

PHOTOPHYSICAL PROPERTIES  
OF  
PORPHYRIN SYSTEMS IN SOLUTION

Submitted by

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To my parents

## S U M M A R Y

The work described in this thesis is directed towards obtaining a clearer understanding of how the nature of the environment affects the photophysical properties of synthetic porphyrins. The porphyrins are used as simple models of the chlorophyll molecules that form the light harvesting and reaction centre complexes in bacterial and green plant photosynthesis. Using steady-state and time-resolved luminescence and flash photolysis studies, the photophysical properties of several types of porphyrin molecules have been elucidated. The results have been interpreted in terms of environmental effects. An introduction to the subject and a full description of the experimental procedures used are provided.

Chapter III investigates the role that proteins and lipids play in controlling the excited state lifetimes of chlorophyll molecules. Zinc porphyrins readily complex at the central metal ion with coordinating ligands and the strength of ligation has a profound effect upon the porphyrin triplet state lifetime. Incorporating the porphyrin into a micelle, vesicles or protein similarly perturbs the triplet state and with a zinc porphyrin bound inside a myoglobin molecule the observed triplet lifetime was some 8 times longer than found in free solution.

In Nature, the chlorophyll molecules are sited in very close proximity to each other to facilitate energy transfer. Chapter IV explores the importance of dimerisation on the photophysical properties of water-soluble porphyrins. Electrostatic forces have to be considered in such work and, consequently, the porphyrin-porphyrin interaction depends upon ionic strength, temperature, any coordinating ligands and the presence of a charged interface.

Chapter V continues this work by investigating the photophysical properties of covalently linked porphyrin dimers. Here, a zinc porphyrin was linked to either a free-base porphyrin or to a different metalloporphyrin. According to the nature of the second porphyrin, fluorescence from the zinc porphyrin was quenched to a certain degree. The reaction mechanism and importance of mutual orientation are both discussed.

In order to model electron transfer in photosynthesis, porphyrins covalently linked to electron acceptors have been studied. These systems are compared to unlinked molecules, and again, the importance of orientation and separation distance becomes clear.

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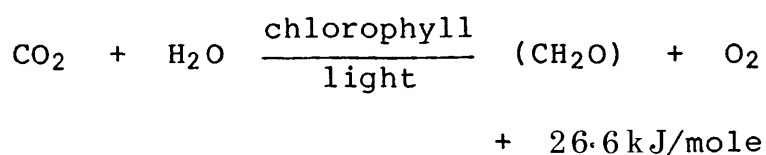
CHAPTER I  
INTRODUCTION

### 1.1 Introduction

To date no system has been developed that can successfully replace the photosynthetic leaf. Its apparently facile conversion and storage of solar energy into useful chemical compounds remains the envy of many research groups all over the world. The interest and excitement that photosynthesis has created is responsible for many areas of research such as the synthesis and study of porphyrin compounds and derivatives and also the modelling of both energy and electron transfer. The study of the latter processes has been greatly aided by the advent of the laser age. One of the intriguing achievements of the plant is the way both energy and electron transfer - both exceedingly complex in their own right - have been linked together in a cooperative fashion to form what is known to us by the simple names of Photosystem I and Photosystem II. With diminishing quantities of natural resources, such as oil, the modelling of photosynthesis has become increasingly popular over the years and areas of research associated with photosynthesis are still expanding.

### 1.2 The systems involved

The entire photosynthetic process can be summarized as:



The capacity of plants to produce free oxygen was discovered by John Priestley in 1772 whilst the requirement for carbon dioxide and chlorophyll was recognised by Jean Senebier in 1782. It was however Julius Robert von Mayer who in 1845 recognised that the fundamental physical function of photosynthesis was the conversion of light energy to chemical energy.

Light energy is absorbed within  $10^{-15}$  seconds by an assembly of pigment molecules, called the photosynthetic unit (PSU) [1]. According to a definition given by Duysens (1966): "The unit consists of a reaction centre and those chlorophyll molecules that have the highest probability of transferring excitation energy to this reaction centre when all reaction centres are in the trapping state". The size of the PSU can vary from plant to plant. Arnold and Emerson [3] estimated 300 chlorophylls to be associated with each photoact. However, reports of up to 5000 chlorophyll molecules per  $\text{CO}_2$  molecule reduced can also be found [4]. In bacteria the figure is significantly less and is put at 50 chlorophylls per reaction center.

In green plants there are two pigment systems and two light reactions [5-7]. Light reaction II, also known as photosystem II (PSII) leads to oxygen evolution and reduction of plastoquinones (PQ), while PSI culminates in the reduction of nicotinamide adenine dinucleotide phosphate ( $\text{NADP}^+$ ) and oxidation of plastoquinones. A scheme showing this sequence of events is given in Fig. 1.1.0.

The ultra fast reaction of photosynthesis takes place within the PSU and involves the transfer of excitation energy from the bulk of the chlorophyll molecules, also known as antennae to the reaction centre. The mechanism of energy transfer is described in most papers as being due to Forster resonance. A description of Forster energy transfer will be given further on in this chapter.

### 1.3 The Pigments Involved in Photosynthesis

The name chlorophyll refers to all classes of porphyrin involved in the primary processes of photosynthesis. The major green pigments of higher plants consist mainly of chlorophyll-a and -b and also bacteriochlorophylls which are involved in bacterial photosynthesis. The various structures of these chlorophylls are shown in Fig. 1.1. The skeleton of chlorophyll consists of a square planar tetrapyrrole macrocycle, the centre of which is chelated to a  $Mg^{2+}$  ion, which if displaced by two hydrogen ions gives the corresponding pheophytin. In chlorophyll-a and -b, the pyrrole constituting ring IV is hydrogenated at positions 7 and 8. Another feature of chlorophylls is ring V - the cyclopentanone ring. Each chlorophyll also contains two carbonyl groups both of which are esterified, one containing a methanol residue, and the other a phytol residue which gives the chlorophyll lipophilic properties. The tetrapyrrole ring provides a system of conjugated double bonds over which  $\pi$  electrons can be delocalised.

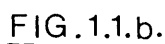
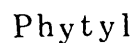
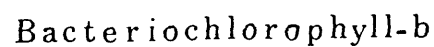
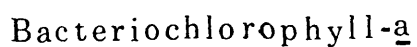
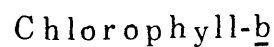
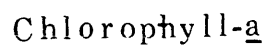


FIG. 1.1b Absorption spectrum of Chlorophyll-a

Both photosynthetic units of green plants contain varying ratios of chlorophyll-a and chlorophyll-b. Approximately 80% of all chlorophyll-b in the chloroplast is associated with PSII. In spinach chloroplasts the Chl a/Chl b ratio for the PSI complex is about 8 whilst for PSII the ratio is 35 [8]. Bacterial photosynthetic systems on the other hand contain exclusively bacteriochlorophyll a (BChl a), one exception being Rhodospseudomonas viridis which contains exclusively BChl b. The action spectra for PSI and PSII are shown in Fig. 1.2 . The Fig. illustrates the inability of PSII to

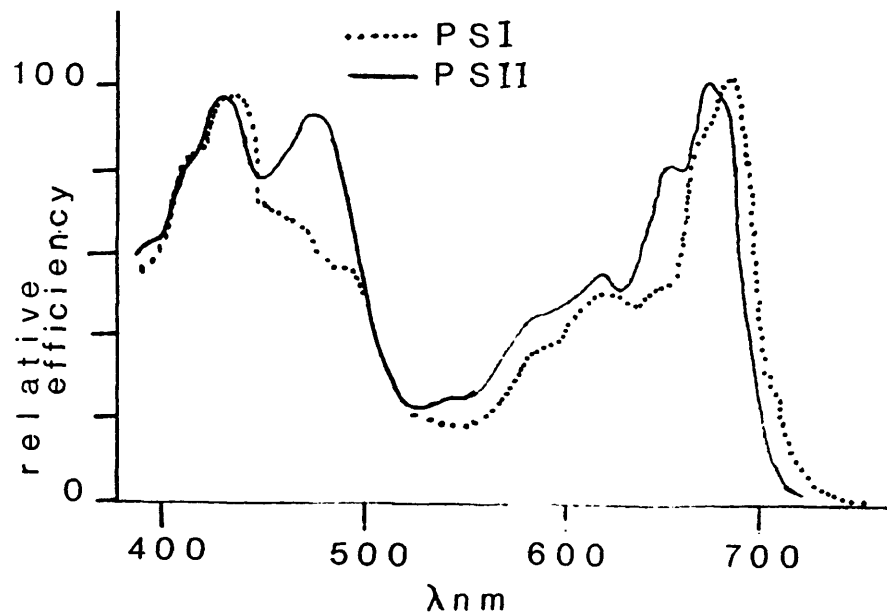


FIG. 1.2 Action spectra for PSI and PSII.

utilise light above 700 nm, whilst below about 680 nm light is absorbed by both photosystems with some preference for PSII [9].

#### 1.4 Chlorophyll-Protein Complexes

Because chlorophylls play a key role in photosynthesis, an important factor is their location in the thylakoid membrane. Biochemical studies on chlorophyll-protein fractions, isolated from detergent solubilised thylakoid membranes, have revealed that virtually all chlorophylls are associated with protein [10,11]. Research activity in this area has uncovered numerous chlorophyll-polypeptide entities but so far little information on their structural and intermolecular interactions has been uncovered [12]. The chlorophyll-protein complexes can, however, be divided into three main groups 1) chlorophyll-protein complexes associated with PSI activity (commonly referred to as CPI) and containing about 30% of the total chlorophyll, 2) chlorophyll-protein complexes associated with PSII activity and containing 20% of the total chlorophyll, and 3) light harvesting chlorophyll-pigment complexes also referred to as LHCs or CPII with a Chl-a/Chl-b ratio approaching 1, as opposed to a value of about 3 in thylakoids. Thus, for example, CPII has been characterised as an apoprotein of 35 kDa complexed with three molecules of chlorophyll-a, three of chlorophyll b and a carotenoid [13]. The second preparation of the antenna protein, LHC, is more stable than CPII and contains a larger number of chlorophyll molecules. Approximately 13 chlorophylls are complexed to a 23 kDa apoprotein with a chlorophyll a/b ratio of 1.2 [14]. An apparently high molecular weight 51 kDa

polypeptide is one of the two dominant proteins of the PSII core complex. It binds Chl a and is the apoprotein of one of chlorophyll protein complexes known as CP47 [15].

Structures for the LHC unit have been elucidated over the past three years [16] using Fourier Transform analysis of crystalline arrays of purified pea complexes. The model is shown in Fig. 1.3 and shows a highly symmetrical unit with a  $C_3$  axis of symmetry. Preliminary results using circular dichroism appear to support this model [17].

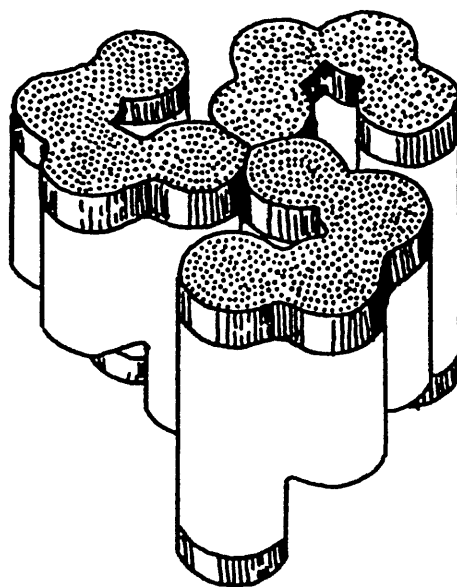


FIG. 1.3

Schematic drawing of one Chl a/b LHC unit based on a three dimensional map generated from Fourier Transform analysis of crystalline arrays of purified pea complexes. The shaded regions show the part of the complex that would protrude from a hypothetical 4.5 nm lipid bilayer. The top flat region probably constitutes the surface that promotes membrane adhesion [16].

### 1.5 Energy Transfer and Migration in the Reaction Centre

The reaction centres of PSI and PSII are surrounded by a range of ancillary pigments such as carotenoids, chlorophylls-a and -b and phycobilins [18,19]. These molecules form the antenna, absorbing light of shorter wavelength and then transferring it to chlorophyll-a. As a result, the action spectrum shown in Fig. 1.2 is considerably broader than the absorption spectrum of pure chlorophyll-a shown in Fig. 1. .

One commonly quoted example where these rapid energy transfer processes have been observed directly is that of Porphyridium cruentum [20]. This red alga possesses water soluble accessory light harvesting pigments contained within structures called phycobilisomes attached to the thylakoid membranes. Phycobilisomes contain three pigments: B-phycoerythrin (B-Ph), R-phyococyanin (R-PC), and allophycocyanin (APC). The chlorophyll a is contained within the thylakoids. Using a Nd/glass laser apparatus it was possible to excite solely the pigment possessing the highest singlet excitation energy - B-Ph in this case - and monitor subsequent fluorescence decays of the four other pigments incorporated in the alga. The sequence of grow-ins and decay patterns of the four pigments is shown in Fig. 1.4 and it clearly follows the predicted energy transfer pathway.

The early models for reproducing chloroplast like conditions in vitro, involved using monolayers. Classical work by Bellamy, Tweet and Gaines [21] showed that a Forster mechanism could be used to describe energy

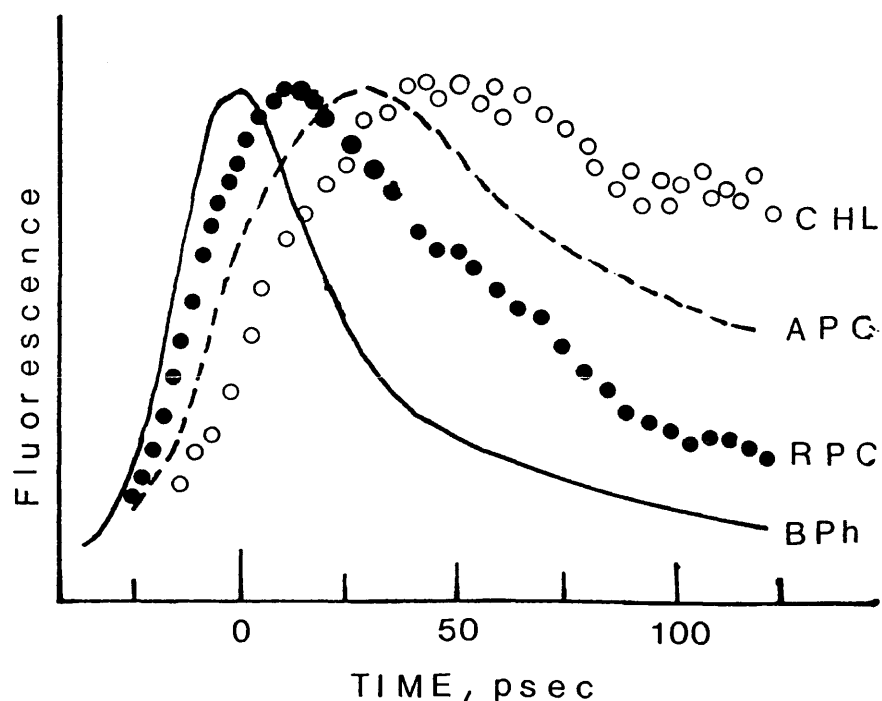


FIG. 1.4

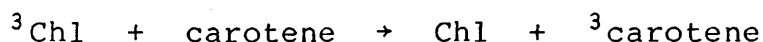
Energy transfer in Porphyridium Creuntum. Fluorescence of BPh at 576 nm decays by transfer in 70 ps to RPC which fluoresces at 640 nm. Finally, this transfers in 120 ps to chlorophyll a which fluoresces at 685 nm and decays in 180 ps by transfer to the trap.

transfer between like and unlike molecules in diluted monolayers. They also observed a marked decrease in the fluorescence yield as the separation of molecules within a layer was decreased but suggested no explanation. Later work [22] used monolayers of chlorophyll-a diluted by various chloroplast lipids. Here too, a Forster mechanism was used to explain the fluorescence results and concentration quenching was also observed. Monte Carlo calculations have shown that the average separation for

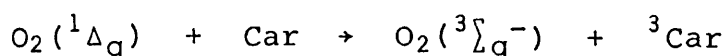
50% quenching between chlorophyll-a molecules is 10 Å [23]. This suggests that an efficient light harvesting antenna of chlorophyll-a must have no molecules separated by less than 10Å but they must also be close enough for efficient energy transfer. A study on a bacteriochlorophyll-protein complex has shown that the average nearest neighbour separation is 12 Å which is almost ideally suited for energy transfer [24]. However the Monte Carlo estimation was purely for a random arrangement of Chl-a molecules, and it did not take into account the importance of relative orientations.

So far the above examples have centred around energy transfer taking place from the excited singlet state. Under conditions of high light intensity however there exists an excess of excitation energy due to the limitation of the photochemical turnover rate by secondary electron transfer reactions. Most of this energy is dissipated by radiative (fluorescence) or non-radiative (heat) decay of the excited singlet states. However these decay routes are not sufficient for complete dissipation of the excess energy as chlorophyll triplets are formed via intersystem crossing from the singlet state. These triplets by virtue of their long lifetimes (microseconds) could be very reactive. They can react with molecular oxygen, which is also a triplet, and give rise to singlet oxygen,  $O_2(^1\Delta_g)$  which causes irreversible photodestructions. In order to prevent these harmful reactions nature has instituted a "safety valve" in the form of accessory pigments called carotenoids [25-28].

Protective action is offered in two ways:- The first involves energy transfer from chlorophyll triplet to the carotene :



Formation of  $^3\text{carotene}$  can be monitored at 520 nm. The second safety measure is the reaction of carotenoids with singlet oxygen:-



#### 1.6 Structure of the Reaction Center and Reaction Centre Models

The high efficiency of biological light energy conversion is almost certainly based on the arrangement and structure of the pigments within the reaction centre proteins. It is only in the last five years that photochemically active crystalline photosynthetic reaction centres have been made available for X-ray crystallography [29-31]. The reaction centre crystals characterised by crystallography were those of the purple photosynthetic bacteria Rhodospseudomonas viridis. A model of the arrangement of the pigments is shown in Fig. 1.5. The most prominent feature the spatial arrangement of the BChl b and BPh b is the approximate two-fold rotation symmetry.

