ODMR OF TRIPLET STATES OF COFACIAL DIMERIC ZINC PORPHYRINS

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The triplet-state zero-field splitting parameters and the triplet sublevel decay rates for several monomeric zinc porphyrins and cofacial bis-zinc porphyrin dimers are reported. In the dimers, weak π-electron interactions between the porphyrin subunits are found to exist. Therefore the commonly used exciton model can be applied to obtain structural information about the excited triplet state of the dimers. In the β-linked dimers 1 and 2, the two porphyrin subunits are rotated with respect to one another about the common out-of-plane axis. These results suggest that these compounds were prepared and studied as the anti-, rather than syn-diastereoisomers. A meso-linked porphyrin dimer 3 was also studied.

1. Introduction

Recent work in porphyrin chemistry has focused on the synthesis and characterization of cofacial porphyrin complexes [1–8] as possible catalysts for the direct four-electron reduction of dioxygen to water [2,4]. In addition, such porphyrin dimers are of considerable interest because of their possible use as models for the reaction center of photosynthetic systems. Chlorophyll dimers have been proposed as electron donors in plant reaction centers as well as in photosynthetic bacteria [9–13]. Several models for the geometry of such a reaction center dimer have been assumed [14–19] and theoretical calculations based on the exciton formalism have been made in an attempt to account for its observed spectral features [20–22]. Spectroscopic studies with simple model compounds may be useful in establishing the validity of the exciton model. The well characterized "face-to-face" porphyrin dimers of Collman et al. might provide useful models for these studies [1–4, 22].

Magnetic-resonance spectroscopy in the pho-

toexcited triplet state has emerged as being one of the more useful methods currently used for investigating the structural and dynamical features of photosynthetic systems [23–30]. Under weak-coupling conditions the triplet state of a dimer has properties which can be calculated from those of the monomer and the geometry of the dimer [29–35]. The assumption which needs to be made is that the triplet states associated with a pair of identical interacting molecules may be conveniently described through the exciton formalism which has been successfully employed in the description of triplet excitons in molecular crystals [31,32,36,37]. Specifically this means that symmetric charge transfer terms may be neglected in the wavefunctions of the excited triplet states. Prior investigations on [2.2]- and [3.3]-phanes [38–43] have shown that this weak-coupling assumption is only valid if the π-electron interaction is small and the two units forming the dimer have a relatively large distance with respect to one another. In this exciton model the triplet zero-field splittings and the decay rates of the individual spin sublevels of

the dimer triplet state are both expected to be functions of the dimer geometry and of the triplet-state properties of the monomer. Therefore, for such dimer systems measurement of these triplet-state properties by EPR or ODMR spectroscopy allows a direct evaluation of the dimer configuration. A review of related problems has recently appeared [44,45]. In this paper we show that the "face-to-face" porphyrin dimers 1–3 shown in fig. 1 [1–4] are model systems, where the conditions of the single exciton model are fullfilled and where structural information can be obtained from triplet zero-field splitting parameters and decay rates of the triplet sublevels.

2. The lowest excited triplet dimer state

Sternlicht and McConnell [31] have shown that in cases where identical individual interacting molecules are excited into a triplet state the spin hamiltonian describing the triplet state of the system can be represented as the average of the spin hamiltonians for the isolated molecules. The only condition which has to be assumed is that the intermolecular exchange interaction between the molecules is larger than the magnetic dipole–dipole interaction between the triplet electrons. This formalism can also be used for a pair of interacting molecules. The lowest excited triplet state associated with such a pair of identical interacting molecules may be described in this exciton formalism by wavefunctions of the form [29–35]

$$^3\psi_i^E(\pm) = 2^{-1/2}(^3\psi_i^A \, ^1\psi_0^B \pm \, ^1\psi_0^A \, ^3\psi_i^B),$$ (1)

where A and B refer to the two molecules forming the pair, $i = x^*, y^*, z^*$ designates the exciton spin sublevels in the averaged principal axis system, $^3\psi_i^{A,B}$ refer to the complete triplet-state functions localized on molecule A or B and $^1\psi_0^{A,B}$ are the complete ground-state functions for the molecules A and B. Both $^1\psi_0^{A,B}$ and $^3\psi_i^{A,B}$ refer to the molecules in their lowest vibrational energy levels.

These wavefunctions can be used to calculate the triplet sublevel zero-field energies of the dimer

[34,35]

$$\begin{pmatrix} X^* \\ Y^* \\ Z^* \end{pmatrix} = \begin{pmatrix} l_X^2 & l_Y^2 & l_Z^2 \\ m_X^2 & m_Y^2 & m_Z^2 \\ n_X^2 & n_Y^2 & n_Z^2 \end{pmatrix} \begin{pmatrix} X \\ Y \\ Z \end{pmatrix} = \Lambda X,$$ (2)

where X, Y, Z are the zero-field energies of the triplet sublevels of the monomers and l_i, m_i, n_i the set of direction cosines which relate the principal magnetic axes (x, y, z) of the monomers to those (x^*, y^*, z^*) of the dimer [29–35].

