

LUMINESCENCE OF PORPHYRINS AND METALLOPORPHYRINS VII: LUMINESCENCE OF PHOSPHORUS TETRAPHENYLPORPHYRINS

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Summary

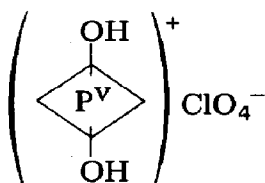
The absorption, fluorescence and low temperature phosphorescence spectra of phosphorus(V) tetraphenylporphine ($P^V\text{TPP}$) appear to be quite normal for a diamagnetic porphyrin although both the fluorescence and phosphorescence quantum yields are low ($\phi_F = 0.059$ and $\phi_P = 5 \times 10^{-4}$). Internal conversion from the first excited singlet to the ground state occurs with a quantum yield of about 0.14 and the triplet lifetime at 77 and 300 K appears shorter than that predicted from the spin-orbital coupling properties of the compound. It is proposed that ion pairing between the cationic $P^V\text{TPP}$ and a perchlorate counter-ion provides a route for non-radiative deactivation of the excited triplet state, although there is no direct evidence to support this idea. The unstable $P^{III}\text{TPP}$ possesses a hyperabsorption spectrum, but no luminescence attributable to the compound could be observed at 77 or 300 K.

1. Introduction

With a few notable exceptions, the photophysical properties of diamagnetic metalloporphyrins have been well documented both experimentally and theoretically, and the nature of the first excited singlet and triplet states is essentially pure $\pi\pi^*$. This is not so when the central metal ion possesses paramagnetic behaviour and despite prolonged investigation the characterization of the photophysical properties of such compounds has advanced only a short distance. The emergence over the last few years of metalloid or non-metal porphyrin complexes has opened up a new section of porphyrin photophysics and there is much current interest in characterizing such species.

The known luminescence properties of metalloid porphyrins and the phthalocyanines were reviewed recently by Sayer *et al.* [1] and it is clear that this subject is still very much in its infancy. So far, arsenic and antimony porphyrins have been studied in some detail [2, 3] and there are a few quali-

tative descriptions [4, 5] of the fluorescence from phosphorus porphyrins. These metalloid porphyrins exhibit luminescence spectra similar to those of diamagnetic metalloporphyrins [1] and it seems likely that the photo-physical properties of arsenic, antimony and phosphorus porphyrins can be explained in terms of existing theoretical frameworks. This feeling is confirmed by the work reported here for phosphorus(V) tetraphenylporphine ($P^V\text{TPP}$) which is found to exhibit quite "normal" behaviour:



(where $\diamond \equiv \textit{meso}$ -5,10,15,20-tetraphenylporphine).

2. Experimental details

2.1. Materials

Ethanol (Burroughs, AnalaR grade) was used as received. $P^V\text{TPP}$ was prepared by a route similar to that described by Sayer *et al.* [4] using pyridine as the solvent. 0.1 g of TPP (Aldrich, chlorine free) were dissolved in 20 cm³ of pyridine (redistilled from CaH₂) and the solution was purged thoroughly with nitrogen. After careful addition of 2 cm³ of PCl₃, the mixture was heated to 90 °C for 1 h and then evaporated to dryness. The residue was dissolved in CH₂Cl₂-H₂O and the aqueous phase was extracted with a large volume of CH₂Cl₂. After drying, the CH₂Cl₂ solution was evaporated to dryness and the residue was dissolved in 10 cm³ of methanol, filtered to remove unreacted porphyrin and diluted with 25 cm³ of water. After filtering, a saturated solution of NaClO₄ was added to precipitate the required product which was isolated by filtration and dried at 50 °C under vacuum. Analysis by thin layer chromatography (TLC) showed the presence of small amounts of metal-free porphyrin and an unidentified product, and the final material was purified by repeated preparative scale TLC using CH₂Cl₂-C₂H₅OH mixtures as eluents. The overall yield was about 4% - 7%.

2.2. Methods

The absorption spectra were recorded using a Perkin-Elmer 554 spectrophotometer and the luminescence spectra were recorded using a Perkin-Elmer MPF 4 spectrofluorometer equipped with attachments for correcting both excitation and emission spectra. Luminescence yields and lifetimes were determined as described in previous papers in this series [6] and zinc TPP was used as the standard for all measurements. The triplet state lifetime, yield and absorption spectrum were recorded by flash photolysis techniques using outgassed ethanol solutions at room temperature. Both conventional

(pulse duration, 10 μ s) and neodymium glass laser (pulse duration, 15 ns) excitation sources were used whilst the singlet excited state lifetime was measured by time-correlated single-photon counting (pulse duration, about 500 ps). Error limits are given in the text.