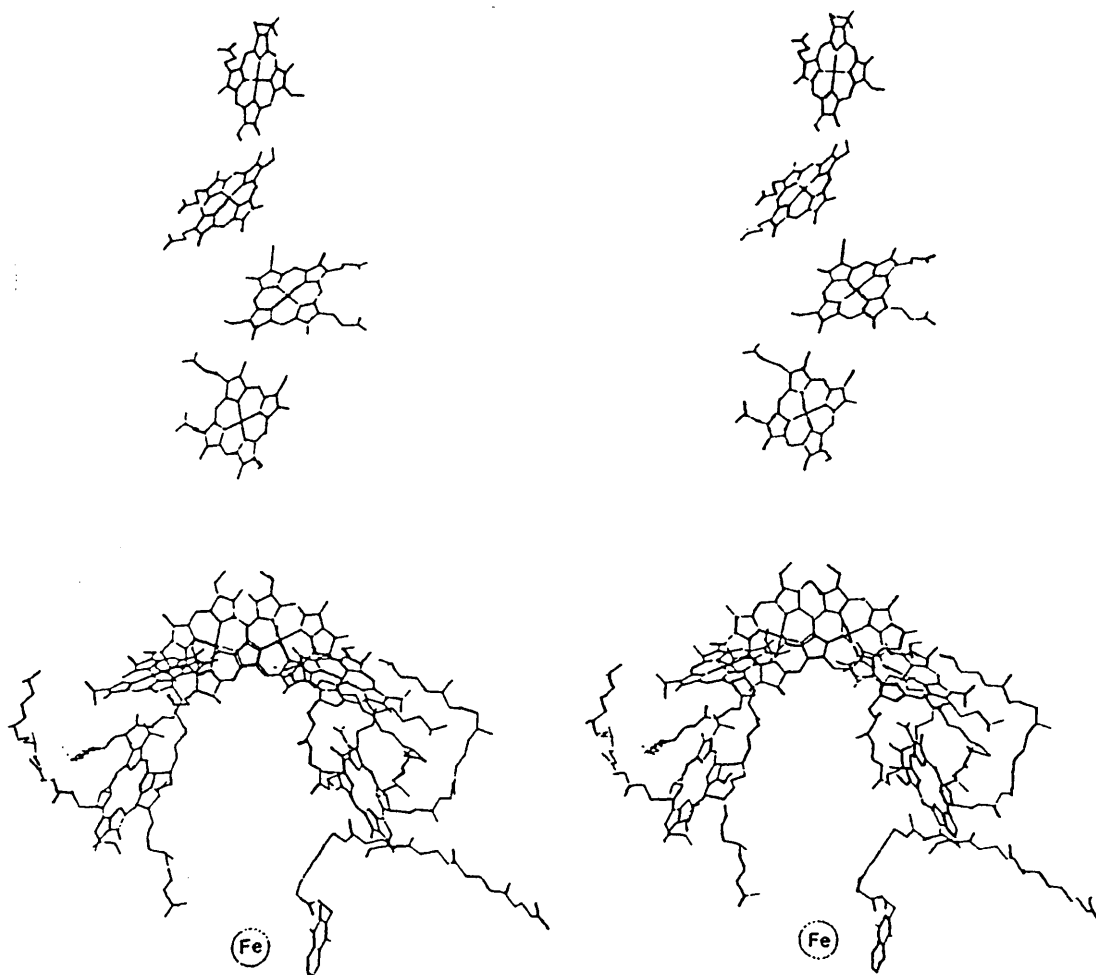


FIG. 1.5a

Stereo drawing of the prosthetic groups of the RC showing 4 BChl-b (BC), 2BPh-b (BP), 1 non-heme iron (Fe), 1 quinone (MQ) and 4 heme groups (HE). The central local symmetry axis runs vertically in the plane of the picture. The plane of the membrane is assumed to be oriented perpendicular to the central local symmetry axis, i.e. horizontal and perpendicular to the plane of the picture. The dotted lines marked O and I indicate the presumed approximate outer and inner membrane surfaces of the bacterial cell. (Reproduced from ref. 32).

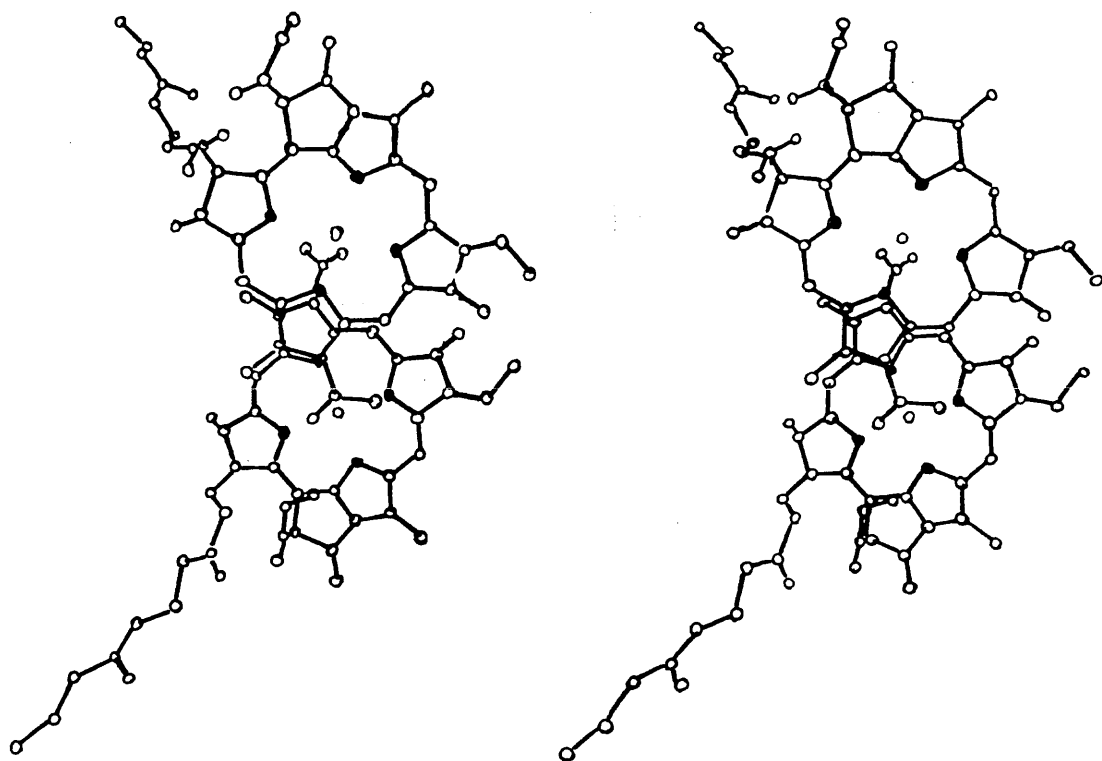


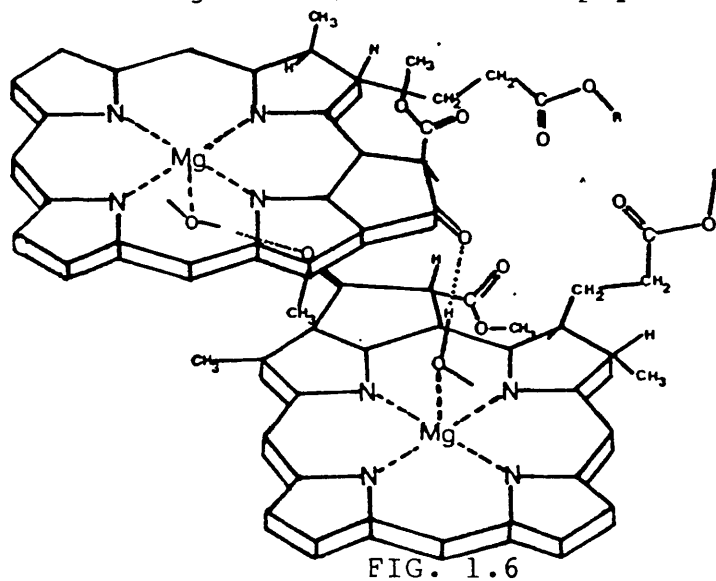
FIG. 1.5b

Stereo drawing of the special pair. The central local symmetry axis runs horizontally between the BChl-bs. Ring numbers are indicated in one BChl-b. Phytol chains are truncated. (Reproduced from ref. 32].

The rotation axis runs through the nonheme-iron atom and two associated BChl-b molecules, whose pyrrole rings I (see also Fig. 1.5b) are stacked on top of each other. The average distance between atoms of one of these pyrrole rings to the plane of the other ring is about 3 Å. Interestingly, the acetyl groups of rings I are in direct contact with a Mg atom of the other BChl-b in the pair. The distance between the BChl-b Mg ion is approximately

7 Å, the angle between the ring planes is  $\sim 15^\circ$ . This structure is interpreted as the "special pair" which was postulated on the basis of results of spectroscopic investigations [33,34]. To each BChl-b of the special pair another BChl-b is associated with Mg-Mg distances of  $\sim 13$  Å and angles between the tetrapyrrole planes of about  $70^\circ$ . Each of these monomeric BChl-b is in contact with a BPh-b. The distances are  $\sim 11$  Å, the angles between the ring planes  $\sim 64^\circ$ . From the non heme iron atom four strong electron density connections extend to four helices of the protein. Menaquinone is the primary quinone. Since chlorophylls-a and -b from chloroplasts and cyanobacteria do not possess an acetyl group at pyrrole ring I, the primary donors in photosynthesis of plants and cyanobacteria may also be different.

Some of the first RC models were put forward by Shipman et al. [35] and Boxer and Closs [36]. In the model below (Fig. 1.6), the chlorophyll macrocycles are



Chlorophyll special pair model of Shipman et al. [35].



In search for a more complete model of a R.C., it is necessary to attach electron donors, acceptors and an antenna. Later work from Shipman and co-workers [39] developed a structurally well defined model [39] shown in Fig. 1.8.

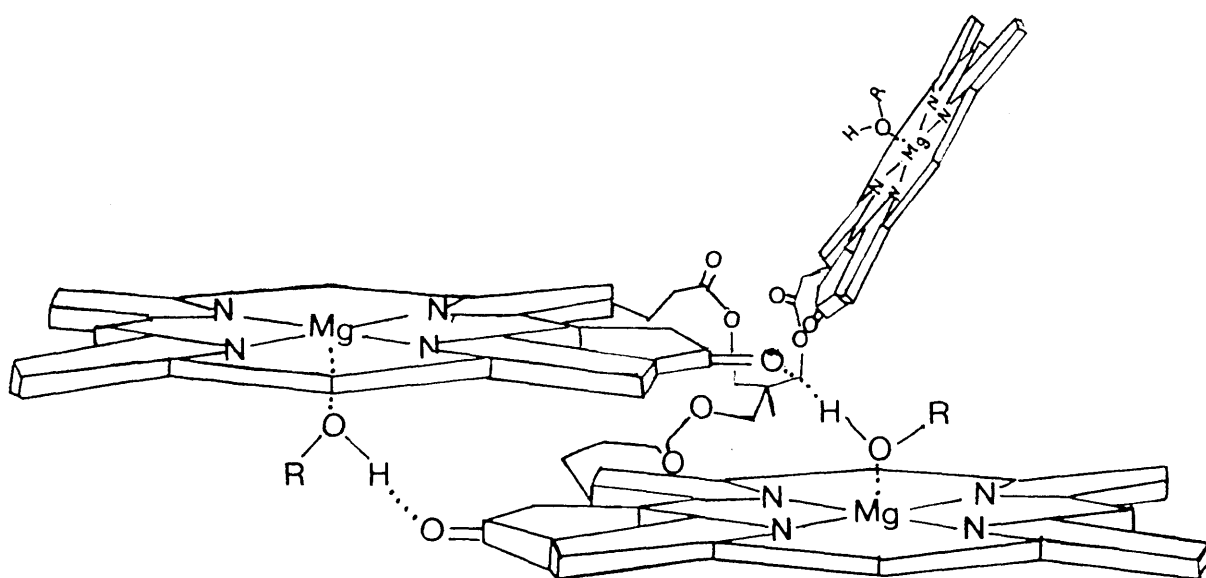


FIG. 1.8

Structure of folded form of covalently linked model to study energy transfer from LHC to a Chl special pair.

When dissolved in a nonpolar solvent to which a small amount of hydrogen-bonding nucleophile has been added, folding occurs between two of the macrocycles whilst the third remains free. The two macrocycles in the folded configuration have an absorption maximum at ~700 nm, and the free macrocycle absorbs light of ~665 nm. Thus the free macrocycle stands in the position of an antenna relative to the cross-linked pair.

### 1.7 Mechanisms of energy transfer

Energy transfer is usually observed as the deactivation or quenching of one excited state with the corresponding promotion of another molecule to an electronically excited state. One of the great contributors to the theory of electronic energy transfer was Theodor Forster [40]. The process of emission from one molecule followed by absorption in another can occur at large molecular separations because a photon can travel long distances: the probability of a photon interacting with any particular molecule is proportional to  $4\pi r^2$ . Forster showed that a comparatively weak interaction between two molecules could be sufficient for transfer to occur provided some kind of resonance condition is fulfilled. After absorption of light, vibrational relaxation occurs very rapidly in solution and then resonance between the transitions in the two molecules will bring about a transfer of energy, providing some coupling between them is present. The process is

schematically shown in Fig. 1.9. The coupling is strongest if the corresponding electronic transitions in the two molecules are allowed for electric dipole radiation. As the dipole-dipole interaction depends on the third power of the separation of the two molecules and the probability of transfer is proportional to the square

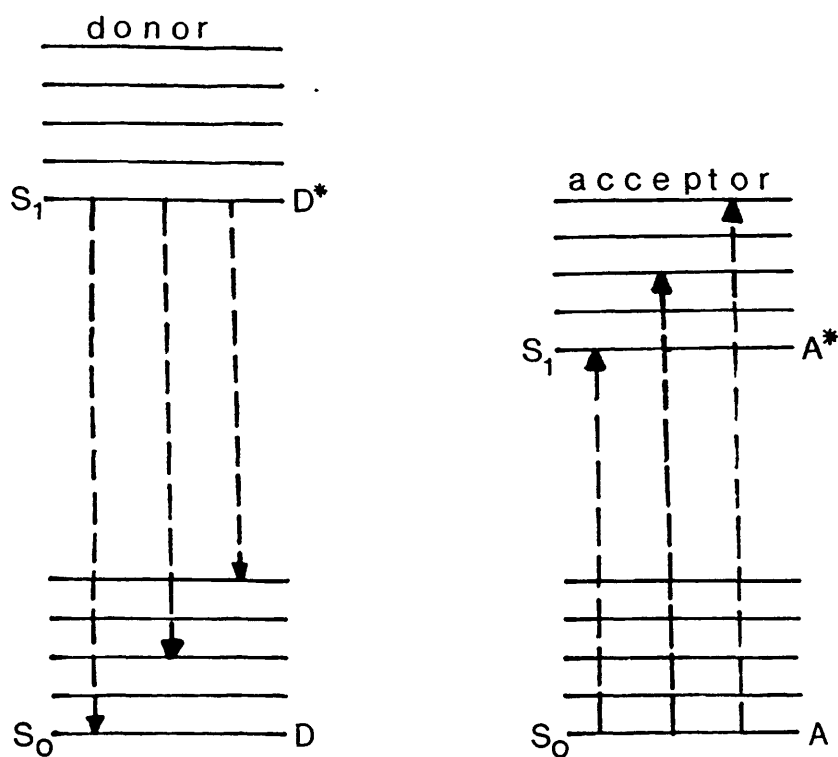


FIG. 1.9

Schematic diagram of long-range non-radiative energy transfer between excited donor ( $D^*$ ) and ground state acceptor ( $A$ ). This is also called resonance energy transfer because the energies of the coupled transitions have to be identical.

of this interaction energy, the energy transfer probability becomes dependent on the sixth power of the distance. Thus for quenching of a molecule D by an acceptor A at separation  $R_i$ , the quenching rate constant  $k_Q(\text{sec}^{-1})$  is given by:

$$k_Q = \frac{1}{\tau_0} \left( \frac{R_0}{R_i} \right)^6$$

where

$$R_0^6 = \frac{(9000 \ln 10) K^2}{128 \pi^5 n^4 N} \phi_f \int_0^\infty \frac{f_D(\nu) \epsilon_A(\nu)}{\nu^4} d\nu$$

where  $n$  is the refractive index,  $N$  is the Avogadro number,  $\phi_f$  is the fluorescence quantum yield and  $K^2$  is an orientation factor. The value of  $K^2$  in fluid solution it has an average value of  $2/3$ . The terms after the integral give the overlap between the emission of the donor and the absorption of the acceptor. The whole term is called the overlap integral  $J_{DA}(\text{cm}^6 \text{ mol}^{-1})$ :

$$J_{DA} = \int \frac{F_D(\nu) \epsilon_A(\nu)}{\nu^4} d\nu$$

where  $f_0(\nu)$  is the relative fluorescence of the donor at wavenumber  $\nu$  and  $\epsilon_A$  is the molar extinction coefficient

of the acceptor. The area under the fluorescence spectrum is normalised.  $R_0$  is defined as the distance at which probability of emission and energy transfer are equal values lie typically in the range 4-7 nm.

## 1.8 Electron transfer

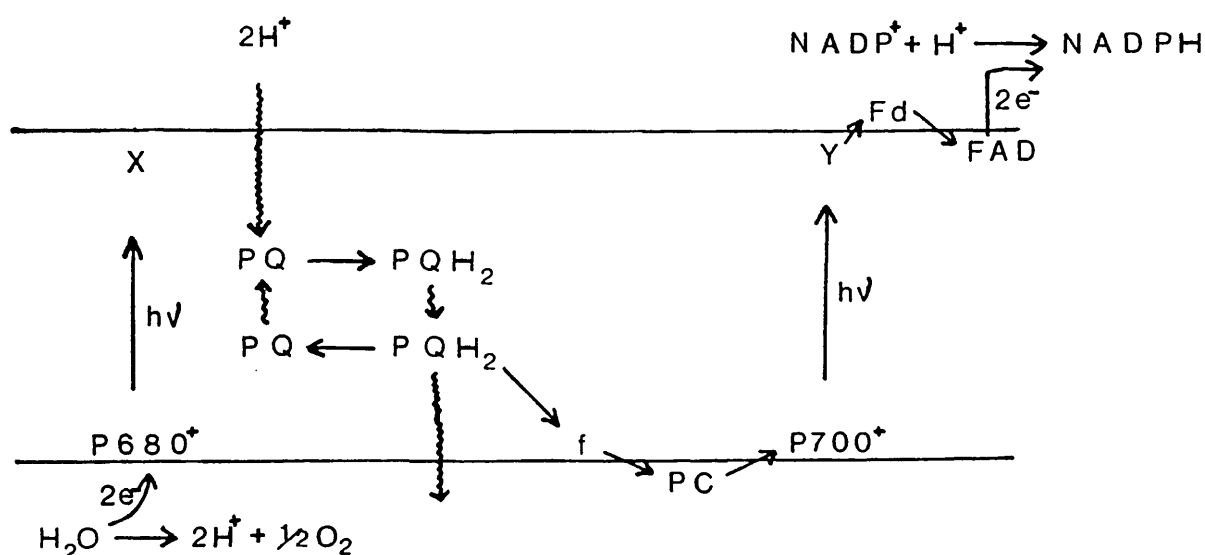


FIG. 1.1.0

Simplified photosynthetic electron-transfer chain showing the positions which the components are thought to occupy in relation to the thylakoid membrane. P680<sup>+</sup>, P700<sup>+</sup> are chlorophyll pigments of photosystem II and I respectively and X and Y are their primary electron acceptors; PQ = plastoquinone; PQH<sub>2</sub> = plastoquinol; f = cytochrome f; Pc = plastocyanin; Fd = ferridoxin; FAD = flavin adenine dinucleotide.

Fig.1.1.0 shows a simplified version of the electron transfer chain in photosynthesis. However it is still a bit too ambitious to model on a laboratory scale. Nature has perfected the scheme such that all the components involved lie in exactly the right position and along an electrochemical gradient such that back electron transfer is minimised. In the in vitro experiments it is typical to model just a very small piece of the overall unit e.g. a porphyrin and an electron acceptor to model the step  $P680^+ \rightarrow X$  shown in Fig.1.1.0 Research then tries to optimise the conditions to improve the rate and yield of electron transfer and at the same time prevent the back reaction which is still very much of a problem in such systems. The ensuing pages aim to give some outline of the various parameters which effect the rate of electron transfer and also give some idea about the types of systems studied.

