INFLUENCE OF AXIAL LIGATION ON THE FLUORESCENCE OF TETRAKISPHENYLPORPHYRINS

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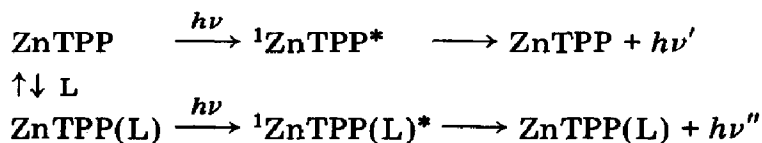(Received July 3, 1984; in revised form August 31, 1984)

Summary

The fluorescence properties of zinc tetrakisphenylporphyrin (ZnTPP) are significantly perturbed on axial ligation with strongly coordinating ligands. The entire spectrum undergoes a red shift relative to that of uncomplexed ZnTPP and there is an increase in the intensity of the $Q(0, 0)$ band relative to the $Q(1, 0)$ band, which is correlated with (a) the red shifts in the fluorescence maxima and (b) the donor number of the ligand. These effects are much less pronounced for magnesium tetrakisphenylporphyrin except in the case when the ligand is pyridine.

1. Introduction

Binding of a donor solvent or a molecule on a vacant coordination site of a metalloporphyrin is known to produce a dramatic change in its ground state absorption as well as its redox properties. This phenomenon is fairly well documented for iron, zinc, cobalt, manganese, ruthenium, tin and osmium porphyrin systems [1 - 16]. In almost all cases the effects of the medium have been traced to specific complexation (ligation) of the metalloporphyrin with one or more ligand/solvent molecules and are not merely due to solvation:

$$MP + nL \longrightarrow MP(L)_n \tag{1}$$

The ligated metalloporphyrin molecules are "new" chemical species with their own distinct properties. Therefore, for development of photosensitizer catalysts based on these compounds, it is pertinent to ask to what extent, if any, the photophysical properties of the metalloporphyrin are altered upon complexation with the added ligands or solvent molecules. We chose to examine the simplest system, *i.e.* the fluorescence of zinc tetrakisphenylporphyrin (ZnTPP)

$$\text{ZnTPP} \xrightarrow{h\nu} {}^1\text{ZnTPP}^* \longrightarrow \text{ZnTPP} + h\nu'$$

$$\uparrow\downarrow \text{L}$$

$$\text{ZnTPP(L)} \xrightarrow{h\nu} {}^1\text{ZnTPP(L)}^* \longrightarrow \text{ZnTPP(L)} + h\nu''$$

for the following reasons.

(i) Zinc is unambiguously in the 2+ state. The four-coordinated zinc will accept one, and only one, axial ligand to form a five-coordinated complex. Since ZnTPP has a d^{10} configuration there are no empty orbitals involved in the bonding.

(ii) Changes in the ground state absorption and redox properties are well characterized for a large number of ligands.

(iii) Zinc porphyrins are increasingly under investigation as potential photosensitizers in various photosystems and microheterogeneous environments. The excited species may change depending on the solvent system and the microheterogeneous environment. Examination of fluorescence in a wide variety of solvents has shown that both the fluorescence maxima and the relative intensities of various vibronic bands undergo large variations which can be correlated with the electron-donating properties of the ligand/solvent molecules.

2. Experimental details

The fluorescence spectra and yields were measured using a Perkin-Elmer MPF 4F spectrofluorometer equipped with a red-sensitive Hamamatsu R928 photomultiplier tube and a correction unit. Commercial ZnTPP (Strem) was treated using the method of Barnett et al. [17] to remove the chlorine impurity and was recrystallized from toluene before use. All solvents used were of spectroscopic grade (Fluka) and were used as supplied. The absorption spectra data (maxima and relative intensities) measured in this work are in good agreement with the earlier data of Nappa and Valentine [5].