Analogous results are obtained for the decay rates k_i^* of the triplet sublevels $(i = x^*, y^*, z^*)$ of the dimer [34,35].

$$k^* = \Lambda k.$$ (3a)

The expressions for both the triplet sublevel energies (X^*, Y^*, Z^*) and for the decay rates (k_i^*) of the dimer are thus related in simple geometrical terms to those of the monomer. This model gives the following essential condition for the decay rates of the dimer k_j^* and the monomer k_i [35,42,45]:

$$\sum_j k_j^* = \sum_i k_i,$$ (3b)

with $j = x^*, y^*, z^*$ and $i = x, y, z$.

The validity of eqs. (3a) and (3b) is restricted to the following assumptions. Both are only valid in the case of an incoherent energy exchange while in addition eq. (3a) is restricted to the case where cross terms of the form $\langle S_0|er|i\rangle\langle S_0|er|k\rangle$ $(i, k = X, Y, Z;$ and $i \neq k)$ can be neglected [45,46]. If the three triplet sublevels belong to different irreducible representations of the molecular point group of the monomer these sublevels are connected via spin–orbit coupling to different singlet levels. Therefore the product of these two matrix elements in the case of a D_{2h} symmetry must be zero because of symmetry reasons. For the coherent energy exchange the decay rates k_i^{*coh} are usually smaller than for the incoherent case. Only if the two units forming the dimer are parallel in all three molecular axes the decay rates for the coherent case are equal to the rates in the incoherent case [35].

An important special case where this model can

be applied occurs when the molecular planes of the two monomeric units are parallel to one another and are only rotated about their common out-of-plane axis. In this case the zero-field energy corresponding to the out-of-plane spin sublevel (z^*) remains unchanged ($D_{dim} = D_{mon}$) and the energy of the two in-plane sublevels (x^*, y^*) varies with the angle of relative rotation. Furthermore, the same behaviour is expected for the decay rates, i.e. k_z^* remains unchanged, while k_x^* and k_y^* vary with rotation angle [34,35].

For the use of the exciton model, it is essential to verify that the lowest triplet state can be adequately described by a wavefunction of form (1). If the interaction between the two molecules is large compared to the triplet zero-field splitting ($2J \gg D, E$), the triplet states can no longer be described by wavefunctions of form (1). Now, one must take into account the small but definite probability of electron transfer between molecules A and B. In analogy to the exciton terms, the symmetric and antisymmetric charge transfer states can be described by the wavefunctions [38,42–45, 47]

$$^3\psi_i^{CT}(\pm) = 2^{-1/2}(^3[\psi_A^+\psi_B^-] \pm ^3[\psi_A^-\psi_B^+]),.$$ (4)

Here only electron transfer from the HOMO of one molecule to the LUMO of the second are considered. The wavefunction for the whole system is then

$$^3\phi_i^{(j)} = C_{1i}^{(j)3}\psi_i^E(\pm) + C_{2i}^{(j)3}\psi_i^{CT}(\pm),$$ (5)

where $i = x^*, y^*, z^*$ and where in general $C_{1i}^{(j)} > C_{2i}^{(j)}$ and $C_{1i}^{(j)} + C_{2i}^{(j)} = 1$. The parameter j runs from 1 to 4 corresponding to the four different ways of combining the symmetric and antisymmetric exciton and charge transfer terms. In general we assume that the set of wavefunctions

$$^3\phi_i^{(1)} = C_{1i}^{(1)3}\psi_i^E(+) + C_{2i}^{(1)3}\psi_i^{CT}(+),$$ (6)

where $i = x^*, y^*, z^*$, describes the lowest excited triplet state of the dimers. This assumption is not restrictive since results analogous to eqs. (7) and (8) would be obtained, even if one of the other three sets of possible wavefunctions were actually to describe the lowest excited triplet state.

When the lowest excited triplet state of the dimer is described by wavefunctions of form (6), then, in all cases, the value of the triplet zero-field splitting parameter D for the dimer is lower than for the monomer,

$$|D|_{dim} < |D|_{mon}.$$ (7)

This reduction is due to the decreased average dipole–dipole interaction between the two triplet electrons, originating from charge transfer contributions. As a result, the average separation between the electrons is larger *. Moreover, in this case the following relationship between the decay rates of the triplet sublevels of the dimer k_j^* and those of the monomer k_i holds,

$$\sum_j k_j^* \gg \sum_i k_i,$$ (8)

where $j = x^*, y^*, z^*$ and $i = x, y, z$. This relationship has previously been shown to be valid for [2.2]- and [3.3]-phanes. It was found that the decay rates for the dimer (k_j^*) increased as the contribution of the charge transfer term increased [42,43].

In general, where charge transfer terms contribute, and where the system in its triplet state is described by wavefunctions of form (6), then knowledge of the triplet state zero-field splitting parameters and the decay rates is insufficient to obtain information about the geometry of the dimeric system in its excited state [42,43]. Therefore, in cases where $|D_{dim}| < |D_{mon}|$ is observed, only by measurement of the decay rates and a subsequent check of the validity of eqs. (3) or (8) can it be established whether or not the exciton model can be used to obtain structural information. Specifically, when condition (8) holds, the triplet-state zero-field splitting parameters and the decay rates do not, in general, yield any information about the geometry of the dimer.