### 1.9 Theory

"Occasionally as scientists we have the good fortune to stumble onto problems whose significance and solution turn out to be more far reaching than may have been anticipated at the time". These are the words of R.A. Marcus [41] who made his first contributions to electron transfer theory almost 30 years ago. Most explanations of the theory make use of two intersecting parabolas as shown in Fig.2. The parabolas represent a one dimensional profile of the potential energy vs. reaction coordinate

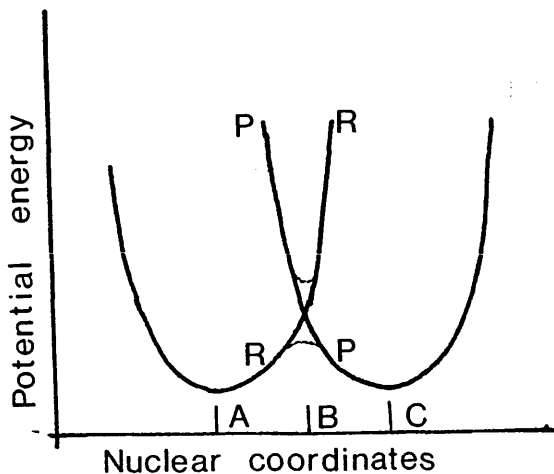


Fig.1.1.1.1. Profile of many dimensional potential surface of reactants plus surrounding medium (R) and that of products plus medium (P). Dotted lines indicate splitting due to electronic interaction of reactants. A and C denote nuclear coordinates for an equilibrium configuration

of reactions and for products respectively; B denotes nuclear configuration at the intersection of the two potential-energy surfaces. Taken from ref [42].

for reactants (R) and products (P). For electron transfer to occur in solution the reactants must first be brought into proximity with one another to enhance coupling between the electronic orbitals. This process is generally diffusion-controlled where the rate of diffusion is given by the expression:-

$$D = kT/6\pi r\eta, \quad (1)$$

where  $k$  = Boltzmann's constant,  $T$  = temperature,  $r$  = hydrodynamic radius of diffusing species and  $\eta$  = viscosity.

In fact viscosity of the solution can be shown to affect the rate of the reaction [43] and becomes a limiting factor especially where reactions take place within a polymer matrix [44]. Once the reactants are brought together the barrier to electron transfer is a matter of intrinsic ( $\lambda$ ) and thermodynamic ( $\Delta G$ ) parameters. The intrinsic factors involve rearrangement of the solvent sphere from the equilibrium position of the reactants to those of the products and are a function of the change in nuclear configuration. Thus for example in the self exchange reaction of cobalt hexamine



the intrinsic factors are quite substantial as the nuclear radius changes drastically on going from  $\text{Co}^{2+} \rightarrow \text{Co}^{3+}$  and vice-versa. The above applies more specifically to what is termed as 'outer sphere electron transfer' and describes a system where the reactants do not share a common bond or where electronic overlap between the reactants is weak. In 'inner sphere electron transfer' the rate is generally not diffusion controlled. Where overlap between electronic orbitals is small the rate is also governed by the fact that the electron is such a light particle. In such instances i.e. outer sphere electron transfer, the Franck-Condon principle has to be applied. This states that during electron transfer the nuclei do not have time to change either their positions

or momenta. Thus electron transfer will only occur at positions along the reaction coordinate in Fig.2 where the total potential energy of the reactants and surrounding medium equals that of the products i.e. at the intersection. Once this point is reached the transition from R  $\rightarrow$  P depends on factors such as the electronic coupling which in turn is dependent upon the separation distance of the reactants.

#### 1.1.0 Calculation of rate constant

In the classical treatment the rate of electron transfer involves calculating the probability of reaching the intersection area in Fig.1.1.1 multiplied by a suitably weighted frequency for crossing the intersection and another probability for crossing from the R to the P surface. The resulting equation for bimolecular electron transfer takes the form:-

$$k = K A \sigma^2 \exp(-\Delta G^*/RT) \quad (2)$$

where  $A \sigma^2$  has dimensions of collision frequency;  $\sigma$  = average center to center distance during the transition state;  $\Delta G^*$  = activation energy related to  $\lambda$ ;  $K$  = the transmission coefficient or averaged transition probability for electron transfer through the intersection region at fixed separation distance  $r$  of the reactants.

For a reaction where electronic coupling between reactants is large i.e. adiabatic reactions,  $K$  is assumed

to be unity. At large separation distances  $r$ ,  $K$  varies as  $\exp(-ar)$ . As mentioned previously the activation energy is governed by intrinsic and thermodynamic factors and can be written as:-

$$\Delta G^* = w^r + \lambda/4(1 + \Delta G^0/\lambda)^2$$

where  $\Delta G^0 = \Delta G^0 + w^p - w^r$  (3)

$\lambda$  are the intrinsic factors

where  $w^r$  and  $w^p$  is the work required to bring the reactants and products to their mean separation distance. In biological systems the electron donors and acceptors are generally fixed at a specific distance and orientation and equation (2) can be rewritten for a first order rate constant as:-

$$k = K(r)v \exp(-\Delta G^*_r/RT) \quad (4)$$

and  $\Delta G^* = \lambda/4[1 + \Delta G^0/\lambda]^2$

where  $r$  = distance and  $v$  has the units of frequency ( $s^{-1}$ ).

#### 1.1.1 Quantum mechanical treatment

In the quantum mechanical treatment the rate of electron transfer at fixed  $r$  is given by

$$k = 2\pi/h H_{AB}^2 (FC) \quad (5)$$

where  $H_{AB}$  is the electronic matrix element describing the electronic coupling of the reactants' electronic state

with that of the products. It is equal to one-half the separation of the dotted curves at the intersection in Fig.2. (FC) is the Franck Condon factor and it is a sum of products of overlap integrals of the vibrational and solvational wavefunctions of reactants with products weighted by Boltzmann factors.

If the solvent molecules are treated as a collection of oscillators then eq(5) can be rewritten as:-

$$k = \frac{2\pi}{h} H_{AB}^2 \sum_{\nu_r, \nu_p} (FC)_{\nu} P(\nu_r) \quad (6)$$

where  $FC_{\nu}$  is the Franck Condon vibrational overlap factor for a given set of vibrational quantum numbers  $\nu_r$  of the reactants' and  $\nu_p$  of products,  $p(\nu_r)$  is the probability of finding the system in the vibrational state  $\nu_r$ , and the sum is over all  $\nu_r$  and  $\nu_p$ .

In this form however the equation is difficult to solve. In order to simplify this we usually introduce some limiting parameters. Mostly these are classical. Thus in this case when all the degrees of freedom are treated in the classical limit  $h\nu_i/2kT \rightarrow 0$ , and when all frequency changes are relatively unchanged and can be neglected then we can write [42,45,46]

$$\sum (FC)_{\nu} p(\nu_r) = (4\pi kT\lambda)^{-\frac{1}{2}} \exp [-(\Delta E + \lambda)^2 / 4kT\lambda]. \quad (7)$$

Thus eq(6) becomes

$$k = \frac{2\pi}{h} \frac{H_{AB}^2}{(4\pi RT)^{\frac{1}{2}}} e^{-(\Delta E^0 + \lambda)^2 / 4\lambda RT} \quad (8)$$

This form resembles the classical expression except that it contains energy terms rather than free energies since we have assumed that changes in entropy are small. In the high temperature region however we can adapt eq(8) to:-

$$k = \frac{2\pi}{h} \frac{H_{AB}^2}{(4\pi\lambda RT)^{\frac{1}{2}}} e^{-(\Delta G^0 + \lambda)^2 / 4\lambda RT} \quad (9)$$

The resemblance to the classical expression is now very clear. The exponential term is identical i.e.

$$\begin{aligned} \exp^{-\Delta G^*/RT} &= \exp^{-(\lambda/4[1+\Delta G^0/\lambda]^2)/RT} \\ &= \exp^{-(\Delta G^0 + \lambda)^2 / 4\lambda RT} \end{aligned}$$

and hence we can equate the pre-exponential terms in eqns(4) and (9) i.e. the classical and semi classical:-

$$K(r)v = 2\pi \frac{H_{AB}^2}{h(4\pi\lambda RT)^{\frac{1}{2}}} \quad (10)$$

As both  $H_{AB}^2$  [47,48,49] and  $K$  decrease exponentially for many systems the above can be simplified to:

$$K(r)v = 1 \times 10^{13} \exp[-\alpha(r-r_0)]s^{-1} \quad (11)$$

where  $r_0$  is the value of  $r$  at which  $Kv = 1 \times 10^{13}s^{-1}$ . This value is a typical frequency for motion of nuclei along the reaction coordinate.

This thesis is concerned with adapting this equation to deal with electron transfer to or from porphyrins. These are non-spherical molecules and the distance we are interested in is the edge to edge distance of the  $\pi$  orbitals on the respective porphyrins. Thus eq(11) becomes

$$Kv = 1 \times 10^{13} \exp(-\alpha r)s^{-1} \quad (12)$$

Where there is strong overlap between the two porphyrins involved  $K = 1$ , i.e. the reaction is adiabatic.  $\alpha$  is a constant which is placed at around  $12nm^{-1}$  for aromatic molecules, and usually has a lower value if an excited state is involved. Hence when we deal with excited state porphyrins we usually use a value of  $\alpha \approx 8.8nm$  as can be seen in Chapter V.

#### 1.1.2 Dependence of $k$ on $\Delta G^*$

The relation between  $K$  and  $\Delta G^*$  as seen from eqs(4) and (7)-(9) suggests that  $K$  increases with increasing  $\lambda$ ,

then reaches a maximum after which  $K$  decreases with further increase in  $\lambda$ . This is known as the inverted effect. In fact the exponential term has Gaussian shape characteristics. Fig.1.1.2 shows a plot of the expected relationship for the Marcus theory and also a plot of results obtained experimentally by other groups notably that of Weller [50].

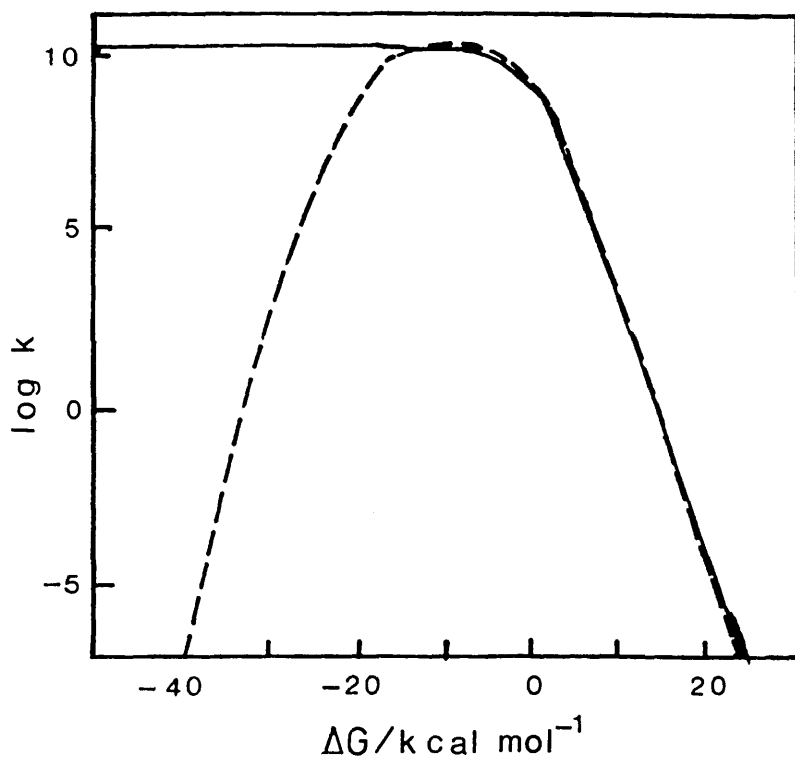


FIG. 1.1.2

Rehm-Weller (—)  
and Marcus (- - -)  
plots for  
 $\Delta G^* = 2.4 \text{ kcal}$  (Taken  
from ref.50)

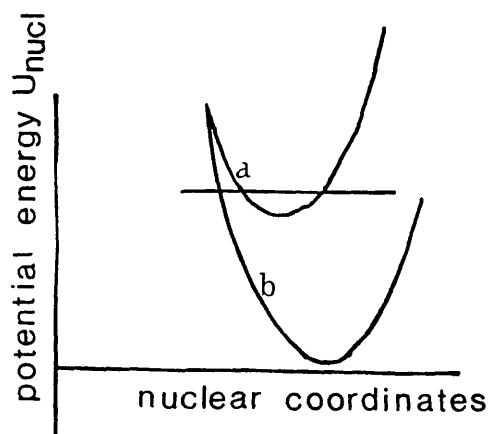


FIG. 1.1.3

Nuclear tunnelling  
in a highly  
exothermic reaction  
from a to b (Taken  
from ref.42)

The inverted effect corresponds to lowering the P surface vertically or raising the R surface. The intersection of the R and P surfaces eventually occurs at the minimum of the R surface such that there is no barrier whilst further lowering raises the point of intersection again as shown in Fig.1.1.3. Thus the expected rate dependence is due to simultaneous requirements for conservation of energy and nuclear position during electron transfer.

Unfortunately most experimental studies in solution have failed to prove the existence of the inverted region at high exothermicities [51-54]. The rate constants reached a maximum at the diffusion controlled limit and remained constant over further increases in exothermicities. The first data to support the electron transfer theories were published only recently [55,56]. In that study the donor and acceptor were separated by rigid hydrocarbon spacers and radical anions were generated by pulse radiolysis. Using other appropriate spacers they were also able to show the effect of rate on distance and prove it decreased exponentially ( $k(v) = v \exp(-r/a)$ ) with  $a = 0.83 \text{ \AA}$ . Indeed the rate was shown to be quite large even over large spacer distances.

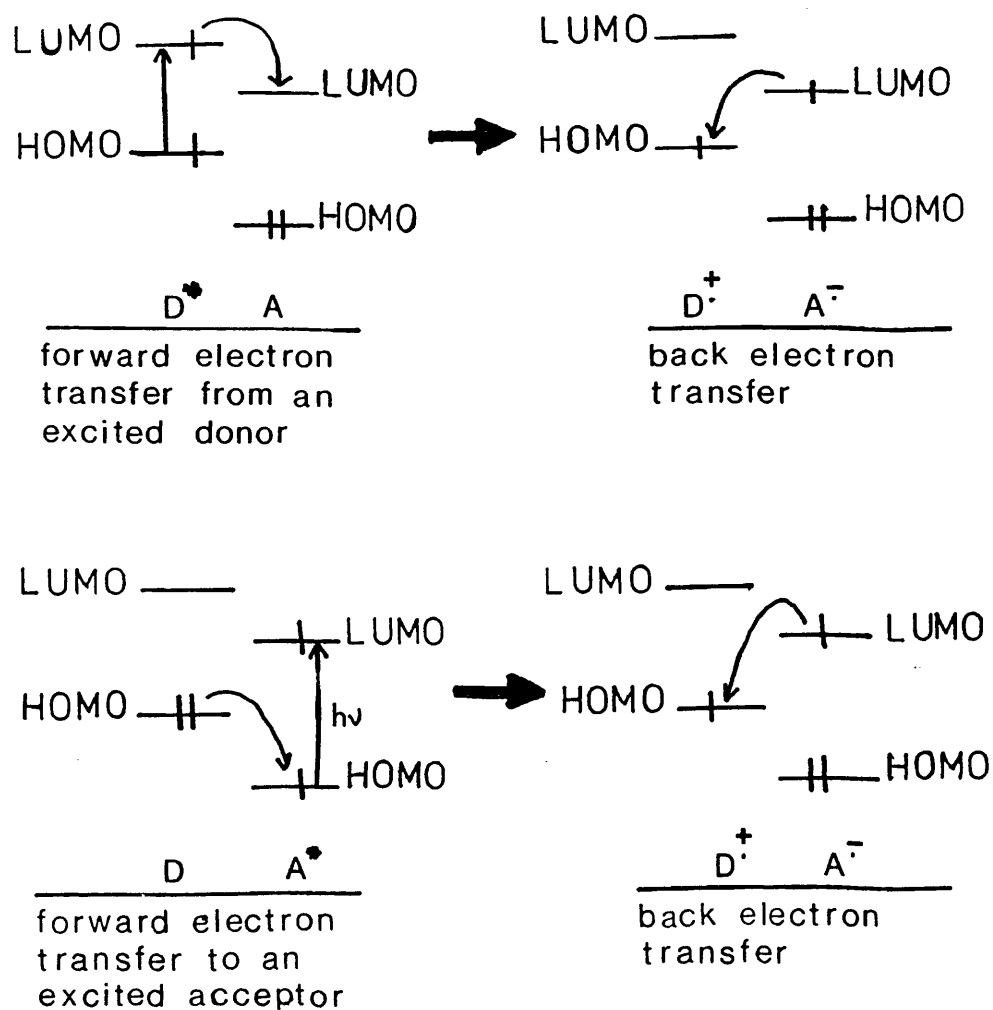
Large distances between redox centres is also quite a common occurrence in nature where electron transfer occurs over distances such as  $15 \text{ \AA}$  [57] and even  $25 \text{ \AA}$  [58]. Another example of long range transfer is in a rigid polymer [59]. The above examples have one thing in common

- their position and conformation with respect to donor and acceptor is fixed. The rates for a transfer are still quite fast and it appears that the inner sphere reorganisational barrier associated with the electron transfer is negligibly small and the implication may well be one of electron tunnelling being involved.

### 1.1.3 Porphyrin related systems

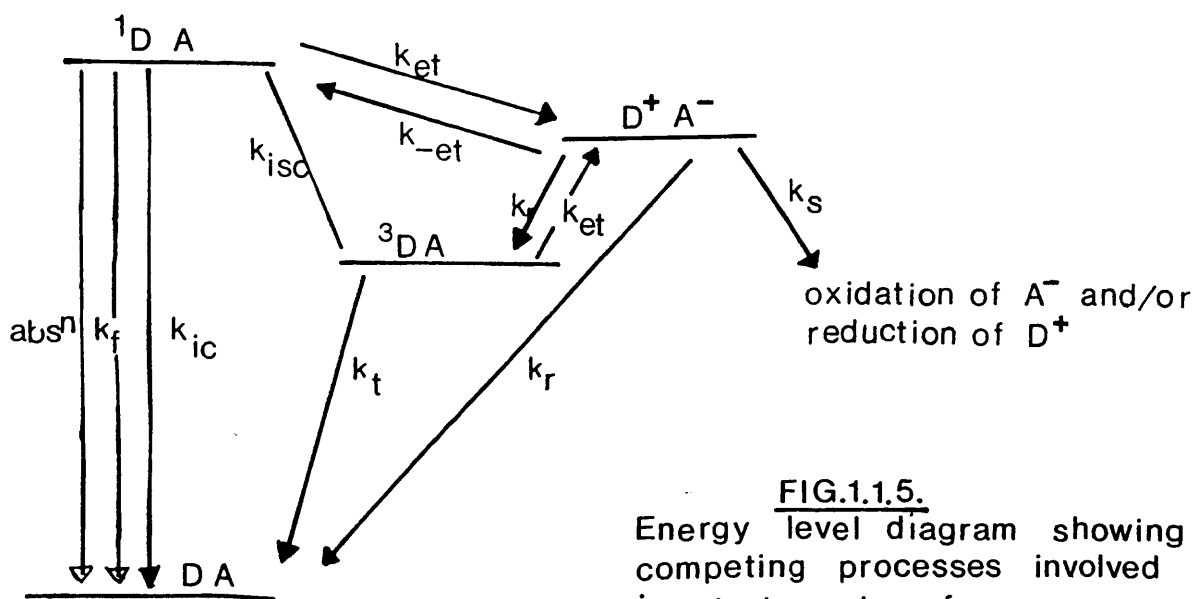
One of the reasons we use porphyrins as redox couples is because their excited states can be used as both reducing agents and oxidising agents as illustrated by the diagram below:-

FIG.1.1.4.