3. Results and discussion

The absorption spectrum of P^V TPP in ethanol solution is shown in Fig. 1. By comparison [7] with diamagnetic metalloporphyrins, such as magnesium TPP, it is a "normal" spectrum with no indication of charge transfer bands in the near-UV or far-red regions. The addition of acetic acid or NaOH solution results in small shifts in the absorption bands which are consistent with protonation-deprotonation of the axial hydroxide ligands although the shifts are less than 200 cm^{-1} . Beer's law is obeyed throughout the concentration range 10^{-7} - $10^{-4}\text{ mol dm}^{-3}$ and there is no spectral evidence to suggest dimerization in ethanol solution.

Fluorescence from P^V TPP in ethanol solution is observed easily at both 77 and 300 K; the Stokes shift is about 60 cm^{-1} and the corrected excitation spectrum correlates well with the ground state absorption spectrum throughout the entire visible region. The fluorescence spectrum (Fig. 2) shows good mirror symmetry with the lowest energy absorption bands. As shown in Fig. 2, low temperature phosphorescence can be observed, albeit with considerable difficulty owing to the low yield, with a maximum at about 775 nm. Thus, the singlet-triplet energy gap is 3700 cm^{-1} , in reasonable agreement with typical values observed for diamagnetic metal TPP com-

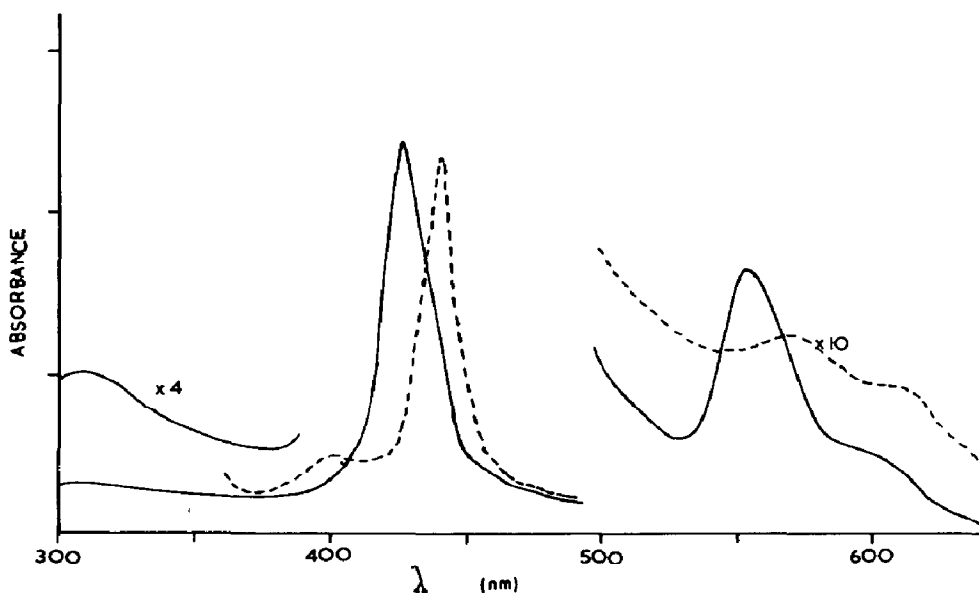


Fig. 1. Absorption spectra of P^V TPP (—) in ethanol solution and P^{III} TPP (---) in pyridine-benzene solution.