3. Experimental

The metal-free dimeric porphyrins H_2-FTF4-

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* A large number of measurements with [2.2]- and [3.3]-naphthalino-phanes [43] have served to establish the invalidity of a previously assumed hypothesis, that the D and E values are decreased by the same factor if charge transfer contributions to the wavefunction occur.
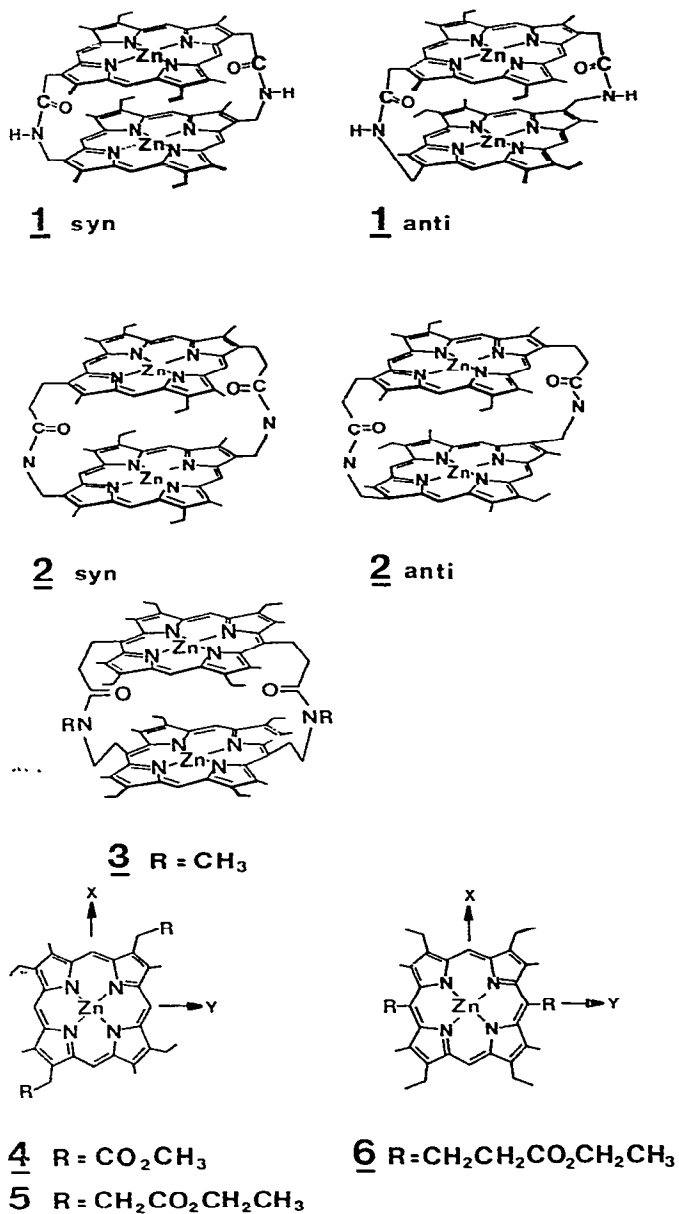
1 syn

1 anti

2 syn

2 anti

3 R = CH₃

4 R = CO₂CH₃

5 R = CH₂CO₂CH₂CH₃

6 R = CH₂CH₂CO₂CH₂CH₃

Fig. 1. Schematic representations of the monomeric and cofacial dimeric porphyrins used in this study.

2,1-NH(1), H₂β-FTF5-3,1-NH(2), H₂-m-FTF6-3,2-NMe(3) and the representative diester monomers 4, 5 and 6 were prepared and purified as reported recently [3,4]. Zinc was inserted in the usual way [48]. Fig. 1 shows the zinc complexes of the monomers 4, 5 and 6 as well as those of the dimeric cofacial porphyrins 1, 2 and 3.

As a result of the synthetic sequence employed, the possibility exists that porphyrin dimers 1 and 2 are formed as a mixture of syn- and anti-diastereomers (fig. 1). Prior NMR experiments [3,4], however, have served to indicate that only one (but not which) of the two possible diastereomers is obtained. Moreover, the dimers used in this study were found to be pure by chromatography (as the free-base porphyrins).

All measurements were performed in glass matrices at 1.3 K. Because of the low solubility of the porphyrin dimers a mixture of n-octane and methyl-tetrahydrofuran (30:1) was used. Concentrations between 10^{-5} and 10^{-6} M of porphyrin dimer could be obtained. A similar concentration range was employed to study the monomers. The emission spectra and the ODMR linewidths (15 MHz) indicate that a minority of solute molecules are in good Shpol'skii sites and these have been studied. The use of MTHF did not interfere with the formation of Shpol'skii sites. As a check, the monomers were investigated in both pure n-octane and n-octane/methyl-tetrahydrofuran matrices. We found that neither the ODMR linewidths nor the emission spectra were substantially affected by the choice of solvent.

In all samples the oxygen was removed by flushing with dry nitrogen before freezing. The samples were placed into a liquid-helium cryostate and the temperature was reduced to 1.3 K by pumping. Optical excitation was performed with an argon-ion laser (Coherent CR6) equipped with a prism monochromator (Anaspec 300S) and an additional interference filter. For the S_0-S_1 excitation of the samples the 514.5 nm line was used. The fluorescence and phosphorescence was monitored perpendicular to the excitation path with a double monochromator (Spex 1402 with holographic gratings) equipped with a cooled photomultiplier (RCA 31034A02; −50°C) in combination with a photoncounting system (PAR 1109).

