summarized in Table III. It should be noted that the simulations only give the relative magnitudes of the p_i 's. Included in the table are the kinetic

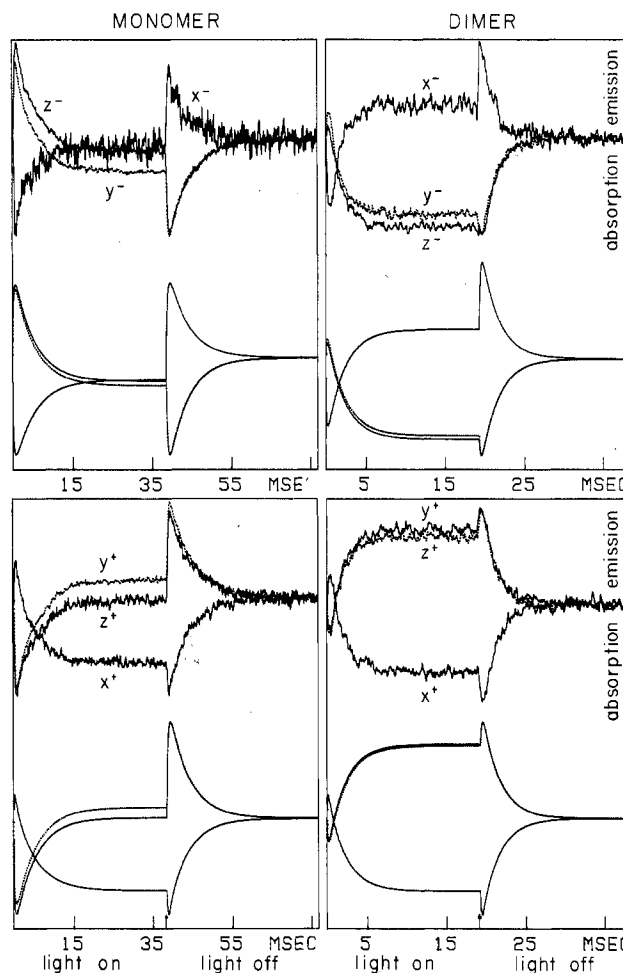


Figure 5. Triplet growth and decay curves recorded with the field set on one of the peaks in the ESR spectrum (cf. Figure 3): left, monomer TPPS; right, TPPS-K⁺-crown dimer. Calculated curves are presented below the experimental curves. Note the differences in time scale of the monomer and dimer plots.

parameters reported for the TPP triplet.³⁹ As expected, the p_i values for TPP and TPPS are closely matched. On the other hand, the triplet decay rates (k_i) differ by about a factor of 2. It is likely that this can be attributed to the difference in solvent matrix. As far as the dimerization effect is concerned, two observations can be made. (a) p_x remains unchanged, whereas p_y decreases and p_z increases. Qualitatively, this parallels dimerization-induced changes of the zfs values. Even so, it is clear that the changes in the relative population rates are too large to fit the dimer geometry derived from the change in zfs values. (b) The relative magnitudes of the decay rate constants are *not affected* by dimerization. Dimerization reduces the triplet lifetime by more than a factor of 2 but leaves the spin selectivity of the decay process unaffected. The reduction in triplet lifetime may be due to a lowering of the triplet energy and additional deactivation pathways provided by intermolecular interaction.³⁵

It must be concluded that the experimental data show that the triplet exciton model does not adequately describe the electronic state of the TPPS dimer. This conclusion also applies for the TPPS-cation dimer. Growth and decay curves of the triplet signals of this species show that the kinetic parameters for this dimer lie

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in between those of the monomer and TPPS-cation-crown dimer.

Magnetophotoselection data also show that the exciton model is too simplistic. The TPPS monomer spectra (cf. Figure 4a) show that the optical transition moment of the $Q_x(0,0)$ band bisects the angle between the zfs axes x and y . As expected, a similar result is obtained with TPP. For both dimer species the results indicate (cf. Figure 4b) that the optical transition moment is close to collinear with the y^* zfs axis in the dimers. With a face-to-face structure in which corresponding axes are collinear, a change in light polarization direction should have the same effect on the monomer and dimer spectra if the exciton theory applies. With an "open-sandwich" structure (x axes collinear), the change in relative intensities of the y and z peaks with change in polarization direction should diminish as the angle between the porphyrin planes gets larger. Evidently, the exciton theory does not give a satisfactory explanation for the magnetophotoselection data.

It is likely that a proper description of the dimers must take into account charge-transfer contributions as well as exciton-transfer effects. We hope to obtain a more thorough understanding of the spectroscopic data reported here by broadening the study to include porphyrin dimers of defined geometry.^{13,15} Also, an

ENDOR study⁴³ of the hyperfine coupling constants in the monomer and dimer triplets would be of value in the study of the electronic structure of these systems.

Finally, it is of interest to note that cation-induced dimer formation has been found for ZnTPPS and PdTPPS. Triplet ESR spectra indicate that these metalloporphyrins form heterodimers with the free base TPPS.⁴⁴ The characteristics of these systems are under investigation.

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Electron Spin Resonance Studies of Divalent Cation-Anion Radical Ion Pairs. The Ninhydrin Anion Radical

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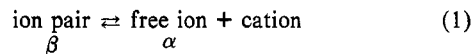
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Additions of divalent cation perchlorate salts to hexamethylphosphoramide solutions containing the ninhydrin anion radical ($N^{\cdot-}$) result in the time-resolved observation of ESR signals corresponding to the free anion and the ion pair. Ion-pair dissociation equilibria are slow on the ESR time scale, thus allowing easy determination of the enthalpies for these reactions. The ΔH_{diss} values determined were 9.1 ± 0.7 , -3.9 ± 0.2 , and -2.1 ± 0.6 kcal/mol for the magnesium, calcium, and barium ion pairs, respectively. Temperature variation of the $Ca^{2+}-N^{\cdot-}$ ion-pair system results in the observation of pronounced line-width alternation, indicating an out-of-phase modulation of two sets of coupling constants as a result of intramolecular cation exchange between the two equivalent coordination sites in the molecule. The magnesium ion pair exhibits an in-phase modulation of all coupling constants which results in line broadening throughout the complete spectrum. No line-width effects were observed for the barium ion pair.

Introduction

Many complexes of organic anion radicals with metal cations exhibit well-resolved ESR spectra which can provide detailed structural and dynamic information about these species in solution.¹ Most organic anion radicals generated by alkali-metal reduction in hexamethylphosphoramide (HMPA) are observed to be essentially free of interactions with the cations.² Residual ion pairing is sometimes observed, as in the case of the ninhydrin anion radical ($N^{\cdot-}$) when generated by potassium reduction in HMPA.³ After initial potassium reduction, the ESR spectrum shows a slight asymmetry as a result of fast interconversion (on

the ESR time scale) between the free ion and ion pair (eq 1).^{3,4}



Additions of alkali metal perchlorate salts drastically change the observed spectrum, which at all times corresponds to the time-averaged species between the free ion and the ion pair.^{3,4}

When divalent cations such as Mg^{2+} , Ca^{2+} , and Ba^{2+} are added as the corresponding perchlorate salts to some organic anion radical solutions in HMPA, time-resolved observation of free-ion and ion-paired signals have been reported.⁵ The double charge on these metal cations results in stronger interactions with the anion

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