As shown above the barriers for forward and back electron transfer are not the same in photoinduced electron transfer. Thus where the donor is in the excited state the forward reaction is governed by the Donor LUMO  $\rightarrow$  Acceptor LUMO gap whilst the back reaction is determined by the Acceptor LUMO  $\rightarrow$  Donor HOMO gap. If on the other hand the Acceptor is in the excited state the Donor HOMO  $\rightarrow$  Acceptor HOMO gap is involved.

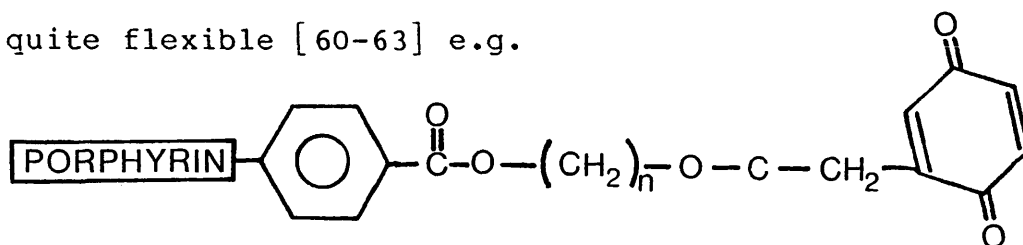
Furthermore in most excited state electron transfer processes the overall forward rate is not only governed by the rate of the back reaction but also by the lifetime of the excited state. The energy level diagram shown below gives some idea of the various competing processes involved:-



Ideally we would like to construct models where  $k_{et} \gg (k_f + k_{ic} + k_{isc})$  and  $k_s \gg (k_r + k_r' + k_{-et})$ .

#### 1.1.4 Examples of models

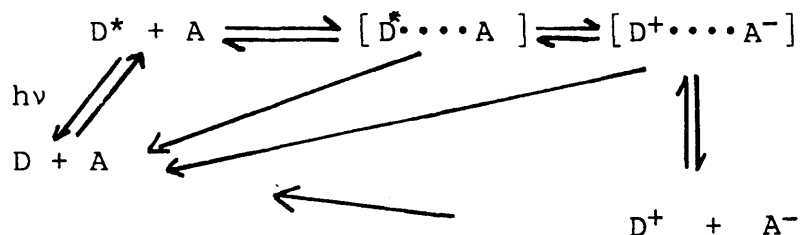
Most of the models synthesised so far have involved attaching an acceptor molecule such as a quinone, viologen or nitro compound to a porphyrin via a covalent linkage. In the first sets of studies these linkages were typically quite flexible [60-63] e.g.



- However electron transfer products were not always observed in these systems and the reason was put down to the conformation of Donor and Acceptor. The situation over the past three years has changed with elegant designs of carefully spaced donor acceptor systems such as [63,65,66] shown on next page.

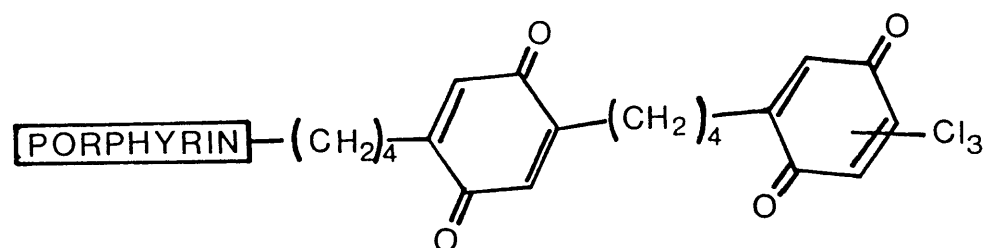
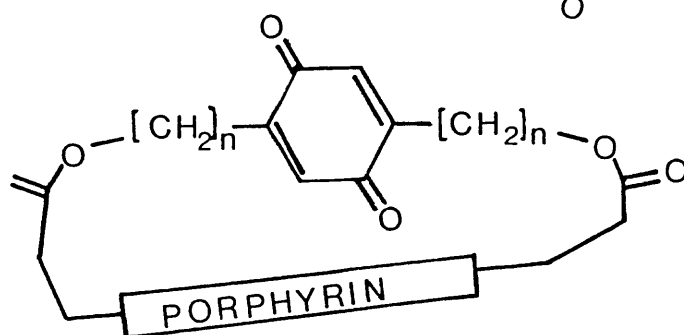
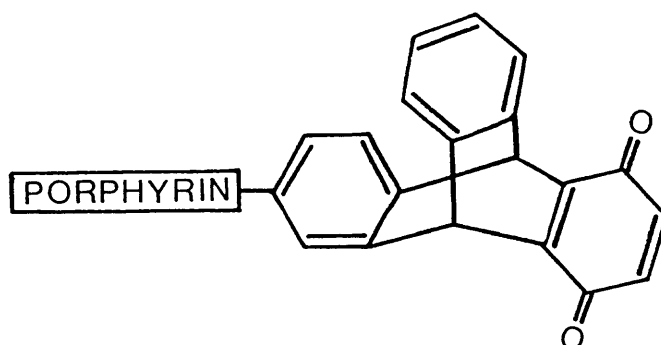
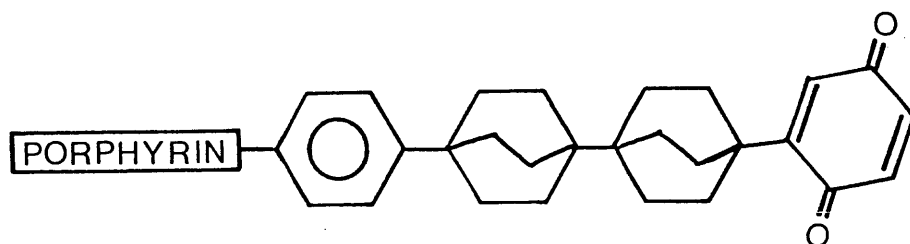
#### 1.1.5 Exciplexes and Electron Donor Acceptor (EDA) Complexes

The scheme in Fig.1.1.5 can be written in the form of an equation as:



As seen one of the intermediates prior to charge separation is a caged ion pair. Sometimes long lived excited state intermediates can be identified and are called exciplexes. The potential energy diagram in

EXAMPLES OF MODELS



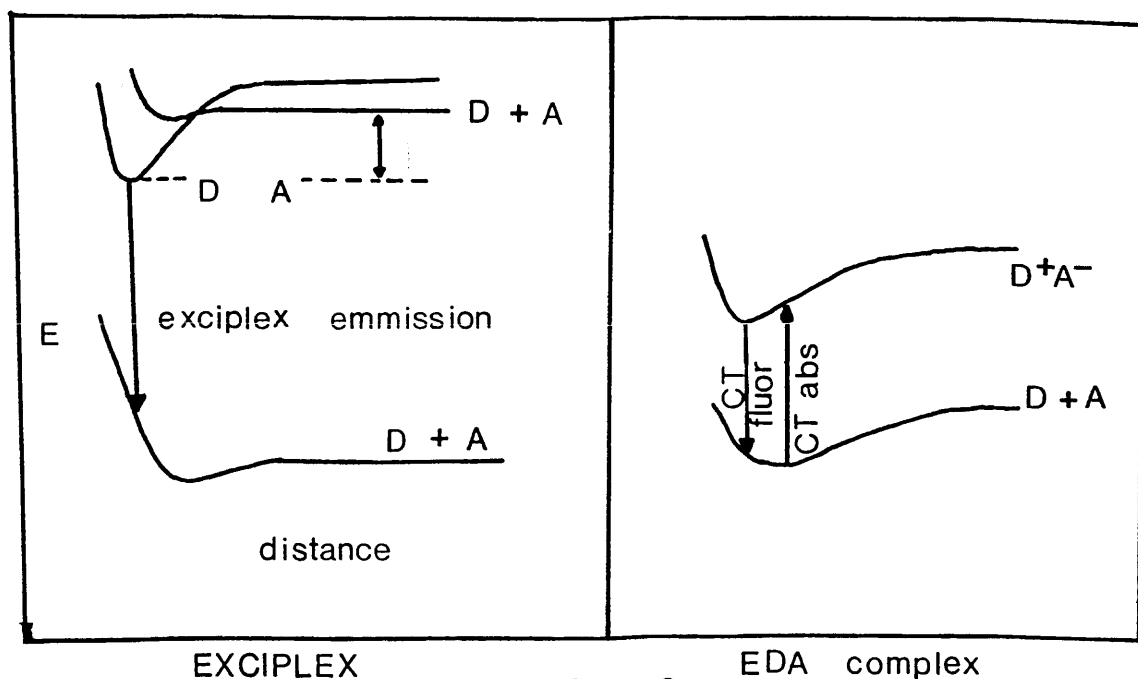


FIG.1.1.6.  
Energy level diagram illustrating the basic difference between an exciplex and an eda complex.

Another type of system where electron transfer is demonstrated is described in Chapter VI.

Fig.1.1.6 illustrates the difference. Typically exciplexes are red-shifted in their emission compared to the monomer. However this need not necessarily be the case as shown in Chapter VI. The components in the exciplex are probably in contact but they could also be described as a pair of ions, individually at equilibrium

with surrounding solvent molecules, bound by coulombic attraction only. Alternatively they could be simply described as a long-lived encounter complex in the excited state. The term exciplex it seems is now an expression for any type of association in the excited state.

#### 1.1.6 Summary

The preceeding pages have described the basis of electron transfer theory. It is not the intention of this thesis to prove the validity of the equations derived but merely to make use of them where necessary and establish a good background to the theory.

#### 1.1.7 Porphyrins

The work described in this thesis uses porphyrins to model photosynthesis. The characteristics of porphyrins are very versatile and are strongly dependent upon the metal in the centre as shown in Table 1.1.

The dominant features of the absorption spectra of metalloporphyrins are intense ( $\pi\pi^*$ ) transitions which occur in the visible region. The most intense band is the B band, which occurs between 400 and 470 nm, and this is the origin of the second ( $\pi\pi^*$ ) excited singlet state. This is illustrated by the spectrum of zinc tetraphenylporphyrin in Chapter III. The nature of the metal in the centre of the porphyrin has a great effect on both the ground state absorption spectra [66-68]. ZnII,

Mn<sup>II</sup> and Ni<sup>II</sup> exhibit very little charge transfer interaction between the metal II and the porphyrin  $\pi$  system and their spectra are assigned to porphyrin ( $\pi\pi^*$ ) transitions. For the remaining first row transition metals however, two other types of excited state need to be considered [69]. These are charge transfer and tripmultiplet. The former involve considerable redistribution of electron density within the metalloporphyrin and may be catagorised as charge transfer between porphyrin and metal, between metal and additional ligands and between porphyrin and ligands. Most apparent of these transitions are those involving the orbitals of the metal ion and the  $\pi$ -orbitals of the porphyrin. Such transitions can be metal $\rightarrow$ porphyrin (from occupied d-orbitals to empty  $\pi^*$  orbitals) or porphyrin $\rightarrow$ metal (from filled  $\pi$ -orbitals to vacant d-orbitals).

With paramagnetic metalloporphyrins, the charge transfer states can interact with the ( $\pi\pi^*$ ) excited states. In the simplest case where the ground state has doublet character,  $\pi\rightarrow\pi^*$  excitation results in formation of two doublets and a quartet. One doublet corresponds to the normal ( $\pi\pi^*$ ) excited singlet mixed with the doublet charge transfer state while the other doublet arises from mixing the charge transfer state with the ( $\pi\pi^*$ ) triplet state [70]. The quartet arises from the spin conversion of the tripdoublet state. Similar, but more complex solutions result when the ground state has a higher spin multiplicity and in such situations the nature and

position of the lowest energy excited states needs to be carefully defined.

The basic concepts underlying all of these results have been well established [66-68]. All chapters in this thesis involve the use of either a free base porphyrin, or a zinc porphyrin, or both, as these two porphyrins appear to be more promising as far as excited state lifetimes are concerned.

#### 1.1.8 Outline of thesis

The photophysical properties of chlorophylls in vivo, such as ground and excited state characteristics, and quenching processes, are not only dependent on their nearest neighbours, but also on the surrounding medium i.e. the membrane environment. Proteins play a great part in controlling both the mutual orientation and separation distance of the pigments, such that the quenching processes are very efficient. This thesis is concerned with modelling the following aspects of the in vivo system:

- 1) The influence of the environment on the ground and excited states of porphyrins. This is tackled in Chapter III where the protein and lipid medium in vivo is modelled by various axial ligands and micelles respectively.
- 2) The effect of various quenchers and the importance of geometric orientation. In Chapter V a zinc porphyrin is covalently linked to a variety of other porphyrins and the quenching characteristics, if any, are studied. The

TABLE 1.1    Some physical properties of porphyrins

| <u>PORPHYRIN</u>     | $\phi_F$           | $\tau_s / \text{ns}$ | $k_{isc} / \text{s}^{-1}$ | $\phi_p$             | $\phi_T$ | $\tau_T$    |   |
|----------------------|--------------------|----------------------|---------------------------|----------------------|----------|-------------|---|
| TPP                  | 0.13               | 13.6                 | $14.7 \times 10^7$        | $4 \times 10$        | 0.82     | 1.5ms       |   |
| Zn <sup>II</sup> TPP | 0.04               | 2.7                  | $3.6 \times 10^8$         | $1.2 \times 10^{-2}$ | 0.88     | 1.2ms       | 5 |
| Ni <sup>II</sup> TPP | $< 10^{-4}$        | 0.25                 | -                         | $< 10^{-5}$          | -        |             |   |
| Mn <sup>II</sup> TPP | $< 10^{-4}$        | -                    | $> 10^{10}$               | $3 \times 10^{-4}$   | -        |             |   |
| Mg TPP               | 0.15               | 9.2                  | $0.9 \times 10^8$         | $1.5 \times 10^{-4}$ | 0.8      |             |   |
| Cd TPP               | $4 \times 10^{-4}$ | 0.065                | 154                       | $4 \times 10^{-2}$   | 1.0      | 0.3ms       |   |
| Pd TPP               | $2 \times 10^{-4}$ | 0.020                | 500                       | $1.7 \times 10^{-1}$ | 1.0      | 430 $\mu$ s |   |
| Hg TPP               | $< 10^{-3}$        | -                    | -                         | $1.0 \times 10^{-4}$ |          |             |   |

contribution of mutual orientation to the quenching is demonstrated by a set of three isomeric systems, consisting of a zinc porphyrin linked to a manganese porphyrin. Energy transfer processes are also shown to take place from a zinc porphyrin to a free base porphyrin where the efficiency of the quenching depends on the separation distance between the two porphyrins. A case of adventitious quenching is shown in Chapter IV where dimerization between porphyrins in solution observed. Finally Chapter VI describes quenching due to electron transfer between octaethyl porphyrins and metal ions.

CHAPTER II  
GENERAL EQUIPMENT

2.1 All aqueous solutions were made up using water which was deionised and doubly distilled from a quartz still.

2.2 Ground state absorption spectra were recorded on a Perkin-Elmer 554 spectrophotometer. Spectra were run at room temperature in quartz cells of path length 0.1 to 10cm.

2.3 Emission spectra were recorded on a Perkin Elmer MPF-4 spectrofluorimeter. Measurements were carried out at room temperature in 1cm path length quartz cells and the fluorescence measured at  $90^\circ$  to the excitation beam.

The wavelength response function of the instrument was corrected according to the method of Argauer and White [72a]. The correction curve thus obtained was stored in a computer programme called "DIGITISE" designed by R.L. Brookfield [72b]. As the name suggests raw data can be digitised and converted to corrected data. Fluorescence quantum yields were determined using the optically dilute method [73]. An optical density of 0.05 at the wavelength of excitation was used. The areas under the corrected spectra were also obtainable from the computer and provided a direct comparison of quantum yields. Fig. 2.1 shows how the spectral profile of ZnTPP is altered after correcting the spectrum.

In fluorescence excitation spectra the spectral range of the ground state molecule was scanned and the fluorescence monitored at a specific wavelength. If the

quantum yield of fluorescence over the spectral range is constant then the absorption and excitation spectra should overlap.

The wavelength response for excitation spectra was corrected by assuming that the absorption and excitation spectra for H<sub>2</sub>TPP monitored for the fluorescence at  $\lambda = 720\text{nm}$  should exactly overlap. Any disparity between the two spectra was the correction factor.

2.4 Gas chromatography measurements were made on a Varian model 920 instrument equipped with a thermal conductivity detector and using Argon as the carrier gas. Hydrogen yields were obtained by removing 50-100  $\mu\text{l}$  samples of the gas phase above the solutions using a gas-tight syringe and injecting the samples into Tandem columns, each 1m long and containing a Linde 5A molecular sieve. The instrument was calibrated by injecting known volumes of hydrogen. For anaerobic experiments, solutions were purged with nitrogen gas for 20 minutes.

2.5 Singlet excited state lifetimes were measured on the single photon counting apparatus using a synchronously pumped mode locked dye laser [74,75] as the excitation source. Excitation was made at 570nm and the time resolution of the instrument was ca. 100ps. I am grateful to Ralph Brookfield for helping me with all the measurements on this apparatus. Further discussion of experimental conditions and results can be obtained from Ralph Brookfield's Ph.D. thesis (University of London) to be submitted.

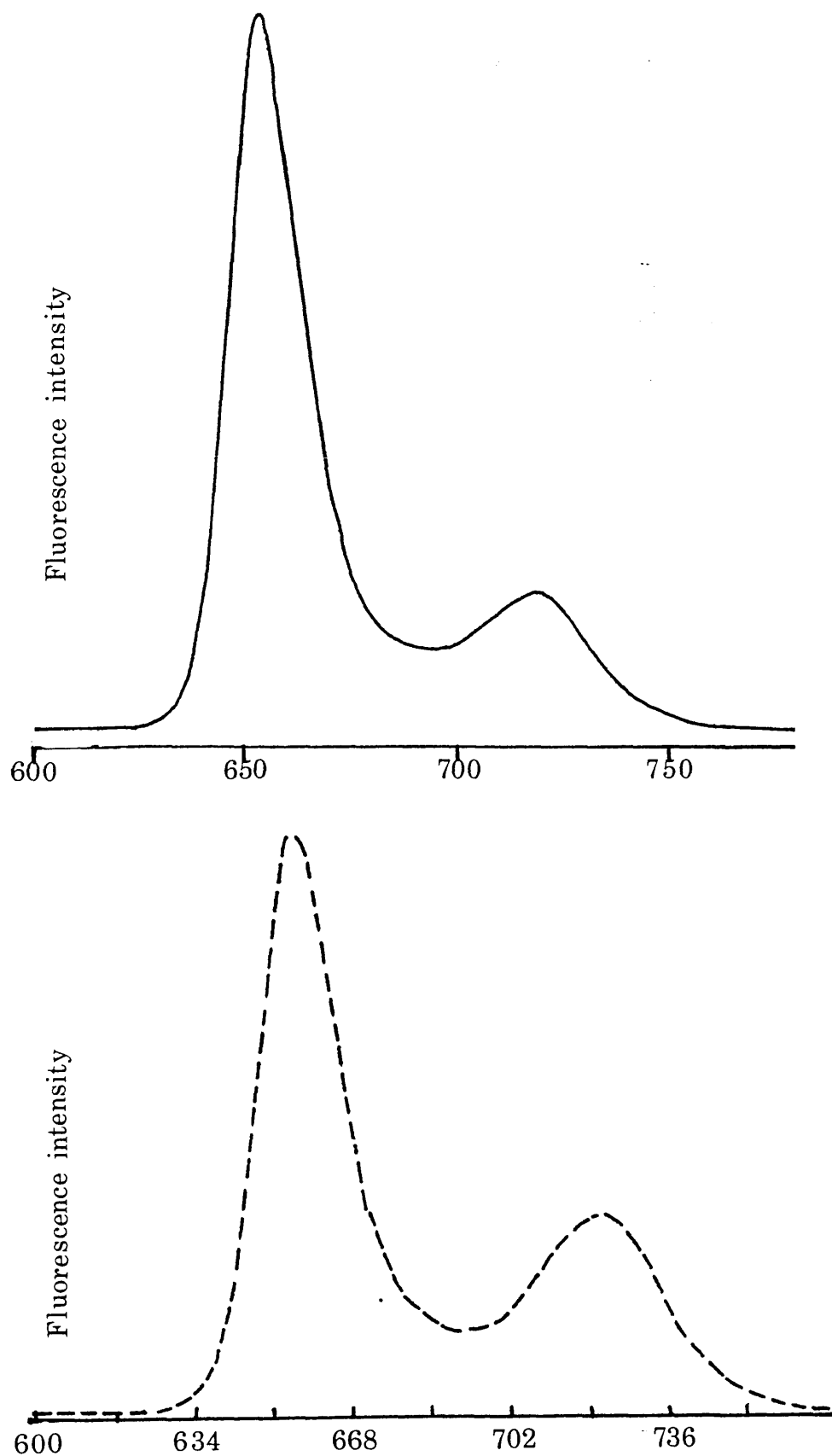


FIG. 2.1

Spectrum of ZnTPP fluorescence before (—) and after  
(- - -) correcting for the photomultiplier response.