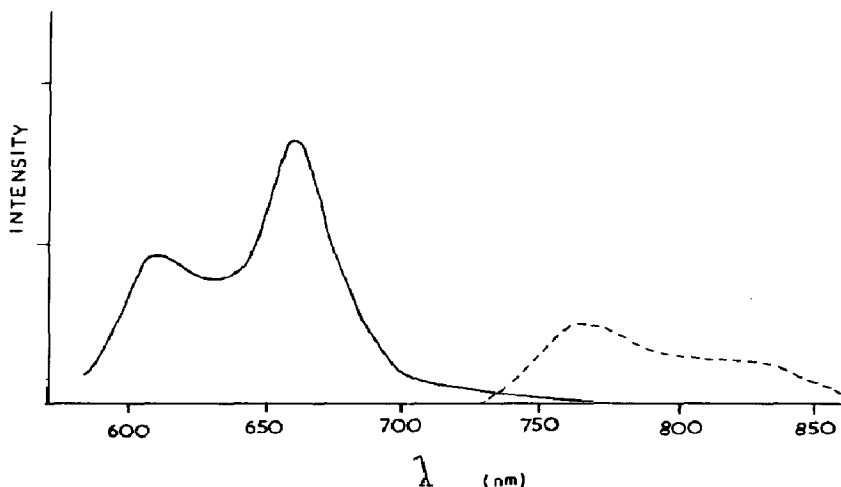


Fig. 2. Room temperature fluorescence spectrum (—) and the phosphorescence spectrum at 77 K (---) of P^V TPP in ethanol solution.

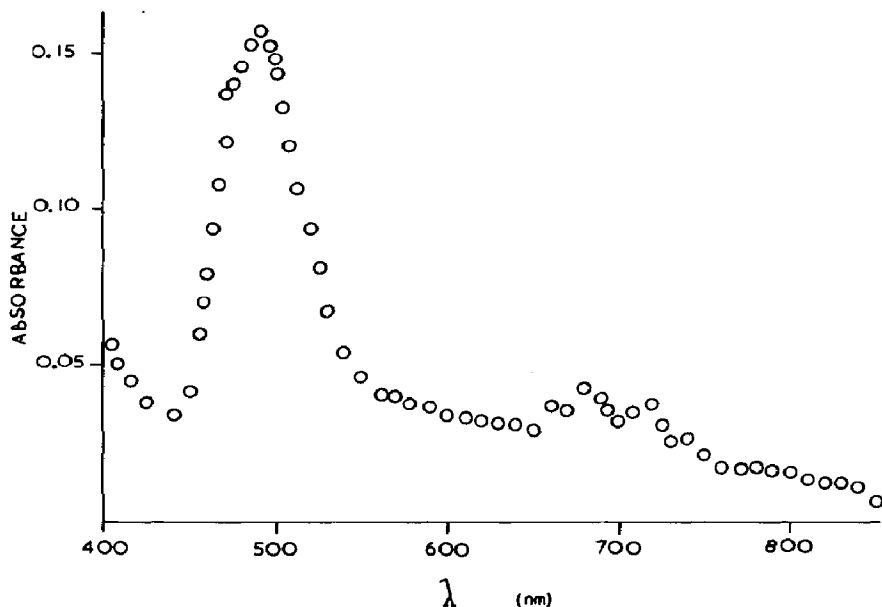


Fig. 3. Triplet absorption spectrum of P^V TPP in outgassed ethanol solution at 300 K.

plexes [7, 8]. No phosphorescence could be observed in outgassed fluid solutions at room temperature but the triplet state exhibited intense absorption throughout the whole visible region (Fig. 3). The triplet spectrum is similar to those found [7] for diamagnetic metalloporphyrins in that there is a series of fairly weak transitions in the far-red region and two intense transitions in the near-UV region. However, there was evidence for a second longer-lived ($t_{1/2} \approx 5$ ms) transient with absorption maxima at about 495 and 700 nm which might be an ionized form of the porphyrin. After repeated flash excitation or steady state irradiation of an outgassed ethanol

TABLE 1

Photophysical properties of phosphorus(V) tetraphenylporphine in ethanol solution

<i>Property</i>	<i>Value</i>
ϕ_F	0.059 ± 0.004
τ_S (ns)	3.7 ± 0.3
k_F (s^{-1})	1.7×10^7
k_{isc} (s^{-1})	2.2×10^8
k_{ic} (s^{-1})	3.3×10^7
ϕ_T	0.80 ± 0.06
ϕ_{ic}	≈ 0.14
ϕ_P 77 K	$(5 \pm 3) \times 10^{-4}$
τ_P 77 K (ms)	7 ± 3
τ_T 300 K (μs)	240 ± 15

solution of P^VTPP there was some loss of the porphyrin absorption bands and a concomitant appearance of a new absorption band centred around 685 nm. Formation of this product was very inefficient and may not be associated with the long-lived transient although neither species has been identified. (The triplet absorption spectrum was recorded in a single shot using a flash spectrographic instrument.)