3. Results and discussion

The absorption and fluorescence spectra of ZnTPP are extremely sensitive to the nature of the solvent. Table 1 gives a summary of the absorption and fluorescence maxima together with the relative intensities of the Q(0, 0) and Q(1, 0) bands (also identified as the α and β bands) in a wide variety of solvents. Figure 1 illustrates the extent of variation observed on going from non-coordinating solvents such as dichloromethane (Fig. 1(a)) to mild donor solvents such as ethyl ether (Fig. 1(b)) to strongly binding solvents such as pyridine (Fig. 1(c)). There is a significant red shift in the entire spectrum and a significant increase in the intensity of the Q(0, 0) band relative to the Q(0, 1) band.

TABLE 1

Influence of axial ligation on the absorption and fluorescence properties of zinc tetrakisphenylporphyrin

Solvent[a]	DN[b]	Dielectric constant	Absorption			Fluorescence			
			$Q(1, 0)$ (nm)	$Q(0, 0)$[c] (nm)	$\varepsilon_\alpha/\varepsilon_\beta$[d]	$Q(0, 0)$[c] (nm)	$Q(0, 1)$ (nm)	τ_{fl}[e] (ns)	Φ_{fl}[e]
1 Cyclohexane	0	2.0	545	584(0.09)	0.09	594(0.42)	639	1.67	1.00
2 Trichloromethane	0	4.8	547	584(0.16)	0.14	595(0.64)	643		
3 Dichloromethane	0	8.9	548	585(0.20)	0.23	596(0.76)	644		
4 Benzene	0.1	2.3	550	589(0.16)	0.17	598(0.74)	646		
5 Ethyl ether	19.2	4.3	552	591(0.26)	0.27	599(0.98)	650		
6 Ethyl acetate	17.1		554	593(0.31)		600(1.10)	651		
7 Methanol		32.7	554	593(0.32)	0.35	601(1.23)	654	1.75	1.12
8 Dioxane	15.0	2.2	554	594(0.36)		602(1.24)	654		
9 THF	20.0	7.6	554	593(0.32)	0.31	604(1.20)	655		
10 Acetonitrile	14.1	38.0	554	593(0.44)	0.44	603(1.44)	655		
11 DMF	26.6	36.1	558	598(0.45)	0.44	606(1.56)	658		
12 DMSO	29.8	45.0	560	600(0.48)	0.47	608(1.60)	660	1.70	0.91
13 TMP	23.0		560	601(0.50)		609(1.60)	661		
14 Pyridine	33.1	12.3	563	603(0.55)	0.51	611(1.75)	664	1.51	1.06

[a]THF, tetrahydrofuran; DMF, dimethylformamide; DMSO, dimethyl sulphoxide; TMP, tetramethyl phosphate.

[b]DN, donor number.

[c]The intensities of the Q(0, 0) band relative to the Q(1, 0) (absorption) or Q(0, 1) (fluorescence) bands are given.