The ODMR apparatus was essentially the same as described earlier [49]. Signal averaging was achieved by using a transient recorder (Biomation 8100) interfaced to a computer system (Dietz 621, 48 K). Tunable band-pass filters or a combination of low- and high-pass filters were used to reduce the harmonic and spurious frequencies of the mi-

crowave sweepers (HP 8620A) by at least 60 dB. Several ODMR techniques were applied as described in the literature [50-53] in order to determine the triplet zero-field splitting parameters D and E, the relative radiative rate constants k_i^r, and the decay rates k_i of the triplet sublevels. The kinetic constants of the triplet sublevels have been determined by a simple method [54] which has been developed in a more general form by Zuclich et al. [53]. During continuous saturation (modulation technique) of a zero-field transition the weak optical excitation of the sample is switched off and the ensuing exponential decay of the phosphorescence is detected.

The total decay rate $\rho = (k_x + k_y + k_z)/3$ can be measured in the same way by saturating simultaneously two zero-field transitions. In addition the total decay rates ρ were determined by the measurement of the phosphorescence lifetime at 70 K. In all cases we observed only small differences ($< 10\%$) in ρ which can be neglected in comparison to the experimental errors. Because of the small decay rates ρ observed in our case we had no microwave saturation problems as studied by Hoff et al. [55].

4. Results

Figs. 2-6 display emission spectra at 1.3 K (fluorescence and phosphorescence) for the dimeric cofacial porphyrins 1, 2 and 3 as well as for
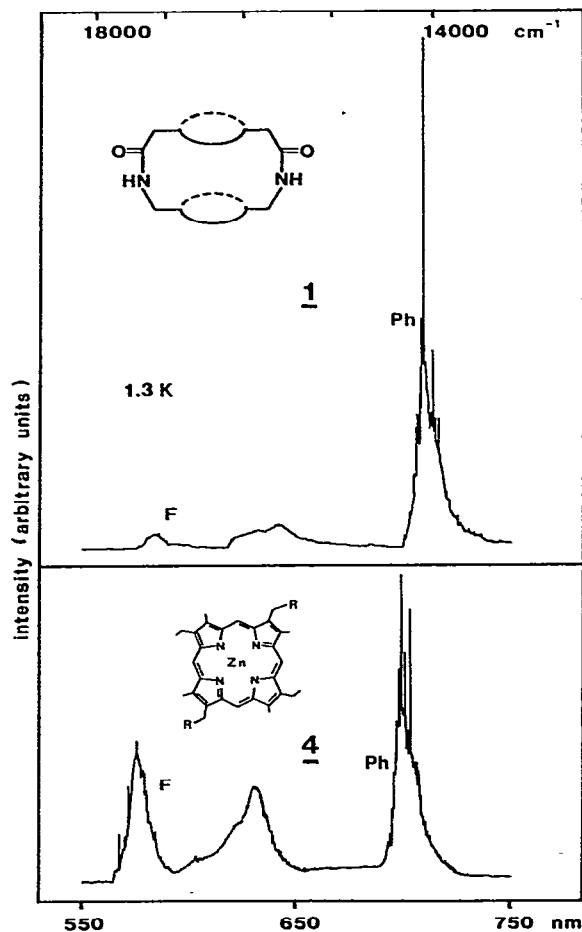

Fig. 2. Fluorescence and phosphorescence emission spectra at 1.3 K of compounds 1 and 4.
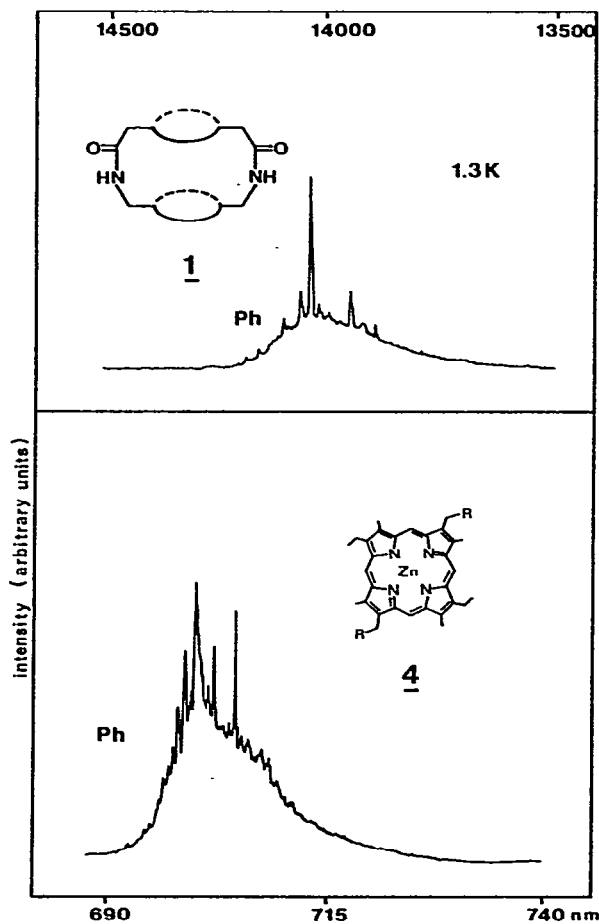