2.6 Steady state irradiation. The light source used was an Applied Photophysics quantum yield reactor with a 900W xenon lamp, high radiance monochromater, and cold water Infra-red filter. The illumination was restricted to appropriate wavelengths using glass cut-off filters.

## 2.7 Flash photolysis

An applied photophysics model KN-020 unit was used. The system was set up as shown in Fig.2.2 and was suitable for microsecond kinetic measurements. A 200J capacitor bank (capacitance  $1\mu\text{F}$ ) was charged by an adjustable 25kV power supply. Typically, voltages of 10kV were used, such that the energy discharged via the two xenon flashlamps, in the sample cavity was about 50J. Solution filter jackets containing 10% w/v potassium dichromate placed around the flashtubes were designed to filter excitation wavelengths below 440nm. The sample cell (10cm long, 20mm diameter) lie in between the two flashlamps. The sample cavity was coated with zinc oxide to provide an even illumination on discharge. Iris diaphragms at each end of the cavity limited incident and emitted light. The flash profile is shown in Fig.2.3 and gives a value of  $10^2\mu\text{s}$  for the flash duration. All triplet state lifetimes reported in this thesis are  $>200\mu\text{s}$  and  $<1\text{sec}$ , well above the flash duration time. A 12V/100W quartz iodine lamp provided the monitoring source. Glass filters placed in front of the monitoring light cut off light of  $\lambda < 420\text{nm}$  or  $\lambda < 580\text{nm}$  before passing through the sample.

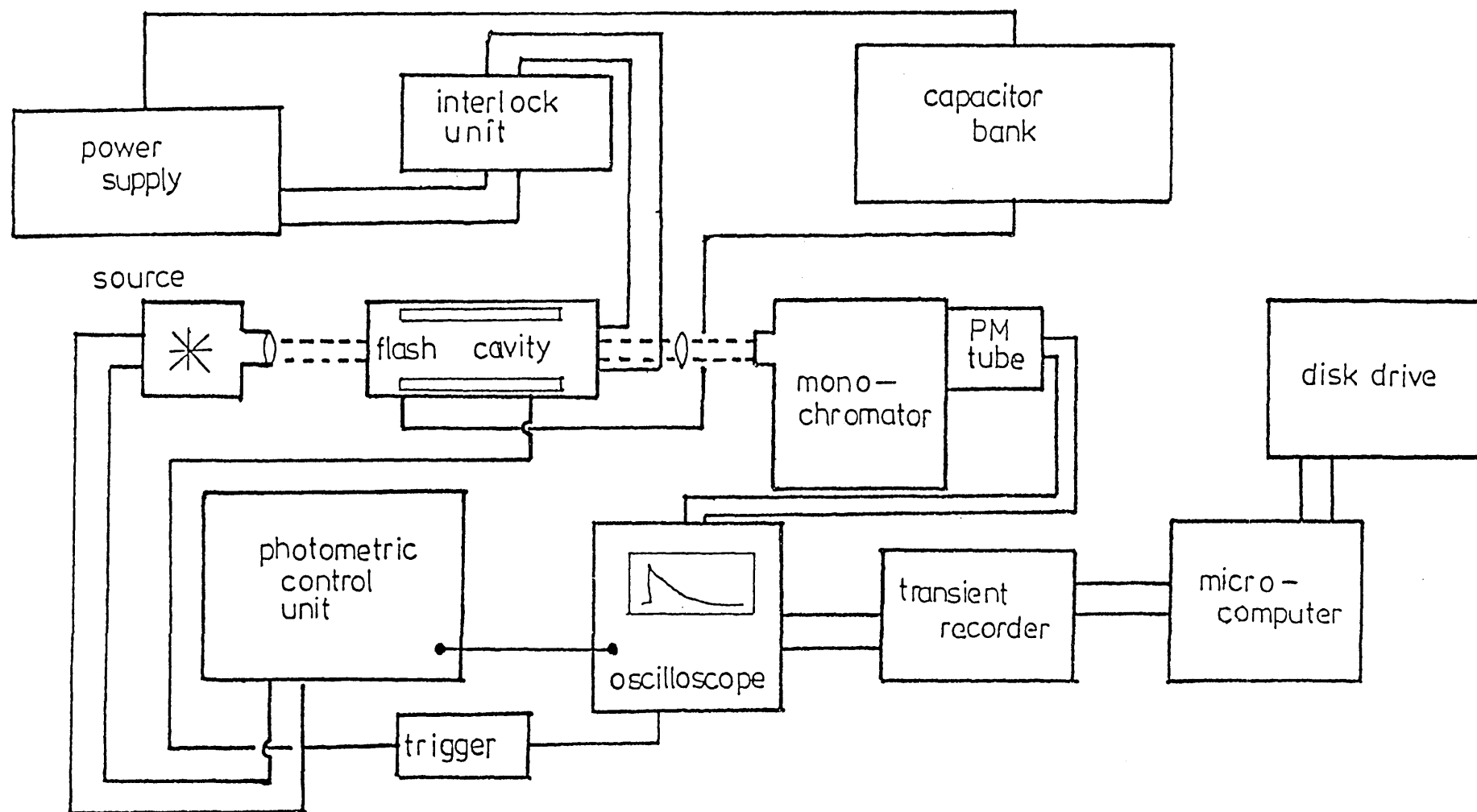


**FIG 2.2.** SCHEMATIC REPRESENTATION OF FLASH PHOTOLYSIS APPARATUS

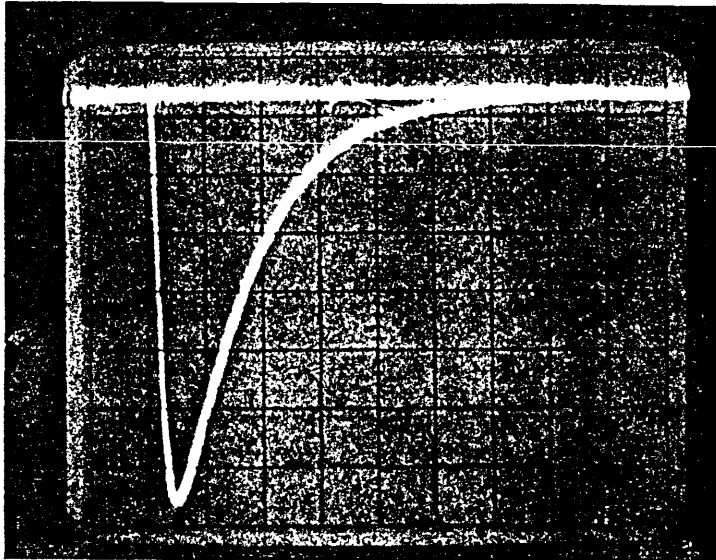


FIG. 2.3  
Flash profile of flashlamps  
in the cell cavity.

All samples were outgassed by the freeze, pump, thaw method until the pressure was less than  $10^{-4}$  Torr.

## 2.8 Analysis of data from flash photolysis

The data were stored in a Datalab DL905 transient recorder prior to analysis by a CBM commodore 4032 computer and the analysed data could be printed out using a Hewlett-Packard 7470A X/Y plotter. For reference, the decay curves were displayed on a storage oscilloscope.

In general, triplet decays follow an equation of the type

$$\frac{-d(^3T)}{dt} = K_1' (^3T) + 2K_2(^3T)^2 + K_3(^3T)(T)$$

$$\text{with } K_1' = K_1 + \sum_i K_i C_i$$

where  $K_1'$  is the measured first order rate constant,  $C_i$  is the impurity concentration (mainly trace oxygen) and  $K_i$  is the corresponding second order impurity quenching constant. However, in well outgassed solutions  $K_1' = K_1$  and this is then the sum of the radiative and radiationless unimolecular decays of the triplet. At low porphyrin concentrations ( $10^{-6} \text{ mol dm}^{-3}$ ) only the first term  $[K_1'(^3T)]$  is important, whilst at higher concentrations the self quenching process ( $^3T + T \rightarrow 2T$ ) becomes dominant. The second order triplet annihilation is significant following large conversions of the ground state to the triplet state. For a unimolecular first

order process, the excited state lifetime  $\tau_T = 1/K_1$  sec. The kinetic measurements for the porphyrins were generally analysed at 470nm where most triplets absorb intensely. In the case of cation radicals, measurements were also made at 680nm, where cation radicals absorb more strongly than triplets.

Triplet absorption spectra were recorded point by point. All the spectra presented in this thesis are reproducible and measurements have been repeated at least three times.

## 2.9 Microsecond flash photolysis studies

A frequency doubled Nd<sup>3+</sup>/glass laser, pulse duration 15ns, maximum energy 150mJ, was used for lifetime measurements between 2 $\mu$  and about 600 $\mu$ s. Solutions of porphyrin for study on this apparatus were adjusted to give an absorbance of 0.15 at 530nm in a 1cm cell. Quantum yields for formation of the triplet excited state were determined relative to tris(2,2'-bipyridyl) ruthenium(II) [76,77] and ZnTPP [68].

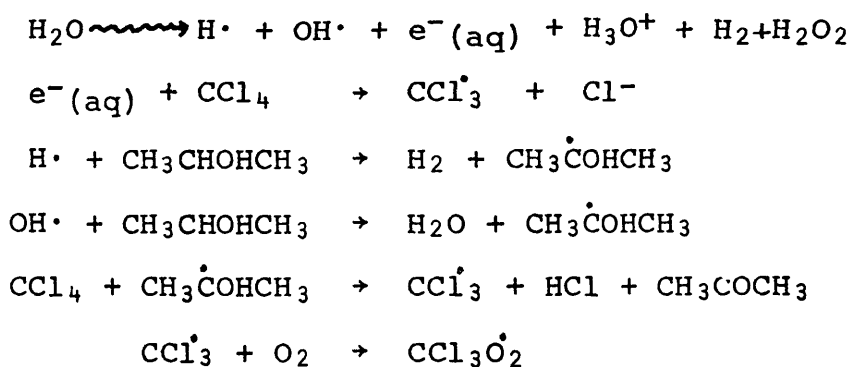
## 2.10 Pulse radiolysis studies

All pulse radiolysis work reported in this thesis was carried out by A. Harriman, while at the Centre for Chemical Physics, National Bureau of Standards, Gaithersburg, U.S.A.

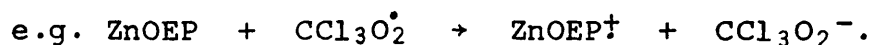
Solutions of porphyrin (about 10<sup>-4</sup>mol dm<sup>-3</sup>) were made up in propan-2-ol (125cm<sup>3</sup>) containing phosphate buffer

( $2 \times 10^{-3} \text{ mol dm}^{-3}$ ) at pH7. The sample was then irradiated with a single 50ns pulse of 2MeV electrons delivered by a Febetron 705 accelerator. The usual dose was 500 rad, as measured by thiocyanate dosimetry [78]; and the concentration of metalloporphyrin  $\pi$ -radical cation ( $\text{MP}^+$ ) formed was monitored at 700nm where the radicals all absorb quite strongly, using a 300W Xe light source and a Bausch and Lomb monochromator (band pass 1nm). Kinetic measurements were made by normal spectrophotometric methods using an irradiation cell of 2cm optical path length. The signals from the photomultiplier were digitised with a Tektronix 7612 transient recorder and analysed with a PD11/34 computer. Cut-off filters were used to protect the sample solutions from undue photolysis.

Radiolysis of the porphyrin solution under the above conditions results in formation of  $\text{CCl}_3\text{O}_2\cdot$  radicals with  $G = 6$  [79]. The following equations describe the sequence of events:



The resulting radicals can oxidise zinc porphyrins in neutral solution:



## 2.11 General materials

Solvents:- Benzene )  
DMF ) gold label purchased from Aldrich  
Pyridine )  
Ethanol - Analar, BDH  
All other solvents were purchased from BDH and were either Spectrosol or Analar quality.

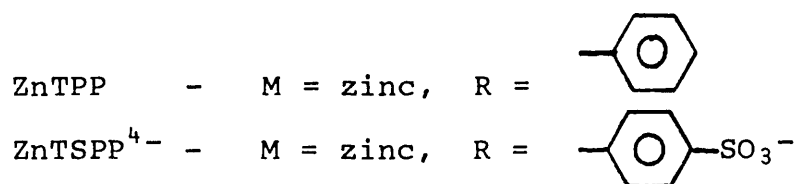
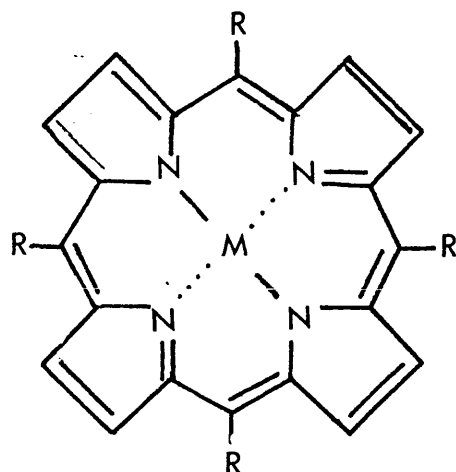
### Micellar media

SLS sodium lauryl sulphate (Sigma) used at  $5 \times 10^{-2} \text{ mol dm}^{-3}$   
CTAC acetyltrimethylammonium chloride (Sigma) used at  $5 \times 10^{-2} \text{ mol dm}^{-3}$   
Igepal used at  $3 \times 10^{-2} \text{ mol dm}^{-3}$ .

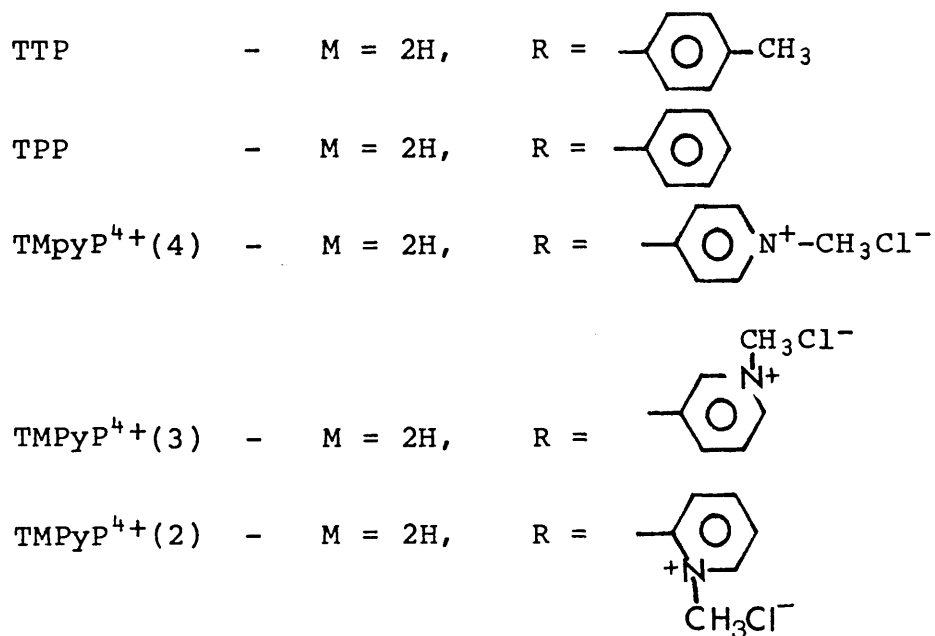
The solutions of micelles were prepared above their critical micelle concentrations. For comparison of the behaviour of porphyrins in different micelle media, identical volumes of concentrated porphyrin solution were added to the appropriate micelle solution in a conical flask. Where the porphyrin was not soluble in aqueous solution, a concentrated solution of porphyrin in benzene was first prepared, and aliquots of this were added to the micelle solution. The benzene was then removed by purging with nitrogen gas.

### Porphryins

All the porphyrins described in this thesis were prepared by A. Harriman. The porphyrins used are described below.



Zinc was inserted into the porphyrin ring by normal methods [80] and the product was chromatographed twice on an alumina column.



The free base porphyrins were purchased from Sigma and used as received.

The covalently linked porphyrin systems described in Chapter V were synthesised by the method of Little and co-workers [81,82].

All other chemicals used were usually of the highest purity.

CHAPTER III

INFLUENCE OF LIGANDS AND HETEROGENOUS MEDIA ON THE  
PHOTOPHYSICS OF PORPHYRINS

### 3.1 Introduction

In the laboratory we are used to seeing porphyrins dissolved in aqueous solution. This, however, is very rarely the situation we encounter in nature. Thus, for example, in haemoglobin the iron porphyrin is associated with a haem protein. A special environment is created so that one distinct chemical event - namely complexation with oxygen [Perutz [83] - can take place and other reactions are prevented from occurring. In cytochromes the protein-made microenvironment has two functions: to protect the haem from unwanted ligands and to adjust the redox potential of the iron to the required level. It is the aim of this chapter to investigate how changes in the environment affect the photophysical properties of the porphyrin. This chapter systematically explains the effect of axial ligands, and micelles on the absorption spectrum, fluorescence spectrum and triplet lifetime of the porphyrin.

### 3.2 Choice of porphyrin for this work

As discussed in Chapter I the photophysical properties of the porphyrin are strongly dependent upon the metal you chose to place in the centre. Table. 1.1 showed how this affected the lifetimes of the porphyrins. Thus paramagnetic species drastically quench both the fluorescence and triplet lifetime of the porphyrin. It is desirable that for the work proposed in this chapter a porphyrin with a reasonable lifetime and fluorescence

yield is chosen so that any changes in these parameters are clearly observed i.e. if the lifetime of the porphyrin is extremely short then any further induced decrease will not be noticed.

Another fact to bear in mind is that the system should be kept as simple as possible. For these reasons zinc porphyrin was the ideal candidate. With the metal unambiguously in the 2+ oxidation state, the four coordinate zinc porphyrin will theoretically accept only one axial ligand to form five coordinate complexes, and since the electronic configuration is  $d^{10}$  there are no empty d orbitals involved in bonding.