[d]The relative intensity ratios are taken from ref. 5.
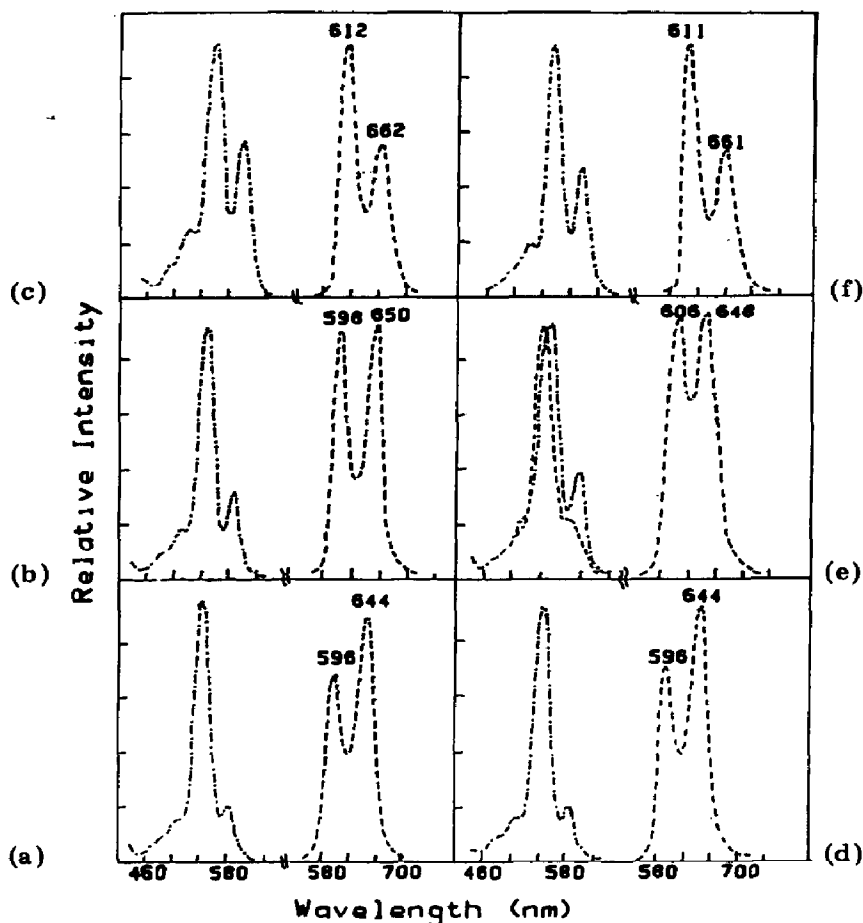
[e]Error estimates, ±20%.

Fig. 1. Fluorescence and fluorescence excitation spectra of ZnTPP in various neat solvents ((a) dichloromethane; (b) ethyl ether; (c) pyridine) and in dichloromethane with various pyridine additions ((d) no pyridine; (e) a pyridine-to-dichloromethane ratio of less than 1:1; (f) tenfold stoichiometric excess of pyridine).

The spectral shifts and the variation in intensity are specific effects due to axial ligation of a donor molecule for they are also seen in non-coordinating solvents such as cyclohexane or dichloromethane in the presence of a one- to tenfold stoichiometric excess of the complexing ligand. (The stability constants for complexation of ZnTPP with nitrogenous bases such as pyridine or picolines are quite high (log β_0 is in the range 3.8 - 4.0).) Figures 1(d) - 1(f) show similar variations in the fluorescence of ZnTPP in neat dichloromethane, in a less than 1:1 pyridine–dichloromethane mixture and in dichloromethane containing a tenfold excess of pyridine. The spectra shown in Fig. 1(e) are mixed emission spectra arising from both the uncomplexed and complexed ZnTPP molecules, as is shown clearly by the dependence of the excitation spectrum on the fluorescence wavelength being monitored.