Fig. 3. Phosphorescence of compounds 1 and 4 at 1.3 K as obtained by the use of two crossed choppers.
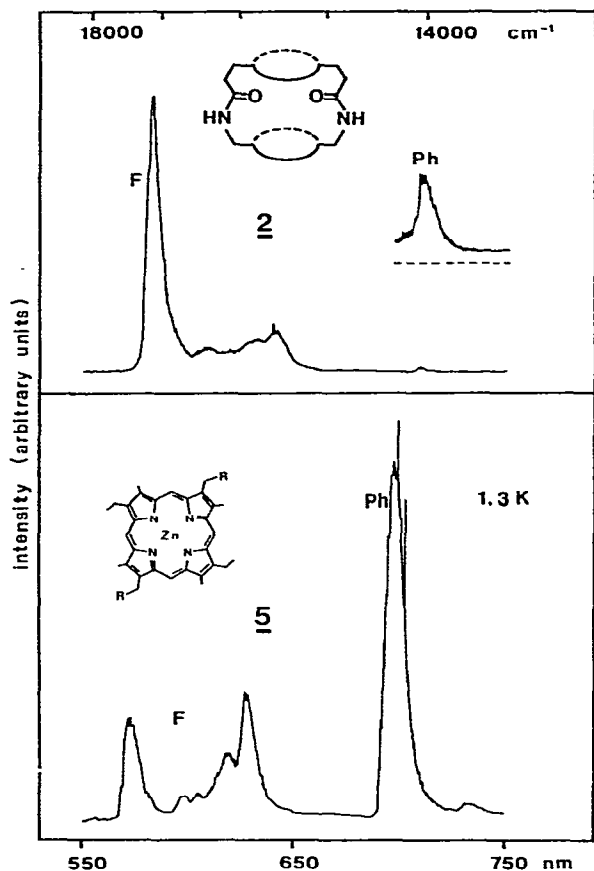
Fig. 4. Fluorescence and phosphorescence emission spectra at 1.3 K of compounds 2 and 5.
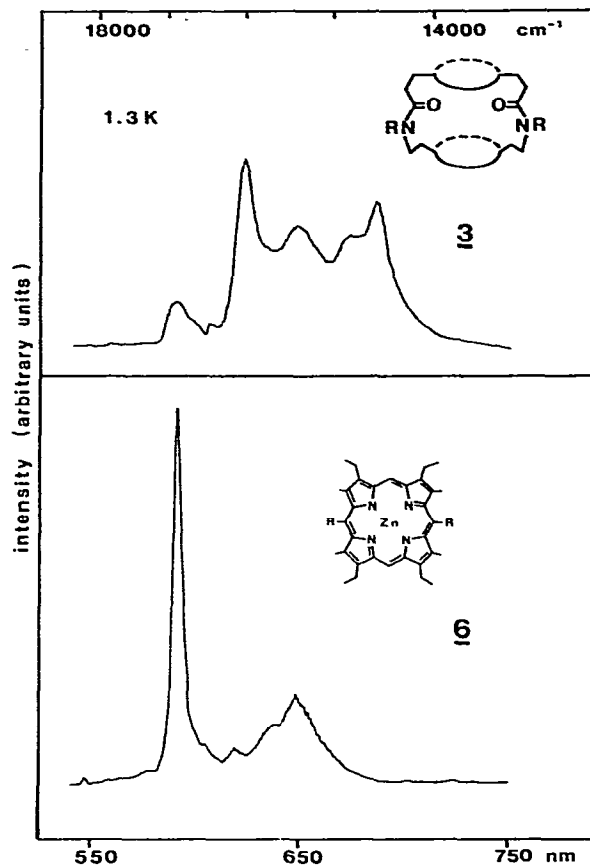

Fig. 5. Emission spectra at 1.3 K of compounds 3 and 6.

the appropriate monomers 4, 5 and 6. Fig. 7 shows a typical set of ODMR transitions obtained at 1.3 K. All work with monomers was carried out using the ester-substituted porphyrins 4, 5 and 6. The corresponding diamino-substituted monomers are unstable in the presence of light and oxygen [2,3,4] and therefore proved difficult to study.

The fluorescence spectrum of dimer 1 is relatively weak and is shifted by ≈ 300 cm^{-1} in comparison with that of the corresponding monomer 4 (fig. 2). The intense phosphorescence of 1 is similar to that of 4 in that it shows sharply defined bands above a broad background. The phosphorescence of the dimer 1 is, however, shifted by ≈ 240 cm^{-1} to the red with respect to 4 (fig. 3). In contrast to 1 and 4 (fig. 2) the spectra of 2 and 5 (fig. 4) show less structure. This decrease in structure is apparently due to the increased length of

the connecting bridges in dimer 2 and to the increased length of the side chains in monomer 5. Similar results have previously been obtained for other monomeric zinc porphyrins [56,57]. Furthermore, 2 shows a much weaker phosphorescence intensity (fig. 4) than do 5 (fig. 4), 1 (fig. 2), and 4 (fig. 2). The meso-linked dimer 3 as well as the monomer 6 (fig. 5) have broad emission bands without any structure. Moreover, the phosphorescence and fluorescence emissions are somewhat superimposed. Fig. 6 displays the phosphorescence of 3 and 6 obtained by the use of two crossed choppers.