### 3.3 Choice of solvent

In order to judge the effect an axial ligand has upon the porphyrin it is advisable to choose a completely non coordinating solvent. This is actually quite hard to do in practice as even a relatively inert solvent such as benzene shows dipole induced dipole interactions due to the high electron density on both the porphyrin  $\pi$  system and the benzene. Solvents such cyclohexane are unsuitable as most of the axial ligands we choose to study are insoluble in this solvent. The solvents eventually used were chloroform and dichloromethane. In these molecules the chlorine atoms do not form as strong axial ligands as molecules containing oxygen, or nitrogen atoms with lone pairs.

Once an idea of the strength of axial ligands

was established, ethanol was used as a solvent; the ligands having much larger stability constants than ethanol with zinc porphyrin.

### 3.4 Examples of ligands

The simplest ligands one can consider are molecules such as ethanol, pyridine, dimethylformamide, piperidine, tetrahydrofuran, dioxan and so on. These molecules all have lone pairs which form axial ligands by electron donation to the metal. Such systems have been well documented in the literature [84-88], and two effects are observed on addition of such ligands to ZnTPP. [84]

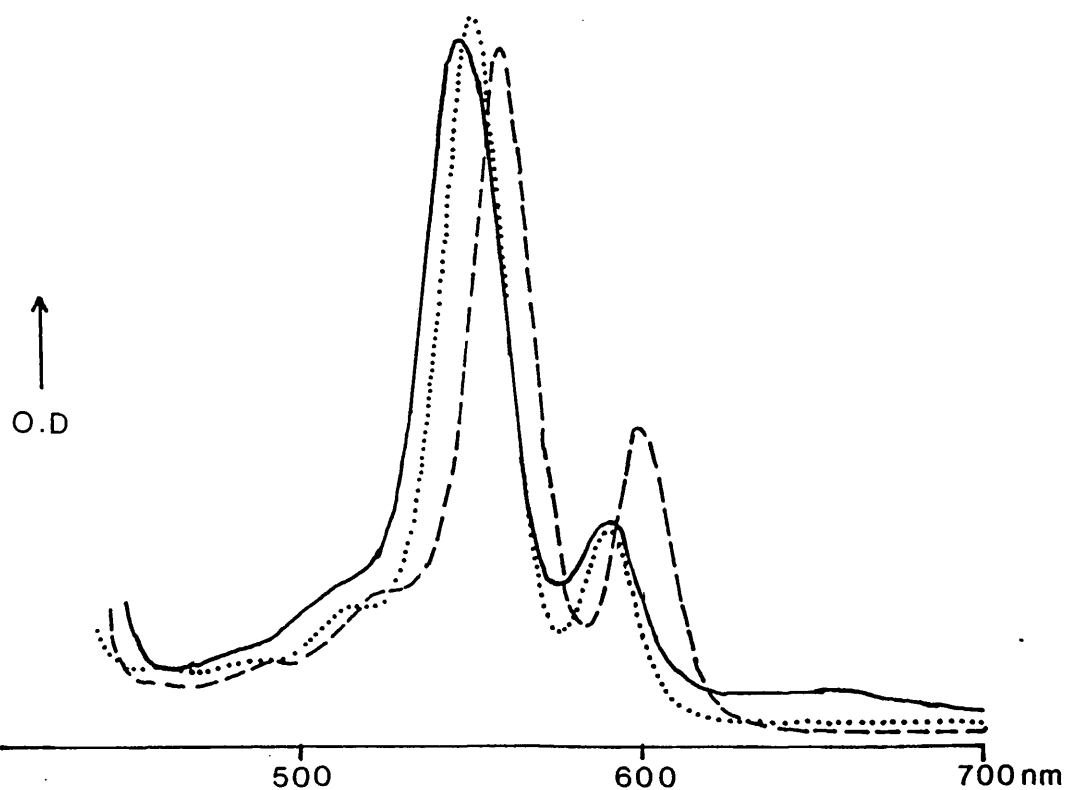


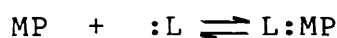
FIG. 3.1

Spectrum of ZnTPP (—); after addition of Dioxan (···);  
after addition of pyridine (- - -).

(1) A shift to the red of the entire absorption spectrum  
 (2) An increase in the ratio of the extinction coefficients  $E_\alpha/E_\beta$  which is proportional to the red shift.  
 Fig.3.1 shows how different ligands affect the absorption spectrum and Fig.3.2 shows how the spectrum changes on stepwise addition of pyridine to a solution of ZnTPP in dichloroethane.

### 3.5 Stability Constants of Ligands with ZnTPP

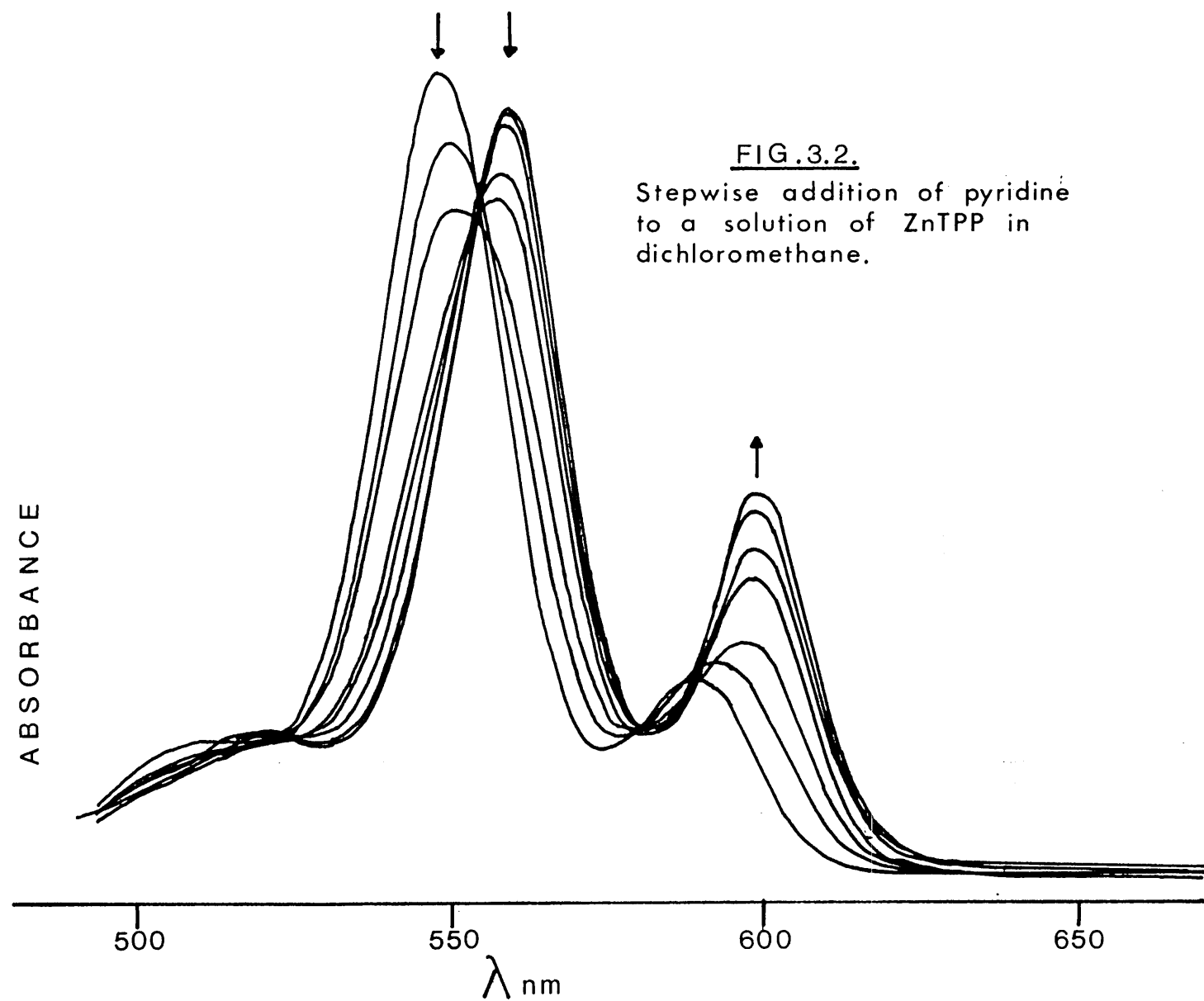
The axial ligands with ZnTPP can be explained in terms of a Lewis Acid (ZnTPP) interacting with a Lewis Base (Neutral Ligands) and can be represented by an equation of the type:-



From data such as that in Fig.3.2 it is possible to determine the number of eg. pyridine molecules which complex with a given metalloporphyrin, as well as the equilibrium constants [87,88,90,91] and thermodynamic factors associated with complex formation [86,89].

Mathematical relations useful in determining the equilibrium constant from the optical density of an equilibrium mixture at a chosen wavelength are:-

$$K = \frac{(\text{L:MP})}{(\text{MP})} \times \frac{1}{(\text{L})} = \frac{R}{(\text{L})} \quad (1)$$



A and X are known then R can be calculated from eq.(3) and K from eq.(1). (The value of (L) in eq.(1) is  $L_0 - F_C C_t$ . where  $L_0$  is the original pyridine concentration of the mixture and  $C_t$  = total concentration of porphyrin). If  $D_C$  is not known then eq.(4) can be employed. A plot of  $1/X$  vs.  $1/L$  will give a straight line from which K can be evaluated from the slope and intercept. The above equation cannot be used, however, if there were any association between the metallo- porphyrins prior to - or after - complexation with the ligand. For the calculation of K described in this chapter, K was estimated by determining the ligand concentration required to give an O.D. half way between zero ligand and excess ligand as shown in Fig.3.3. Table 3.1 gives values of K for various ligands determined by this method at room temperature.

Table 3.1

| <u>Ligand</u>     | <u>K</u> | <u>Lit. value</u> |
|-------------------|----------|-------------------|
| Pyridine          | 6000     | 6030 [85]         |
| Ethanol           | 20       |                   |
| DMF               | 10       |                   |
| Piperidine        | -        |                   |
| Polyvinylpyridine | 250      |                   |

where  $R$  = ratio of complexed to uncomplexed metalloporphyrin

$$F_c = \frac{X}{A} = \frac{\text{complexed metalloporphyrin}}{\text{total metalloporphyrin}} \quad (2)$$

where  $F_c$  = fraction of metalloporphyrin complexed.

$$R = \frac{F_c}{1-F_c} = \frac{X}{A-X} \quad (3)$$

$$\frac{1}{X} = \frac{1}{KA(L)} + \frac{1}{A} \quad (4)$$

The optical densities of the solutions are determined at any wavelengths where the extinction coefficients of the two species differ appreciably. For a series of such solutions, a set of values for  $X$  is readily determined by subtracting the O.D. of the solution containing zero pyridine concentration from the O.D. of the other solutions. If the  $K$  of the reaction is fairly large, the value of  $A$  will also be known, for the O.D. will become a constant in the solutions containing the higher pyridine concentrations, and this constant will be  $D_c$ . If, however,  $K$  of the reaction is relatively small, then  $D_c$  cannot be determined since, even in pure pyridine, there would still be some uncomplexed metalloporphyrin. If both

An assumption of the above equations is that the extinction coefficient is independent of medium effects introduced by changing the donor concentration.

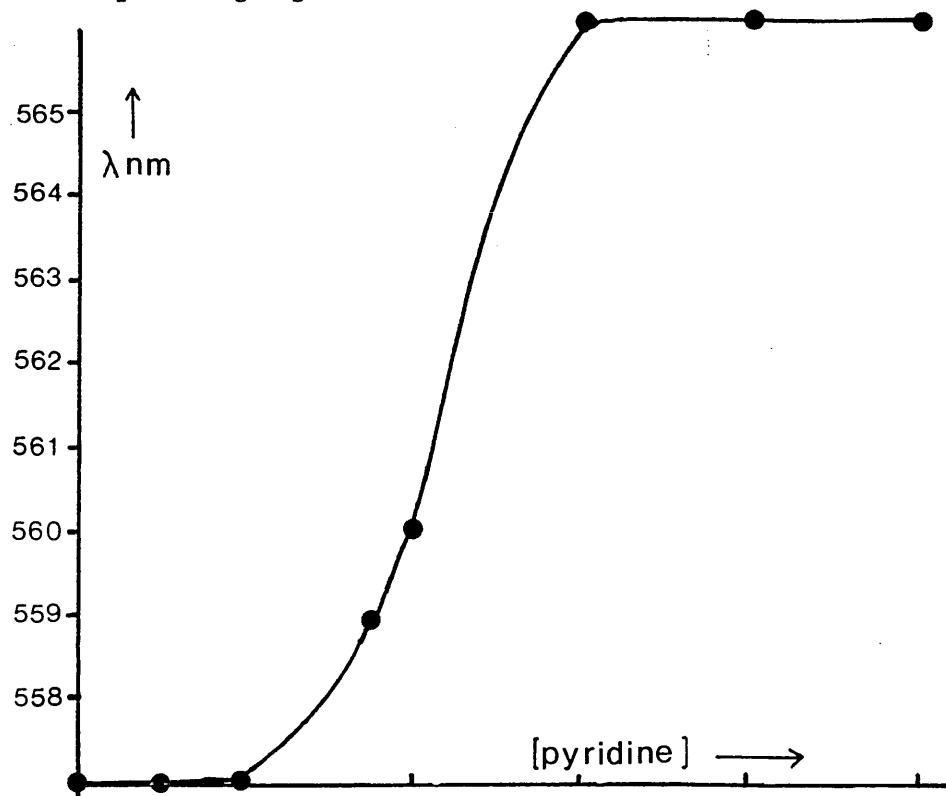


FIG. 3.3

Plot of shift in wavelength vs. ligand concentration.

In the case of small values of  $K$  where absorption of complex cannot be measured directly however, the method of Miller and Dorough [87] can lead to uncertainties in  $K$  as large as a factor of 10 [92].

A procedure which allows one to obtain equilibrium constants without measuring the extinction coefficient of the complex  $E_C$  directly and enables one graphically to analyse the data has been reported [91] and is derived below:-

$$K = \frac{C}{(A_0 - C)(B_0 - C)} \quad (5)$$

where  $A_0$  and  $B_0$  are the initial concentration of the metalloporphyrin and donor respectively and  $C$  is the equilibrium concentration of the complex. Since both the metalloporphyrin and complex absorb in the same region, the total absorbance at a given wavelength is given by:

$$a = E_c C + E_a A \quad (6)$$

where  $A$  = concentration of free metalloporphyrin at equilibrium and  $E_c$  and  $E_a$  are the extinction coefficients of complex and free metalloporphyrin respectively. Combining (5) and (6) with  $A_0 - C = A$  and  $a_0 = E_a A_0$  yields the Rose Drago equation

$$K^{-1} = \frac{a - a_0}{E_c - E_a} - \frac{A_0 - B_0}{A_0 B_0} + \frac{E_c - E_a}{a - a_0} \quad (7)$$

This equation contains two unknowns,  $K$  and  $E_c$ , and can be solved graphically [91].

### 3.6 Nature of Porphyrin-Ligand Interaction and Possible Explanations for the Red Shift

The  $Zn^{2+}$  ion has an effective ionic radius [93] nearly as large as that of high spin  $Fe^{2+}$ . This and X-ray crystallography data gathered by Hoard and co-workers [94,95] support the view that the  $Zn^{2+}$  ion lies above the plane of the porphyrin ring. This is thought to be

another factor contributing to the difficulty of forming diligated zinc porphyrin species.

Values of K for various ligands have been used to derive various thermodynamic parameters such as enthalpy and entropy [85], and they have also been used in  $\log K - pK_a$  and Hammett type correlations [90,88]. Furthermore Drago et al. [96-98] proposed a equation where the enthalpy of adduct formation can be broken up into covalent and electrostatic contributions. The significance of such calculations and their implication to spectral changes will be discussed below.

### 3.7 Enthalpy and Entropy

Knowledge of K can lead to  $\Delta G$  by applying:

$$\Delta G = RT \ln K \quad . \quad (8)$$

By calculating K and  $\Delta G$  at different temperatures and using the following equation,

$$\Delta G = \Delta H - T\Delta S \quad (9)$$

values for  $\Delta H$  and  $\Delta S$  can be obtained from the intercept and gradient respectively of a plot of  $\Delta G$  vs T. Table 3.2 shows how these parameters vary with different ligands and Table 3.3 (taken from ref.86) correlates  $-\Delta H$  with the shift in the Soret Band.

Table 3.2

| <u>Donor</u>                    | <u>-ΔH</u> | <u>ΔS</u>  |      |
|---------------------------------|------------|------------|------|
| Pyridine                        | 10.0       | 13.5 ± 0.9 | [86] |
|                                 | 9.2 ± 0.1  | 14.0 ± 0.4 | [85] |
| Me <sub>2</sub> SO <sub>2</sub> | 8.7        | 12.2 ± 1.4 | [86] |
| Bridge Ether                    | 7.1        | 11.7 ± 1.3 | [86] |
| THTP                            | 6.7        | 12.5 ± 2.0 | [86] |
| TMU                             | 6.5 ± 0.2  | 13.3 ± 0.6 | [85] |
| TPPP                            | 7.7 ± 0.6  | 19.4 ± 0.4 |      |

---

The two values of  $-\Delta H$  obtained for pyridine are due to adduct formation in benzene and cyclohexane. The higher value in benzene is thought to be due to some interaction of pyridine with benzene.

The above table indicates that  $\Delta H$  is dependant on the donor atom and appears to increase in the order N P O S. However there does not appear to be any connection between  $\Delta H$  and the red shift.

### 3.8 log K-pKa and Hammett type correlations

The Hammett equation attempts to quantify ligand effects on the central metal atom to which they are attached. It has been applied most commonly to N donors.

$$\text{Thus:} \quad -\log(K/K_0) = \sigma\rho \quad (10)$$

where  $K_0$  = stability constant for the pyridine reaction,

and  $\underline{K}$ , is the corresponding value for a substituted pyridine.  $\underline{\sigma}$  is the Hammett substituent constant [99] defined in terms of substituted benzoic acids and  $\underline{\rho}$  is the reaction constant, which is a measure of the effect of the electron density at the reaction site, i.e. the zinc ion.

Figures 4 and 5 show plots of  $\log K$  vs  $pK$  and  $\log K/K_0$  vs  $\sigma$  respectively for the list of ligands in Table 3.4.

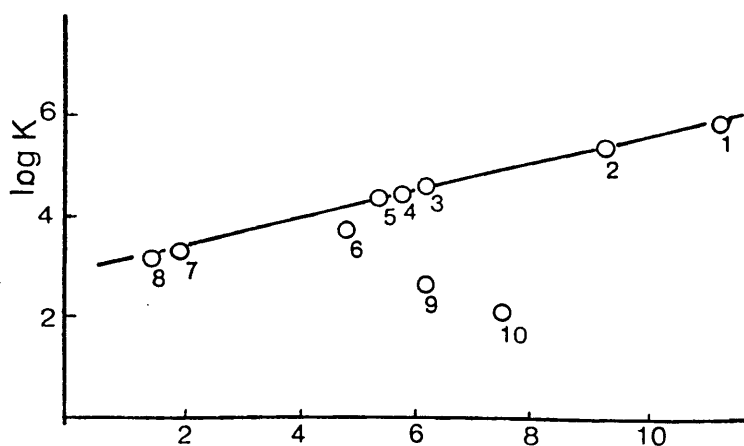
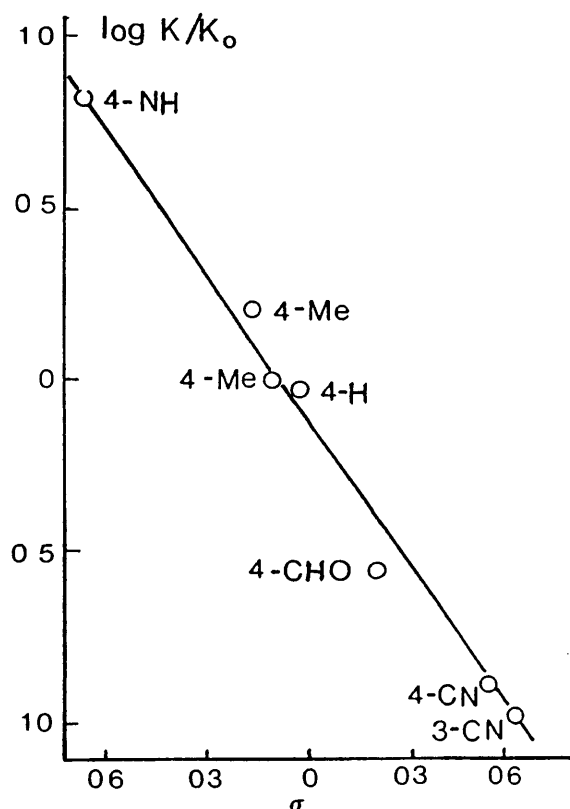


FIG.3.4 Plot of  $\log K$  vs  $pK$  for the reactions of substituted pyridines with ZnTPP.