The fluorescence maxima and the relative intensities increase gradually with increasing Lewis basicity of the solvent. As shown in Fig. 2 the
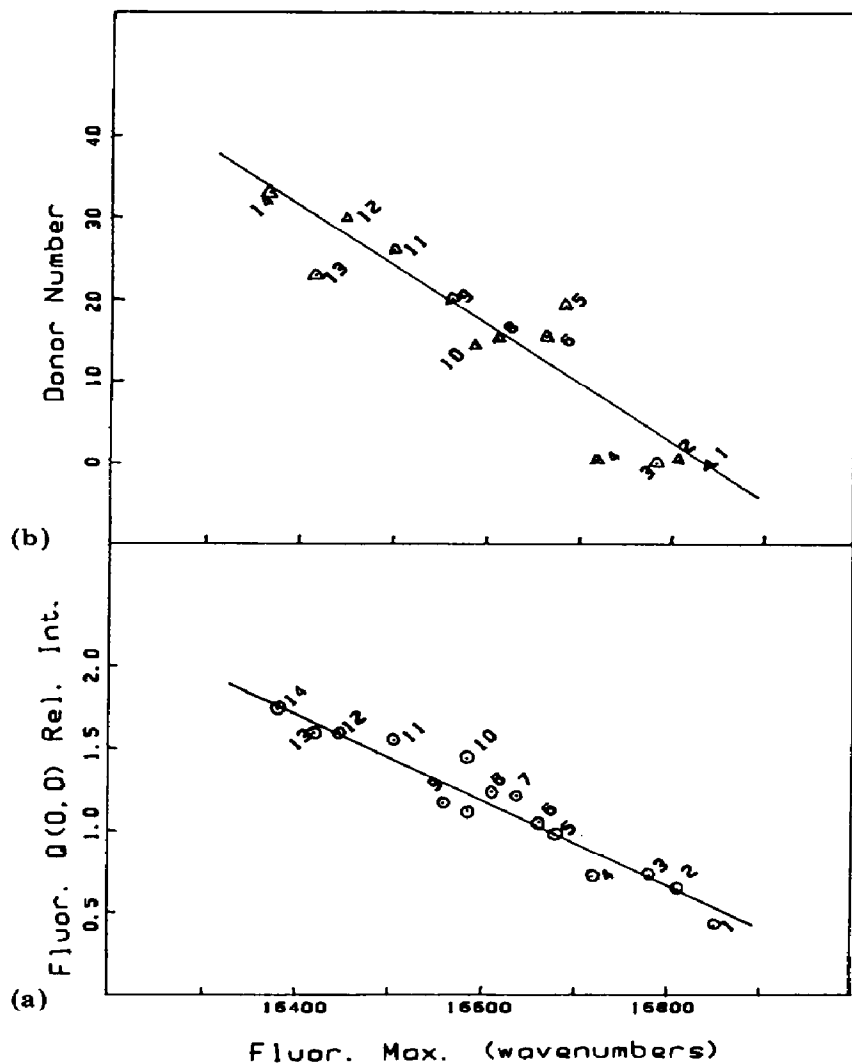
Fig. 2. Variation in the fluorescence maximum of ZnTPP(L) with (a) the intensity of the Q(0, 0) band relative to the Q(0, 1) band and (b) the DN of the solvent. The numbers on the points refer to the solvents as identified in Table 1.

intensity of the Q(0, 0) (or α) band relative to the Q(0, 1) (or β) band correlates fairly well with the position of the Q(0, 0) fluorescence band for all the solvents studied. There is also a good correlation of the fluorescence maxima with the donor number (DN) (donicity) of the solvent. The DN is a relative empirical scale introduced by Meyer and Gutman [18] to express, at least in a semiquantitative manner, the donor strength of a solvent (electron-pair donor molecule). It is defined as the absolute value of the enthalpy changes in kilocalories per mole of the reaction

$$\mathrm{SbCl_5(dissolved) + D(dissolved) \rightleftharpoons SbCl_5 \cdot D(dissolved)}$$

measured calorimetrically for dilute solutions in an inert medium such as 1,2-dichloromethane. In terms of hard and soft acids (class a and class b acids), ZnTPP can be considered as a borderline Lewis acid (class a).

It is rather surprising that axial ligation in a closed-shell (d^{10}) system such as ZnTPP should produce such large spectral shifts (up to 20 nm or 450 cm^{-1}). It should be noted that shifts of a similar magnitude have also been observed in the absorption spectra (in both the maxima and the relative intensities (for data see Table 1)), and what is observed in fluorescence is a manifestation of the strict observation of the mirror-image relationship even in the five-coordinated ZnTPP(L) molecules. Electrochemical studies in the presence of about 20 nitrogenous bases [8, 9] have shown that the redox potentials for the one-electron oxidation–reduction of ZnTPP(L) can be varied by as much as 100 mV by appropriate tuning of the basicity of the complexing ligand.