The origins of the fluorescence and phosphorescence of compounds 1–6 are given in table 1. In addition, in table 1 the redshifts of the fluorescence and phosphorescence of the dimeric cofacial porphyrins 1–3 with respect to their monomers 4–6 are included. Table 2 shows the
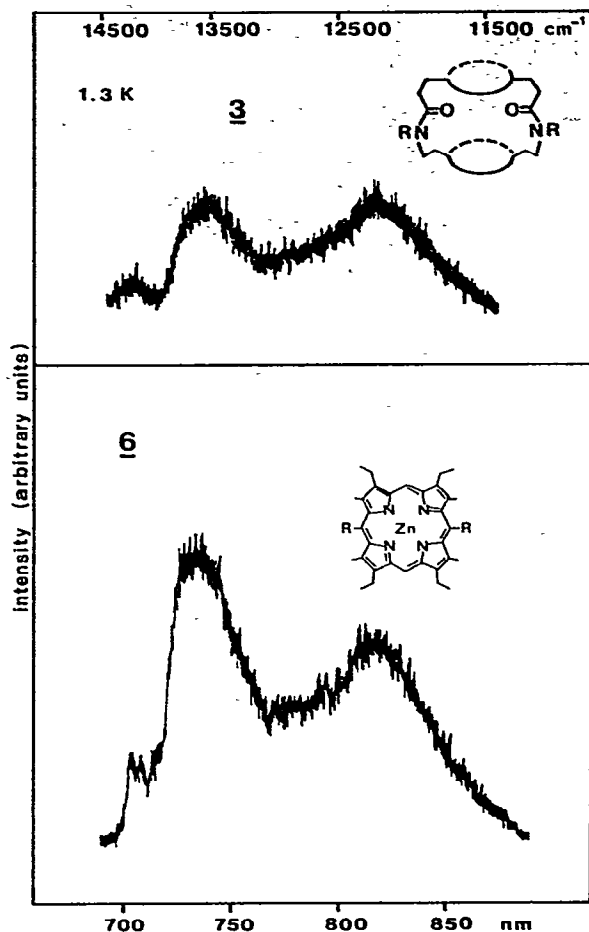
Fig. 6. Phosphorescence of compounds 3 and 6 at 1.3 K as obtained by the use of two crossed choppers.
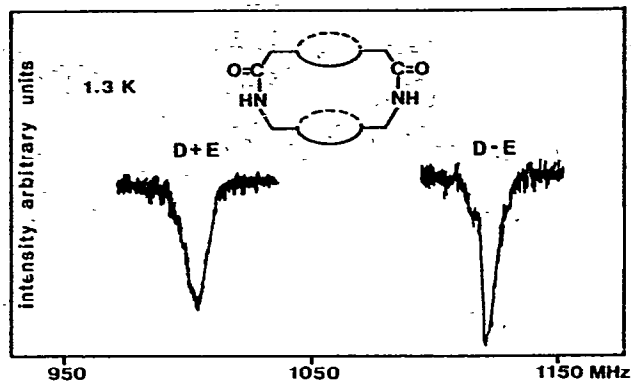

Fig. 7. ODMR transitions obtained at 1.3 K for compound 1. These signals are the result of 50 accumulations. The monitored wavelength was 710 nm and the resolution of the monochromator was smaller (2.5 Å) than the optical linewidth of the Shpol'skii site.

triplet zero-field splitting parameters of several different sites (vide infra) of monomers 4–6 together with those of dimers 1–3. In all cases the detection wavelengths and the ODMR linewidths of the observed microwave transitions are given as well.

From the ODMR measurements on the phosphorescence of monomers 4 and 5 it is evident that the sharp emission lines of these monomers belong for the most part to 0–0 transitions of different sites and only to a small extent to transitions into higher vibrational levels of the ground state (c.f. section 5). The observation that porphyrins and zinc porphyrins in n-alkane matrices can be trapped in different sites is not new [57–62]. In earlier work two main sites (A and B sites) as well

as numerous less prominent sites were detected [57–62]. The main A and B sites were explained in terms of "two or three n-alkane molecule vacancy cages". The porphyrin molecule was thought to be distorted in a slightly different fashion in each of the different cages [57–62]. The fact that the polycrystalline n-octane matrices used in this study contained small quantities of MTHF makes it understandable that a larger number of intensive sites could be observed.

For monomers 4 and 5 evidence for several distinct sites is provided by the observation of several different sets of zero-field splitting parameters where relatively large differences in E values but similar D values are obtained (table 2). In practice, for each site a set of D and E values was measured, and the lowest E values were obtained

Table 1
Origins of the fluorescence and phosphorescence of compounds 1–6, as well as the redshifts of the fluorescence and phosphorescence for the dimeric cofacial porphyrins 1–3 with respect to their monomers 4–6

	S^1 (cm^{-1})	T^1 (cm^{-1})	$\Delta E(S^1_{mon} - S^1_{dim})$	$\Delta E(T^1_{mon} - T^1_{dim})$
1	17390±30	14250±30		
4	17700±30	14480±30	310±30	230±30
2	17480±30	14180±30		
5	17700±30	14480±30	220±30	300±30
3	17300±30	14390±30		
6	18520±30	14490±30	1220±30	100±30