FIG.3.5 Hammettplot for the data in Table 3.4.



For the plot in Fig. 5 Kirksey et al. obtained a value of +1.50 for  $\rho$ . Both the  $\log K$ - $pK$  correlation and the positive  $\rho$  value suggest that the association is predominantly ligand to metal  $\sigma$  bonding and virtually no  $\pi$  back bonding occurs in this system [100]. This contrasts with the Fe(II) porphyrin system where  $\pi$  back bonding does occur and the  $\log K$ - $pK_a$  plot shows an inverse relation with ligand basicity.

Table 3.3 (taken from ref.86)

| <u>Donor</u>              | $\begin{matrix} E & C \\ B, & B \end{matrix}$ | $\frac{-\Delta H}{\text{Kcal/mol}}$ | $\frac{\Delta\lambda}{\text{nm}}$ |
|---------------------------|-----------------------------------------------|-------------------------------------|-----------------------------------|
| Benzene                   | 0.11,1.40                                     | 1.4                                 | 1.6                               |
| Methylacetate             | 0.903,1.61                                    | 5.7                                 | 4.6                               |
| Acetone                   | 0.987,2.33                                    | 6.5                                 | 5.2                               |
| Ethyl Acetate             | 0.975,1.74                                    | 6.1                                 | 5.3                               |
| Tetrahydrofuran           | 0.978,4.27                                    | 7.6                                 | 6.2                               |
| Bridge Ether              | 0.887,4.16                                    | 7.1                                 | 6.3                               |
| Me <sub>2</sub> SO        | 1.34,2.85                                     | 8.7                                 | 8.5                               |
| Dimethylacet amide        | 1.32,2.58                                     | 8.4                                 | 8.8                               |
| Trimethylphosphite        | 1.03,5.99                                     | 9.0                                 | 9.5                               |
| Pyridine                  | 1.17,6.41                                     | 10.0                                | 9.9                               |
| Triethylamine             | 0.991,11.09                                   | 12.0                                | 10.1                              |
| Hexamethylphosphoramide   | 1.52,3.55                                     | 9.9                                 | 10.4                              |
| 1-Azabicyclo[2.2.2]octane | 0.704,13.2                                    | 11.8                                | 11.1                              |
| THTP                      | 0.341,7.90                                    | 6.7                                 | 11.8                              |
| Diethyl sulphide          | 0.339,7.40                                    | 6.4                                 | 11.2                              |
| Pentamethylene sulphide   | 0.375,7.40                                    | 6.4                                 | 11.4                              |

### 3.9 The Enthalpy Equation [96-98]

The equation was formulated in order to correlate the magnitude of the donor-acceptor interactions with electronic properties of the acids and bases. The experiments were carried out in poorly solvating media to reduce the importance of solvent effects. The equation is simply written as

$$-\Delta H = E_A E_B + C_A C_B \quad (11)$$

and is interpreted as the susceptibility of the acid and base to undergo electrostatic interaction [E] or form a

Table 3.4

| <u>Ligand</u>       | <u>Log K</u>    | <u>pK of ligand</u> |
|---------------------|-----------------|---------------------|
| 1. Piperidine       | 5.05 $\pm$ 0.05 | 11.1                |
| 2. 4-Aminopyridine  | 4.65 $\pm$ 0.04 | 9.17                |
| 3. 4-Methyl         | 4.02 $\pm$ 0.05 | 6.11                |
| 4. 3-Methyl         | 3.81 $\pm$ 0.02 | 5.68                |
| 5. 4-Hydrogen       | 3.78 $\pm$ 0.02 | 5.29                |
| 6. 4-Carboxaldehyde | 3.24 $\pm$ 0.02 | 4.77                |
| 7. 4-Cyano          | 2.9 $\pm$ 0.1   | 1.91                |
| 8. 3-Cyano          | 2.80 $\pm$ 0.04 | 1.45                |
| 9. 2-Methyl         | 2.30 $\pm$ 0.04 | 6.11                |

---

covalent bond [C]. Thus acids with large values for  $E_A$  interact strongly with bases have large  $E_B$ . The same is true for  $C_A$  and  $C_B$ . Also the  $E_B$  term may be related to the lone pair dipole moment and the  $C_B$  term to the lone pair polarizability. The calculation of  $E_B$  and  $C_B$  for numerous systems is described very well by Drago and Wayland [96]. Hence  $E_A$  and  $C_B$  for ZnTPP can be obtained by a knowledge of  $\Delta H$  (from experiments) for a particular system. These values of  $C_A$  and  $E_A$  can then be used to calculate  $-\Delta H$  for ligands where direct measurement is not possible. Literature calculations [86] give a value of  $E_M = 5.15 \pm 0.13$  and  $C_A = 0.624 \pm 0.038$  for ZnTPP. In other words the susceptibility of

ZnTPP forming any type of covalent bond is very small. The small C/E ratio for ZnTPP might indicate that the interaction is largely dipole-dipole as a result of the  $\text{Zn}^{2+}$  ion lying out of the porphyrin plane and the absence of low energy d-orbitals to participate in a covalent interaction.

Table 3 gives values of  $E_B$  and  $C_B$  for various donors. Again, however, there is no apparent correlation between these values and the red shift.

### 3.10 Discussion

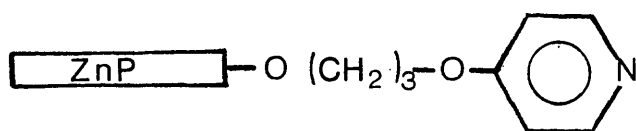
All the above information tells the nature and strength of the bond but the reason for the red shift is still vague. Thus whilst the work described so far suggests no significant involvement of  $-\Delta H$  and  $\Delta S$  with red shift, work on Gas-Solid Interactions of ZnTPP with various volatile ligands [101] finds such a correlation to be true for a variety of ligands including not only a wide range of nitrogen compounds but also hydrocarbons and compounds containing oxygen, sulphur and phosphorus.

Another line of thought used to explain  $\Delta\lambda$  is that it is not dependent on the bond strength of the ligand or the dielectric constant but is due to the charge and polarisability of the ligand [84]. Nappa and Valentine strongly implicate charge as one of the major factors contributing to  $\Delta\lambda$  as all the anion complexes they tried were more red shifted than the neutral ligand complexes e.g. using  $\text{Br}^-$ ,  $\text{Cl}^-$  and  $\text{F}^-$  as ligands,  $\Delta\lambda$  increased in the

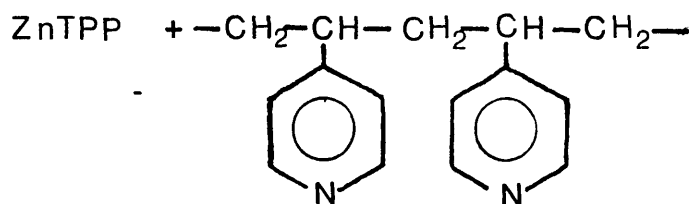
order Br Cl F even though  $-\Delta H$  and  $K$  increased in the reverse order. Thus the shift could be due to negative charge transferred to the porphyrin ring via the Zn atom, explaining why larger shifts are observed with nitrogen donors as more negative charge is transferred to the ring. Another explanation offered for  $\Delta\lambda$  is that different ligands pull Zn out of the porphyrin plane by varying degrees.

### 3.11 Elaboration on the simple ligand systems

As mentioned in section 3.1, the photochemistry of porphyrins in nature is strongly affected by the protein environment. In simple terms proteins are polyamino acids and it is easy to envisage carboxyl or amino groups forming axial ligands quite readily with metalloporphyrins. It has been established now that N donors such as pyridine form axial ligands very easily with ZnTPP and the complex has a large stability constant. From this simple system we can extend to systems such as:-



and



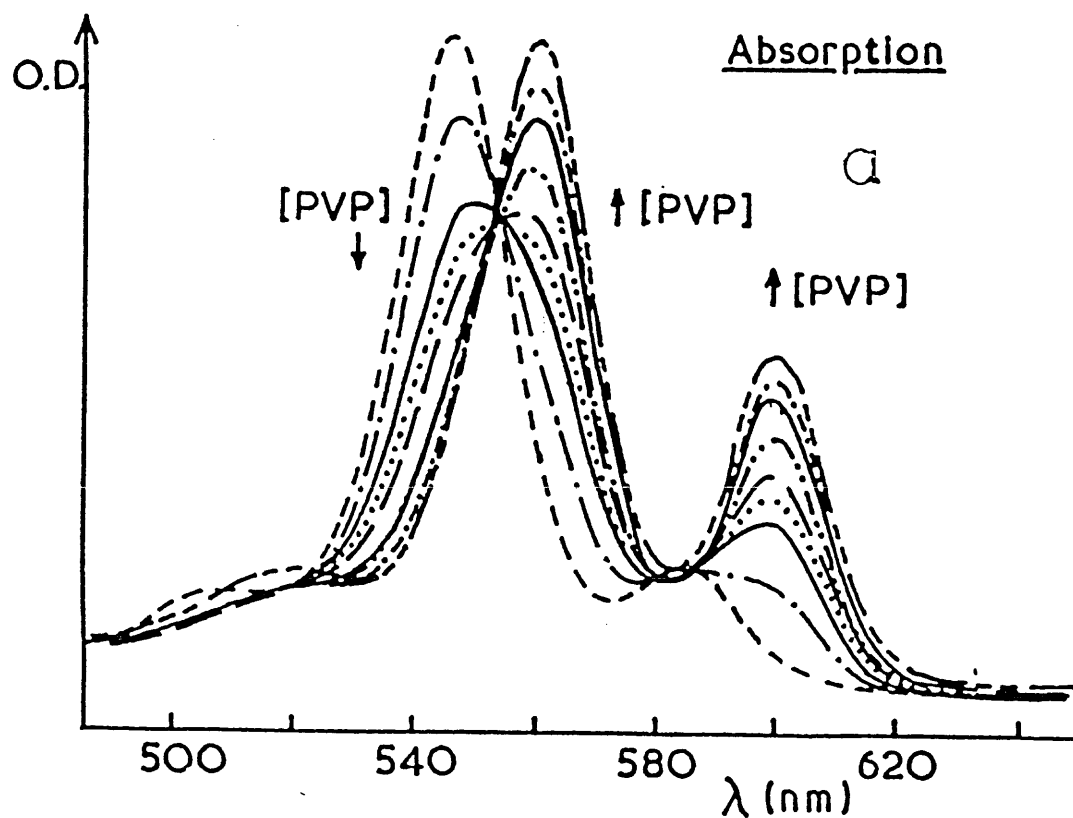
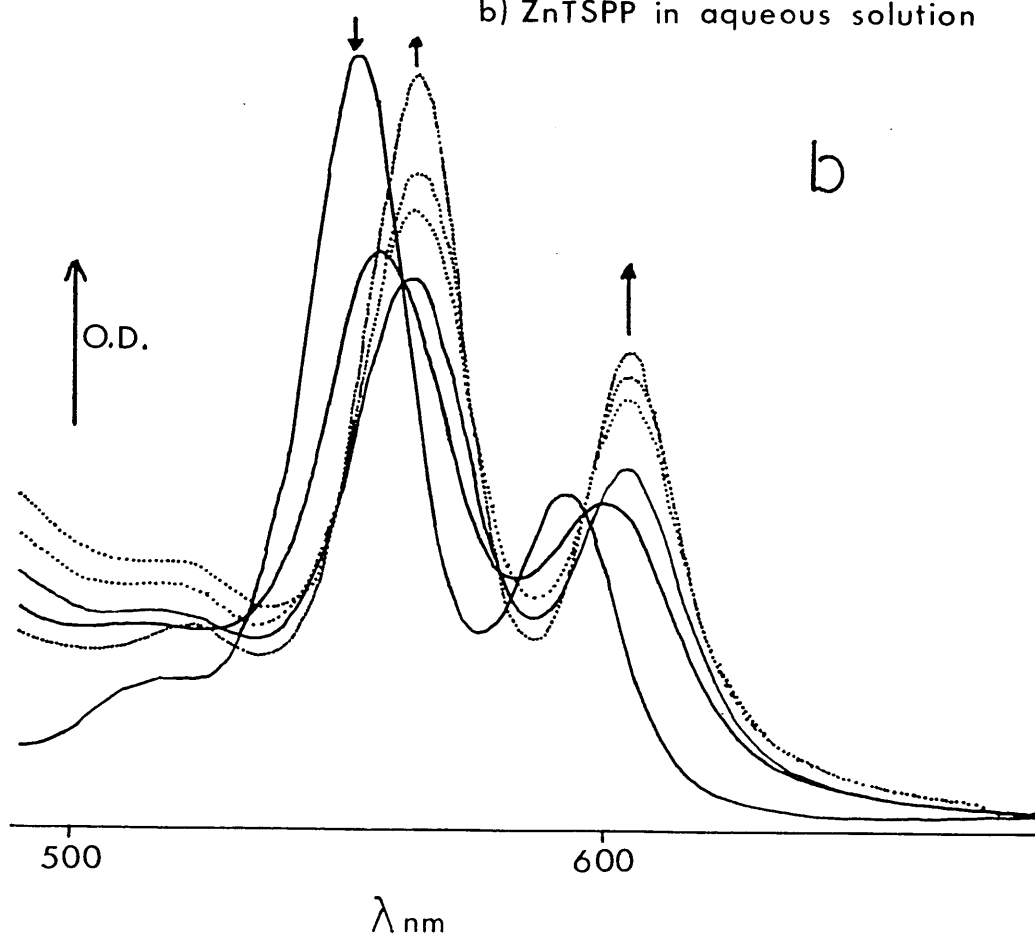


FIG. 3.6  
Addition of PVP to a) ZnTPP in ethanol  
b) ZnTSPP in aqueous solution



System II can be classed as a polyligand system and approaches protein to a certain extent in the sense that many liganding sites are available on the same backbone. In both cases the spectrum of zinc porphyrin is shifted to the red and the ratio  $E_\alpha/E_\beta$  follows the same trend as with pyridine (Fig.3.6a). The stability constant for II this time has a value of 250 using ethanol as solvent. This however is a deceptive figure as it does not account for the fact that spatial parameters do not permit ZnP to attach itself to each ligand site. Much higher values for  $K_{eq}$  ( $2.74 \times 10^8 M^{-1}$ ) [102] have been reported when PVP is adsorbed onto silica. One explanation offered for this observation is that the ZnP plane is preferentially orientated parallel to the silica surface thus yielding an extinction coefficient  $3/2$  that of a randomly ordered sample.

### 3.12 Effect of ligands on fluorescence and triplet lifetime

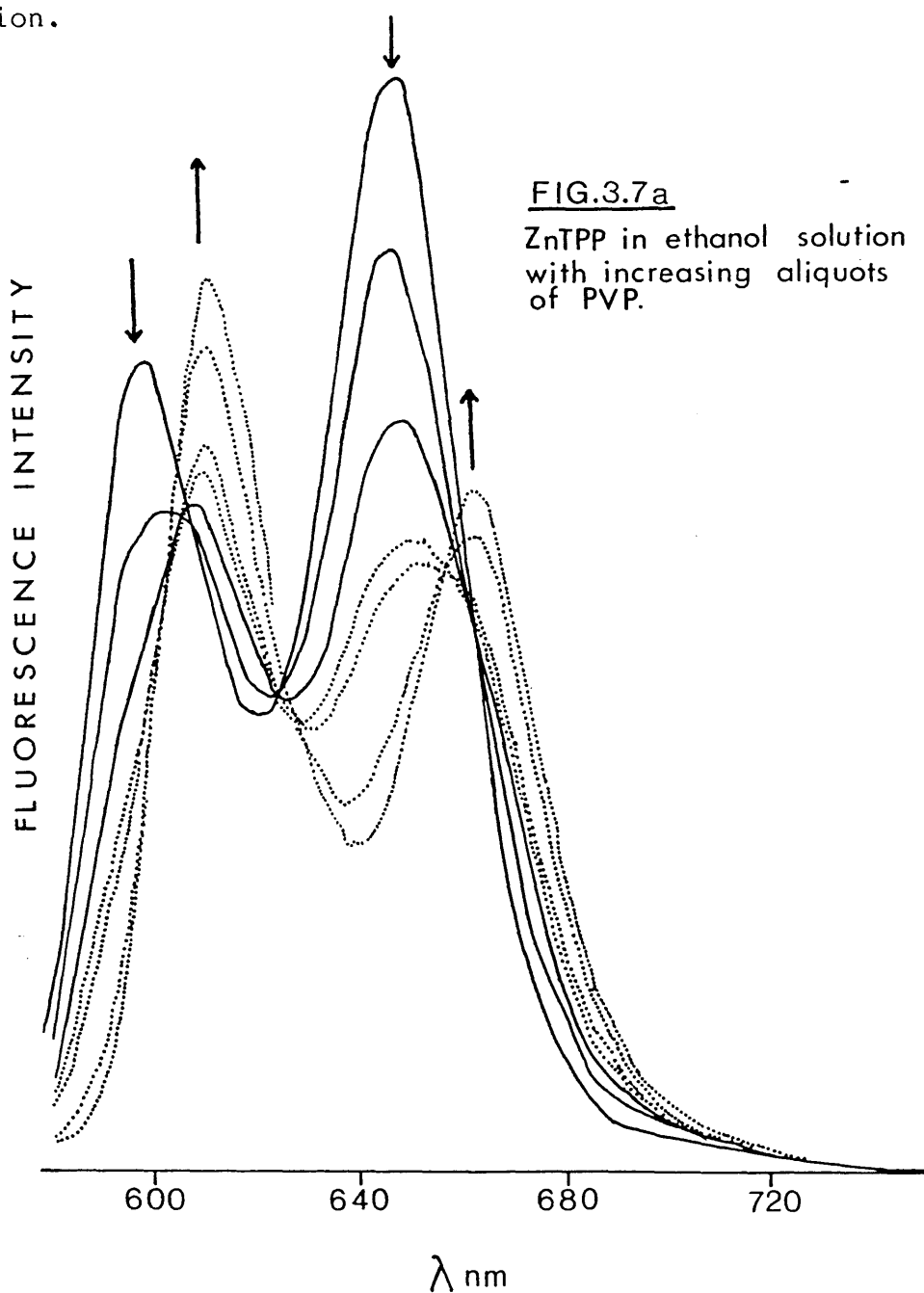
So far only changes in the ground state spectrum have been discussed. Much of the chemistry that involves porphyrins in nature, however takes place in the excited state. For this reason steady state fluorescence and triplet lifetimes ( $\tau_T$ ) were used to characterise the systems.