Since the nature of the axial ligation of ZnTPP has been investigated in detail [1 - 16] using absorption spectroscopy, nuclear magnetic resonance (NMR) and electrochemical methods, it is worthwhile recalling here some of the possible interpretations and conclusions reached. The most comprehensive discussions were those of Nappa and Valentine [5] and the more recent analysis by Kadish and Shiue [8]. For complexing ligands/solvent molecules it is appropriate to seek correlations between the measured spectral properties and the properties of the donor ligand. Since the effect of axial ligands on the absorption spectrum is similar to that observed when the metal is changed in a series of closed-shell metalloporphyrins, it is probable that complexation with ligands that donate charges to the metal should have a similar effect. There is no simple quantitative method of estimating the strength of the zinc–ligand σ bond. Correlations that have been investigated to date include those with the DN, the pK_a of the ligand, the dielectric function of the donor ligand and the Drago parameters E_B and C_B. The ^{15}N NMR chemical shifts observed upon binding a series of substituted pyridines to ZnTPP correlate with Hammett's σ constant. Kadish and Shiue [8, 9] in their electrochemical studies of various nitrogenous bases, generally found good correlation for a given closely related set of ligands (substituted pyridines) but "inclusion of imidazoles added either scatter or curvature to the plots".

We have also investigated the variation, if any, of the fluorescence quantum yields and lifetimes of ZnTPP upon ligation. Relative quantum yield measurements in dichloromethane or cyclohexane with added ligands (sufficient quantities to cause complete conversion to ligated species) as well as in neat solvents showed that the variation of the quantum yields was very small (within ±10% which is approximately the same range as the error in these measurements). Similar results were obtained for fluorescence lifetimes measured using single-photon-counting techniques. This result is rather surprising in view of the large variations observed in the relative intensities and spectral shifts and also contrasts with the effects observed in the lifetimes and quantum yields of non-solvated and

pyridinated tetraalkylporphyrins of osmium and ruthenium. Presumably the charge transfer interactions between the axial ligand and the metal in metalloporphyrins with incomplete metal d shells are much stronger than those in closed-shell systems such as ZnTPP. In addition, pyridine does not appear to quench the triplet state of ZnTPP, as indicated by the similarity of the triplet lifetimes in toluene and pyridine (1.25×10^3 s^{-1} and 1.15×10^3 s^{-1} respectively) reported by Pekkerinen and Linschitz [19].

Only a few direct studies of the influence of axial ligation on the emission properties of metalloporphyrins have been performed. Large spectral shifts analogous to those reported here (about 14 nm) were observed for zinc etioporphyrin(I) and magnesium etioporphyrin(I) on changing the solvent from methylcyclohexane to pyridine [20]. The fluorescence and phosphorescence intensities were also found to decrease upon complexation (by about 50% and 25% respectively for complexation with pyridine) in contrast with the present results for ZnTPP. Harriman and Hosie [21] observed large variations in the fluorescence lifetimes and yields of tetrakisphenylporphyrin on changing the solvent. The results for free-base porphyrins are difficult to interpret owing to the possible protonation equilibria of ligands such as pyridine with the pyrrole N-protons of the porphine.

We have also made some preliminary measurements of similar ligation effects on the fluorescence of magnesium tetrakisphenylporphyrin (MgTPP). Unlike ZnTPP, MgTPP is known to bind up to two ligands:

$$MP + L \rightleftharpoons MP(L)$$

$$MP(L) + L \rightleftharpoons MP(L)_2$$
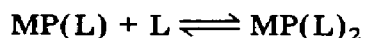
It has also been reported that the optical absorption spectra of uncomplexed MgTPP and the monoligated complexes are very similar. Examination of the spectra in a variety of solvents (dichloromethane, trichloromethane, dimethylformamide and dimethyl sulphoxide) showed that the absorption and fluorescence spectra were indeed very similar and exhibited very small shifts ($\pm(2 - 3)$ nm). Larger shifts in the fluorescence were observed only with pyridine. The addition of increasing amounts of pyridine to MgTPP in dichloromethane produced a shift in the fluorescence maxima from 611 and 664 nm to 626 and 671 nm (corresponding to emission from non-complexed MgTPP and the monopyridinate MgTPP(py) respectively). During the formation of MgTPP(py) shifts in the absorption spectra of only 2 - 3 nm were observed.

Acknowledgments

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