Table 2

Triplet state zero-field splitting parameters of the dimers 1–3 and those of several different Shpol'skii sites of the monomers 4–6. The wavelengths in the table refer to the monitored Shpol'skii site. The resolution of the monochromator was smaller (2.5 Å) than the optical linewidth of the monitored Shpol'skii site

	λ_{detect} (nm)	$|D|$ (cm⁻¹)	$|E|$ (cm⁻¹)	Linewidth (MHz)		
				$|D|+|E|$	$|D|-|E|$	$2|E|$
1	710	0.0354	0.0020	6	11	
	692	0.0356	0.0045	15	10	15
4	695.9	0.0336	0.0074	10	7	
	698.4	0.0346	0.0084	10	8	
2	708	0.0346	0.0025	30	30	
	692.6	0.0347	0.0040	30	30	25
5	695.3	0.0353	0.0063	30	30	
	699.7	0.0366	0.0099	4	4	
3	700	0.0365	0.0110	100	70	75
6	690	0.0388	0.0117	70	70	55

from sites with the highest S_0–T_1 energies. Earlier work on other molecules in glass matrices [63–65] leads us to suggest that as the porphyrin molecule in its excited state is increasingly distorted the electronic energy of the triplet state should be lowered with a concomittant increase in the value of E. Therefore, for the purpose of comparison with dimers 1 and 2, we used the zero-field splitting parameters from the sites of monomers 4 and 5 which displayed the lowest E values, and which represent the sites with lowest distortion. It is worth noting that the E values obtained for these sites, 134 MHz for 4 and 121 MHz for 5, are

among the lowest observed to date for monomeric porphyrins.

For monomer 6 only one set of triplet zero-field splitting parameters is observed (table 2) as is to be expected in the light of the unstructured emission spectra which this compound displays (figs. 5 and 6).

Unique D and E values were also obtained for the dimers 1–3. It is worth noting that although the emission spectra of 1 and 2 display sharp, distinct lines, the actual number of lines observed for the dimers is significantly lower than for the corresponding monomers 4 and 5. This point is

Table 3

Comparison of the triplet state zero-field splitting parameters and decay rates for the dimeric (1,2,3) and monomeric (4,5,6) porphyrins

	$|D|$ (MHz)	$|E|$ (MHz)	$p = \Sigma_i k_i$ (s⁻¹)	k_x (s⁻¹)	k_y (s⁻¹)	k_z (s⁻¹)	α
1	1063 ± 5	60 ± 5	6.7 ± 0.4	5.1 ± 0.4	5.9 ± 0.4	8.6 ± 0.4	60°–65°
4	1067 ± 7	134 ± 5	6.9 ± 0.4	5.4 ± 0.4	6.3 ± 0.4	9.0 ± 0.4	
2	1039 ± 7	74 ± 7	7.5 ± 0.9				50°–55°
5	1041 ± 5	121 ± 5	5.7 ± 1.0				
3	1095 ± 20	330 ± 20	7.9 ± 1.0				0°
6	1165 ± 20	350 ± 20	13.8 ± 15				

illustrated in fig. 3 where the phosphorescence of 1 and 4 are shown with high resolution. There exists, of course, the possibility that the dimers are indeed trapped in several different sites but that these sites show only small differences in their triplet-state zero-field splittings.

Table 3 gives the triplet-state zero-field splitting parameters, D and E, for the dimers 1–3 along with appropriate values for the monomers 4–6. The values listed for the monomers are those which are used for comparisons with the dimers in order to obtain structural information about the dimer configuration (c.f. section 5). Table 3 also lists the individual triplet sublevel decay rates, k_i, to the extent that they could be measured. This table also includes values for the total decay rates $\rho = \frac{1}{3}\Sigma_i k_i$.

5. Discussion

The redshifts of the fluorescence and phosphorescence emissions of the porphyrin dimers 1–3 with respect to the monomers 4–6, are of the order of a few hundred cm^{-1} (table 1); this shows that the condition $2J > |D|$ is fulfilled. This is one of the conditions which must be met in order to use the exciton model [29–35]. Furthermore, these redshifts are much smaller than those observed in dimeric systems where only 2 or 3 bridging CH_2 groups are used to link the subunits. For instance, measurements on [2.2]- and [3.3]-phanes [38–43] showed redshifts of the order of a few thousand cm^{-1}. These data indicate that in the porphyrin dimers 1–3 linked by 4, 5 and 6 bridging atoms the π-electron interaction between the two subunits is much weaker than in the [2.2]- and [3.3]-phanes. In the following discussion the results obtained with dimers 1 and 2 will be considered separately from those of dimer 3.

The data listed in tables 2 and 3 indicate that, within experimental error, the values of the parameters D for the dimers 1 and 2 are the same as those of their corresponding monomers, compounds 4 and 5 respectively. In addition the sum of the triplet sublevel decay rates for each of the dimers is the same as that for its corresponding monomer. In the light of these observations we conclude that the exciton model [29–35] may be

used for the determination of the relative orientation of the monomeric subunits in the "face-to-face" dimers 1 and 2 and that the energy transfer between the two sublevels is incoherent.