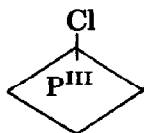
Table 1 gives values for the fluorescence quantum yield ϕ_F and the excited singlet state lifetime τ_S measured in dilute ethanol solution at room temperature and for the phosphorescence quantum yield ϕ_P and lifetime τ_P measured in an ethanol glass at 77 K. Also given in Table 1 are the quantum yield ϕ_T for formation of the triplet excited state and the fluorescence rate constant k_F calculated from the Strickler-Berg equation. These values were used to calculate rate constants k_{isc} and k_{ic} for intersystem crossing from singlet to triplet excited states and for internal conversion from the first singlet excited state to the ground state respectively. It is seen that the sum of the fluorescence and triplet formation quantum yields does not approach unity, suggesting that internal conversion makes an important contribution towards the overall deactivation of the first singlet excited state. Unfortunately, the experimental errors associated with the ϕ_T measurement are too high for much significance to be attached to the derived ϕ_{ic} value but, relative to diamagnetic metalloporphyrins where $\phi_F + \phi_T \approx 1$, there does appear to be some type of non-radiative decay from the first excited singlet to the ground state for P^VTPP.

Even allowing for internal conversion, the triplet manifold is populated with high yield and, at room temperature, it possesses a lifetime τ_T of 240 μs . This lifetime is much shorter than that found [6 - 8] for magnesium, zinc or aluminium TPP complexes ($\tau_T \approx 1.2$ ms), and in fact the phosphorescence lifetime is anomalously short [7]. The low temperature phosphorescence yield is very low, even in the presence of iodoethane, and is more in keeping with the metal-free compound than with the diamagnetic metalloporphyrins

[7]. In previous work with porphyrins that do not possess low-lying dd or charge transfer states unexpectedly short $\pi\pi^*$ triplet excited state lifetimes have been associated with the spin-orbital coupling properties of the central metal ion and/or axially coordinated ligands. The combined spin-orbital coupling terms for $P^V\text{TPP}$ should be relatively low since neither the hydroxide groups nor the phosphorus(V) ion contain heavy atoms. Furthermore from the absorption spectrum it appears that the central phosphorus(V) ion does not interact particularly strongly with the porphyrin π system [7] and, following the treatment described earlier [7], we might expect to observe lifetimes for the triplet state of $P^V\text{TPP}$ of $\tau_P \approx 20$ ms and $\tau_T \approx 1.0$ ms. Thus, compared with diamagnetic metalloporphyrins, there appears to be some additional process that enhances non-radiative deactivation of the excited triplet state of $P^V\text{TPP}$ at both 77 and 300 K.

It is possible that this extra decay pathway is responsible for the long-lived transient species observed in the microsecond flash photolysis studies although the identity of this transient remains obscure. Quite probably the effect is connected with the fact that $P^V\text{TPP}$ is a cation and exists in ethanol solution as an ion pair with a closely associated perchlorate ion. There are numerous examples where the formation of an ion pair results in enhanced non-radiative deactivation of both excited singlet and triplet states and it may be that photoinduced charge transfer from the metalloporphyrin to the perchlorate ion plays some part in the non-radiative deactivation process. Therefore the observation that $P^V\text{TPP}$ shows a surprisingly short triplet lifetime may be explainable in terms of ion pairing between the porphyrin and the counter-ion. However, the nature of the bonding between the small phosphorus(V) ion and the porphyrin π system as well as the intimate relationship between the cationic porphyrin and the perchlorate counter-ion are not well understood at present. In the absence of detailed molecular orbital calculations and an accurate structural determination, it would be wrong to attach too much significance to the above explanations even though they give a good qualitative account of the observed spectroscopic properties.

Unlike $P^V\text{TPP}$, the lower valence $P^{III}\text{TPP}$ derivative could not be isolated as a stable product nor could it be obtained by chemical reduction of $P^V\text{TPP}$:



Problems with the stability of $P^{III}\text{TPP}$ have also been experienced in recent studies concerned with the electrochemical reduction of $P^V\text{TPP}$ [9]. The absorption spectrum (Fig. 1) observed during the early stages of the preparation of $P^V\text{TPP}$ is believed to be due to the $P^{III}\text{TPP}$ compound [1] although there must be many impurities present in the reaction mixture. No fluores-

cence could be detected from the pyridine reaction solution diluted with benzene.

Acknowledgments

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