From the fact that for each of the pairs, 1 and 4, and 2 and 5, the parameters D are the same within experimental error, we conclude that in these dimers both units must be parallel to one another. On the other hand, from the observation that the E values for the dimers 1 and 2 are approximately half of those of the corresponding monomers 4 and 5 we conclude that the monomeric subunits are rotated about their common out-of-plane axis (z). By fitting the triplet zero-field splitting parameters of the dimers and the monomers to the set of eqs. (2) we obtain values for the rotation angle α of 60°–65° and 50°–55° for 1 and 2 respectively [*]. These results suggest that our ODMR measurements as well as earlier electrochemical studies [2,4] were performed with just the anti-stereoisomers of 1 and 2. The anti-stereoisomers are expected to display configurations with approximately the same degree of relative rotation between the monomeric subunits as were observed in this ODMR study [**]. By contrast, little or no relative rotation between the subunits would be expected in the case of the syn-stereoisomer. Our conclusion is reasonable from a synthetic point of view: in the "face-to-face" coupling reaction the less hindered anti-stereoisomer is expected to be the more readily formed of the two synthetically possible stereoisomers [2]. It is important to note that use of this exciton model does not yield information about possible relative displacements of the subunits parallel to any of the three principle axes x, y, z. It thus

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[*] An analogous picture for the relative configuration of the subunits emerges even if D and E values from sites other than those listed in table 3 are used (table 2). Under these conditions, however, the calculated value for the rotation angle, α, would be somewhat larger.

[**] In order to obtain the exact configuration of the anti-stereoisomers of 1 and 2 from their respective syn-stereoisomers, it is necessary to rotate one of the subunits 180° around one of its in-plane (x or y) axes in addition to effecting a relative rotation between monomeric subunits. Simple 180° "flips" of this nature cannot be observed by ODMR measurements since the same zero-field splitting parameters are obtained.

remains possible that in the case of the dimers 1 and 2, small plane parallel shifts are occurring in addition to the observed rotations.

For dimer 1 and monomer 4 we were also able to measure the individual decay rates (table 3). In principle these values should give rise to an independent determination of rotation angle α. However, because, of the relatively large errors (5–10%) associated with the individual decay rates of the triplet sublevels, any resulting calculated value for α would be substantially less accurate than that obtained from the zero-field splitting parameters. We therefore simply verified that using a value of α obtained from the zero-field splitting parameters led to calculated decay rates which agreed within error with those measured experimentally.

For the meso-linked porphyrin dimer 3 the situation is, unfortunately, not so clear. The principle reason for this is that monomer 6, which we use for comparison purposes, displays obvious interactions with the host matrix. Evidence for this interaction results from the values for the total decay rates; within experimental error this decay rate for 6 is at least 50% larger than that for 3. For dimer 3 a value for the total decay rate of $\rho = 7.9 \pm 0.8$ s^{-1} is found which is similar to those found for compounds 1, 2, 4 and 5. In monomer 6, however, this value is substantially higher ($\rho = 13.8 \pm 1.5$ s^{-1}). It is worth noting that contributions from charge transfer states can be ruled out for dimer 3. For, if this were the case, just the opposite situation would pertain, i.e. $\rho_{dim} > \rho_{mon}$. In addition to an increase in the decay rates, an interaction between the host and the guest often leads to a small reduction in the zero-field splitting parameters. Since, however, this effect is usually of the order of a few percent, we shall ignore it for the purposes of this discussion.

In the light of the problems associated with monomer 6, any conclusion reached about the configuration of dimer 3 based on comparisons between the zero-field splitting parameters of compounds 3 and 6 must be considered with caution. In spite of the small apparent differences in the E values for 3 (330 ± 20 MHz) and 6 (350 ± 20 MHz), these values could be considered equal within experimental error. Such an equality would suggest that the subunits are oriented in a plane-

parallel fashion and not rotated relative to one another about a common out-of-plane axis. A parallel orientation appears reasonable in the light of an X-ray structure determination made with a single crystal of the bis-copper analogue of 3 [3], where the planes of the two subunits were found to be oriented parallelly. The two centers of the porphyrin macrocycles, however, were shifted by 4.95 Å with respect to one another.

On the basis of the small differences observed in the D values of compounds 3 and 6 (at least 3% outside of the experimental error), we are tempted, on the basis of our model, to suggest that in the frozen n-octane/MTHF matrix the monomeric subunits are actually not arranged in a parallel fashion. It rather appears that each of the porphyrin subunits is twisted, by $\approx 8°$–$10°$, around the in-plane axis defined by the two substituted meso positions. On the basis of this degree of rotation and the experimental zero-field splitting parameters for monomer 6, calculated values of 1115–1096 MHz and 333–227 MHz are obtained for the D and E values of dimer 3. These calculated values are in reasonable agreement with those obtained experimentally (1095 ± 20 MHz and 330 ± 20 MHz). As noted earlier, these ODMR measurements do not give any information about possible plane-parallel shifts, and hence, we cannot judge the extent to which these shifts might be occurring in dimer system 3.

It should be emphasized that these ODMR measurements were carried out on samples trapped in glass matrices and not on single crystals. In light of the flexibility inherent in the 6 atom bridges in 3, a large number of configurations might exist both in solution and in a glass matrix. Therefore, the configuration we calculate for 3 may actually reflect an average of several possible orientations.

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