Fig.3.7a shows how the uncorrected fluorescence spectrum changes on stepwise addition of PVP. The fluorescence spectra mirror the changes in the absorption

spectrum of the same system. The quantum yields of fluorescence ( $\phi_F$ ) for axial ligands change as follows.

| <u>System</u>    | <u><math>\phi_F</math></u> |
|------------------|----------------------------|
| ZnTPP            | 0.030                      |
| ZnTPP + pyridine | 0.027                      |
| ZnTPP + PVP      | $0.22 \pm 0.002$           |

The trend therefore appears to be decrease in  $\phi_F$  on ligation.



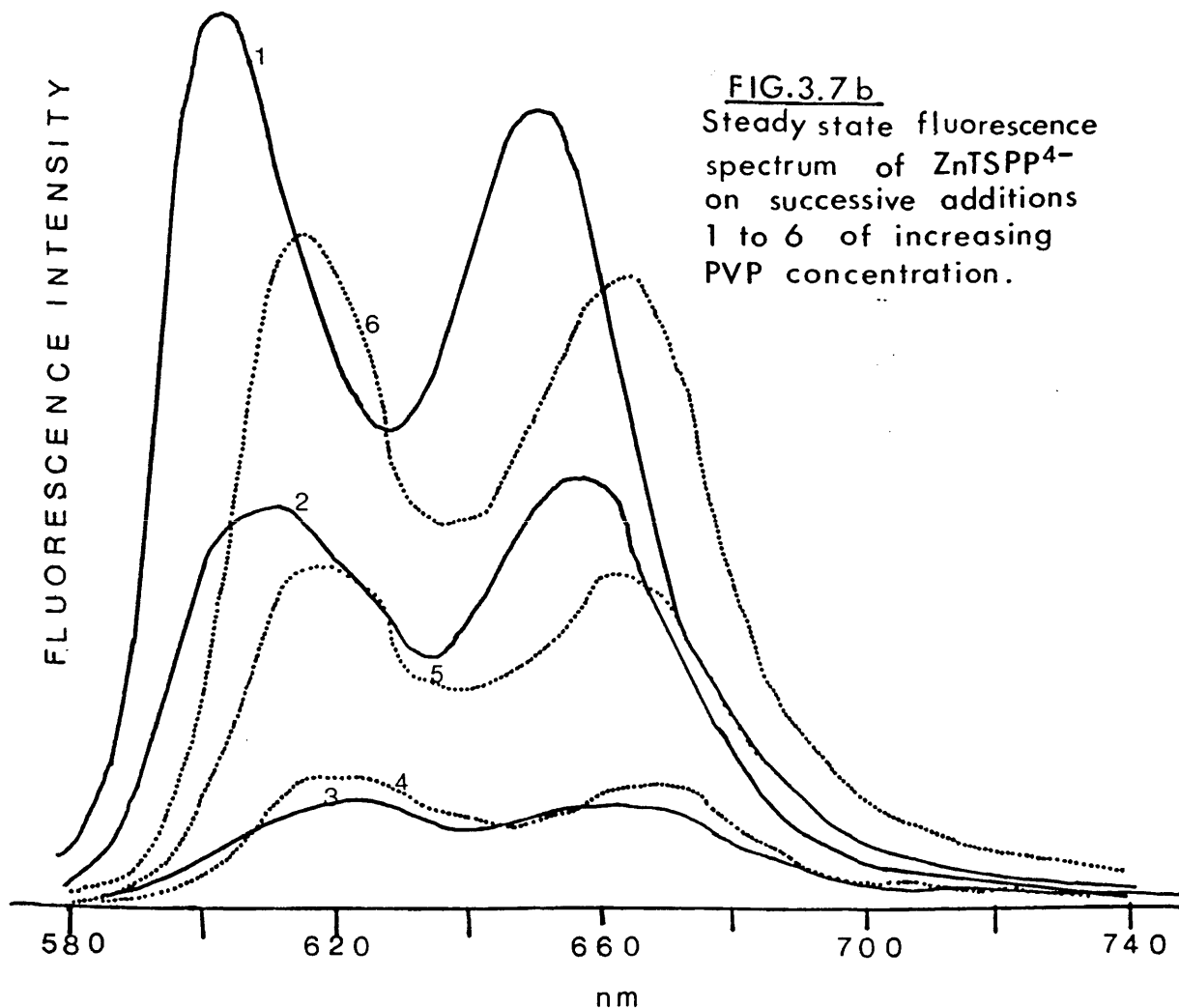
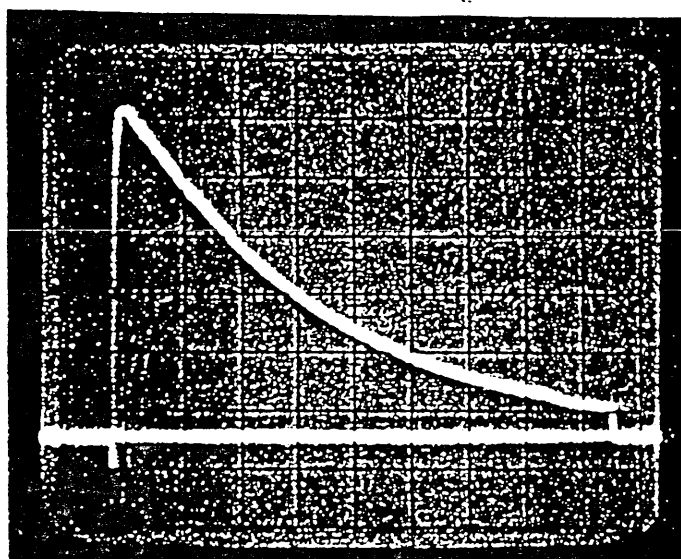


FIG.3.7 b  
Steady state fluorescence  
spectrum of  $\text{ZnTSPp}^{4-}$   
on successive additions  
1 to 6 of increasing  
PVP concentration.

The triplet lifetimes on the other hand highlight the effect of environment more dramatically. Thus we observe values for ZnTPP of:-

|                        |                                 |
|------------------------|---------------------------------|
| The decay profiles are | 1.2mS in ethanol                |
| shown in Fig.38.       | 2.5mS in ethanol + 10% pyridine |
|                        | 3.3mS in ethanol + PVP          |

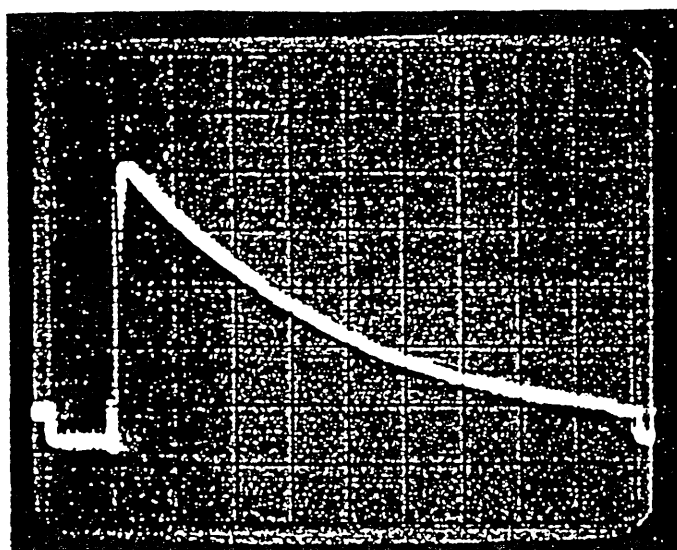
It therefore appears that the more rigid or complex the microenvironment we provide, the longer is the triplet lifetime. In fact A. Harriman in our laboratories has synthesised a zinc porphyrin in myoglobin and the lifetime of that system is an astounding 10mS. More lifetime and fluorescence data with ZnP in micelles is provided later in this chapter.



ZnTSPP in  
outgassed  
aqueous  
solution

$$\tau_T = 1,7 \text{ ms}$$

← 5ms →



ZnTSPP in  
outgassed  
solution with  
PVP

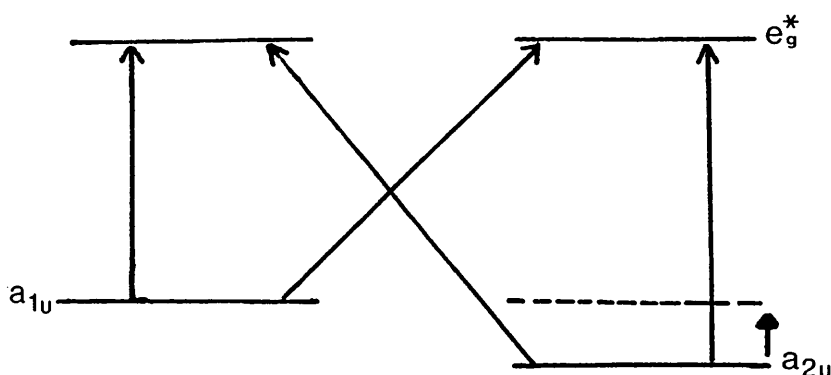
$$\tau_T = 3.3 \text{ ms}$$

← 10ms →

FIG.3.8

### 3.13 Possible explanation for excited state data

The observations so far suggest that the ligation causes (a) a decrease in  $\phi_F$ , (b) an increase in  $\tau_T$ . No straightforward theory has so far been published to explain this phenomenon. Nevertheless this does not prevent one from speculating. According to Gouterman's 4 electron model the orbitals responsible for the observed transition are  $a_{1u}$  and  $a_{2u} \rightarrow e_g^*$  as shown below



Increasing the electron density on the porphyrin as a result of axial ligation (see section 3.10) could increase the energy of the  $a_{2u}$  orbital. Decreasing the energy gap between  $a_{2u}$  and  $e_g^*$  enhances the population of  $e_g^*$  and would explain the increase in extinction coefficient for the  $Q(1,0)$  band as the absorption spectrum shifts to the red. As the energy gap between ground and excited states decreases so should the rate of non radiative decay ( $K_{NR}$ ) increase and thus result in a lower  $\phi_F$ .

The only explanation for change in  $\tau_T$  with ligands is a change in spin orbit coupling. This is dependent on two factors i symmetry and ii electron density. Hence it is probable that ligands change the porphyrin symmetry (even by pulling the  $Zn^{2+}$  out of the porphyrin plane) so as to reduce the spin orbit coupling and hence increase  $\tau_T$ . A change in symmetry would also account for the increased ratio of  $E_\alpha/E_\beta$ .

### 3.14 Aqueous systems

Again referring to nature as a perfect model we find that most reactions such as electron transfer take place in aqueous solution. It would therefore be interesting to see if complexation in aqueous solution optimises the system. Still using Zn porphyrin but with sulphonated groups ( $ZnTSPP^{4-}$  and PVP having 15% of the pyridine sites present as pyridinium ions, spectral data were collected for this system and compared with equivalent data in the organic medium (see Figs.3.6b and 3.7b).

### 3.15 Observations

The complexed species absorbs at 565nm which is similar to the organic system (563nm). However a slight difference in spectra on stepwise addition of polymer species is observed. In the organic system, the isosbestic point at 555nm is very clearly defined. This is not true for the aqueous system where no distinct

isosbestic appears. In addition to this some kind of phase change is taking place:- as PVP is added to a clear solution of  $\text{ZnTSPP}^{4-}$ , the solution appears to become cloudy. Further addition of PVP then renders the solution clear once more. The fluorescence spectral changes on addition of PVP are also remarkably different in the organic and aqueous media (Figs.3.7a and 3.7b). Thus whilst the organic system shows a shift and isosbestic point, the fluorescence in the aqueous system first decreases significantly and then increases again.

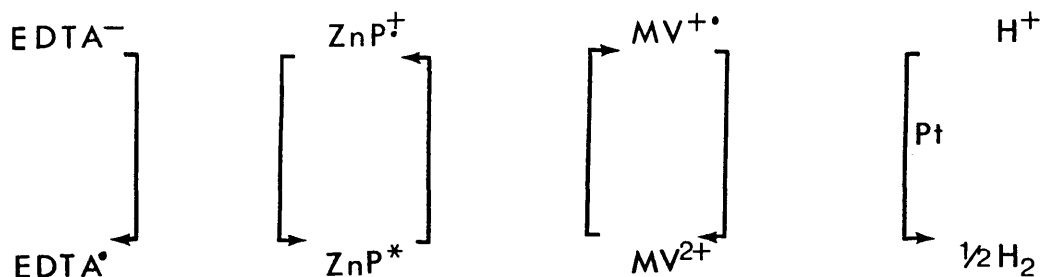
### 3.16 Interpretation of results

The decrease in fluorescence and the cloudy appearance of the solution are due to dimerisation of the porphyrin. At low concentrations of polymer we can imagine that the porphyrin flocks to the polymer to compete for available sites (this phenomenon can be termed "the magnetic effect"). This is encouraged by the fact that the polymer is slightly positively charged and electrostatic interaction with negatively charged porphyrin is possible. As polymer concentration is increased more sites become available for the porphyrin and dimerisation stops becoming a problem. The ratio of porphyrin:pyridine sites just when the solution becomes clear is 1:60. Dimerisation is not normally observed in organic media. It appears therefore that the ratio of porphyrin to ligand species is crucial to the properties we observe in this system.

The  $\tau_T$  fortunately follows the same trend in both systems. Thus  $\text{ZnTSPP}^{4-}(\text{aq}) = 1.5\text{ms}$  and addition of PVP increases this to 3.3ms.

### 3.17 Experiments using the aqueous system

So far we observe increases in  $\tau_T$  as the system gets more complex. A long  $\tau_T$  would be desirable in reactions involving intermolecular electron transfer from the excited state. One example involves the events leading up to photogeneration of hydrogen from water. The reagents generally employed for photoreduction of water in vitro are outlined below and have been well documented in the literature [103-104].



In the above scheme electron transfer occurs from the triplet excitation of the  $\text{ZnP}^*$  to methylviologen ( $\text{MV}^{2+}$ ). This involves the formation of an encounter complex which is diffusion controlled. The viologen radical then transfers the electron to platinum colloid which catalyses the formation of hydrogen.  $\text{EDTA}^-$  is a sacrificial electron donor.

The systems compared in this set of experiments were:-

- 1)  $\text{ZnTSPP}^{4-}$  (aq)
- 2)  $\text{ZnTSPP}^{4-}$  (aq) + pyridine
- 3)  $\text{ZnTSPP}^{4-}$  (aq) + PVP

### 3.18 Observations

From previous experiments carried out by A. Harriman and M.C. Richoux [103] it has been well established that system 1) is unfavourable for photogeneration of hydrogen since  $\text{ZnTSPP}^{4-}$  and  $\text{MV}^{2+}$  form a very strong encounter complex and charge separation is not encouraged. System 2) also behaved the same as 1). But quite suprisingly system 3) evolved a significant amount of  $\text{H}_2$  and furthermore the quantity produced seemed to be dependent on the concentration of polymer used [Fig.3.9]. The optimum yield was found to occur when the ratio of pyridine sites: porphyrin was 80:1. The yield of  $\text{H}_2$  was at least 100 fold greater than that of  $\text{ZnTSPP}^{4-}$  on its own.

### 3.19 Discussion

Obviously the polymer has some inherent property which facilitates  $\text{H}_2$  production in this particular system, since otherwise we would have expected to obtain the same results with system 2). Also it is necessary to question why there is an optimum ratio of porphyrin: PVP for maximum  $\text{H}_2$  yield. In order to answer these question it is necessary to know something about the conformation of

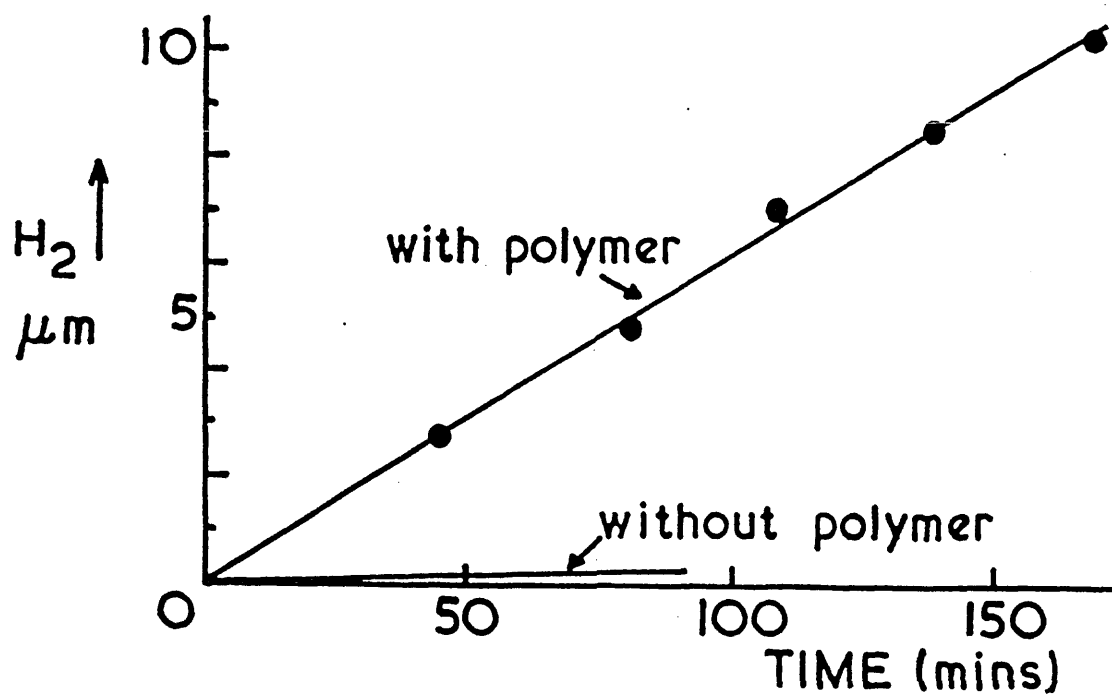


FIG.3.9  
Hydrogen yield of ZnTSPP photosystem  
in presence and absence of PVP.

polymers. In solution the polymer is not one straight chain but a tangled web schematically shown in Fig.10. The spaces so formed within solution are called domains. Within each domain we note two distinct regions - one close to the polyelectrolyte chain and the other occupying the rest of the volume and this is the bulk supporting electrolyte solution. The coulombic interactions of potential fields of polyelectrolytes can be very important in influencing the rates and yields of chemical reactions.

In this particular system we assume that the reactions which involve  $\text{ZnTSPP}^{4-}$  i.e. the reactions with  $\text{EDTA}^{2-}$  and  $\text{MV}^{2+}$  take place close to the polyelectrolyte chain.  $\text{EDTA}^{2-}$  can attach itself electrostatically onto the positive parts of the polymer chain and is in equilibrium with  $\text{EDTA}^{2-}$  in solution. What appears to be happening in this system is that the effective charge on the porphyrin is reduced by complexation with the polymer and this permits charge separation to take place between  $\text{ZnTSPP}^{4-}$  and  $\text{MV}^{2+}$  once electron transfer has taken place.

The maximum yield of  $\text{H}_2$  takes place when there are ~80 sites to each porphyrin. As explained in section 3.8.2, the absorption and fluorescence spectra indicate that below a ratio of 60:1 sites, dimerisation is a problem and hence the very poor yield of  $\text{H}_2$  at low concentrations of polymer might be due to this effect. At a ratio of 80:1 sites dimerisation is eliminated and  $\text{H}_2$  is produced much more efficiently. On further increase of polymer concentration however we are generating more

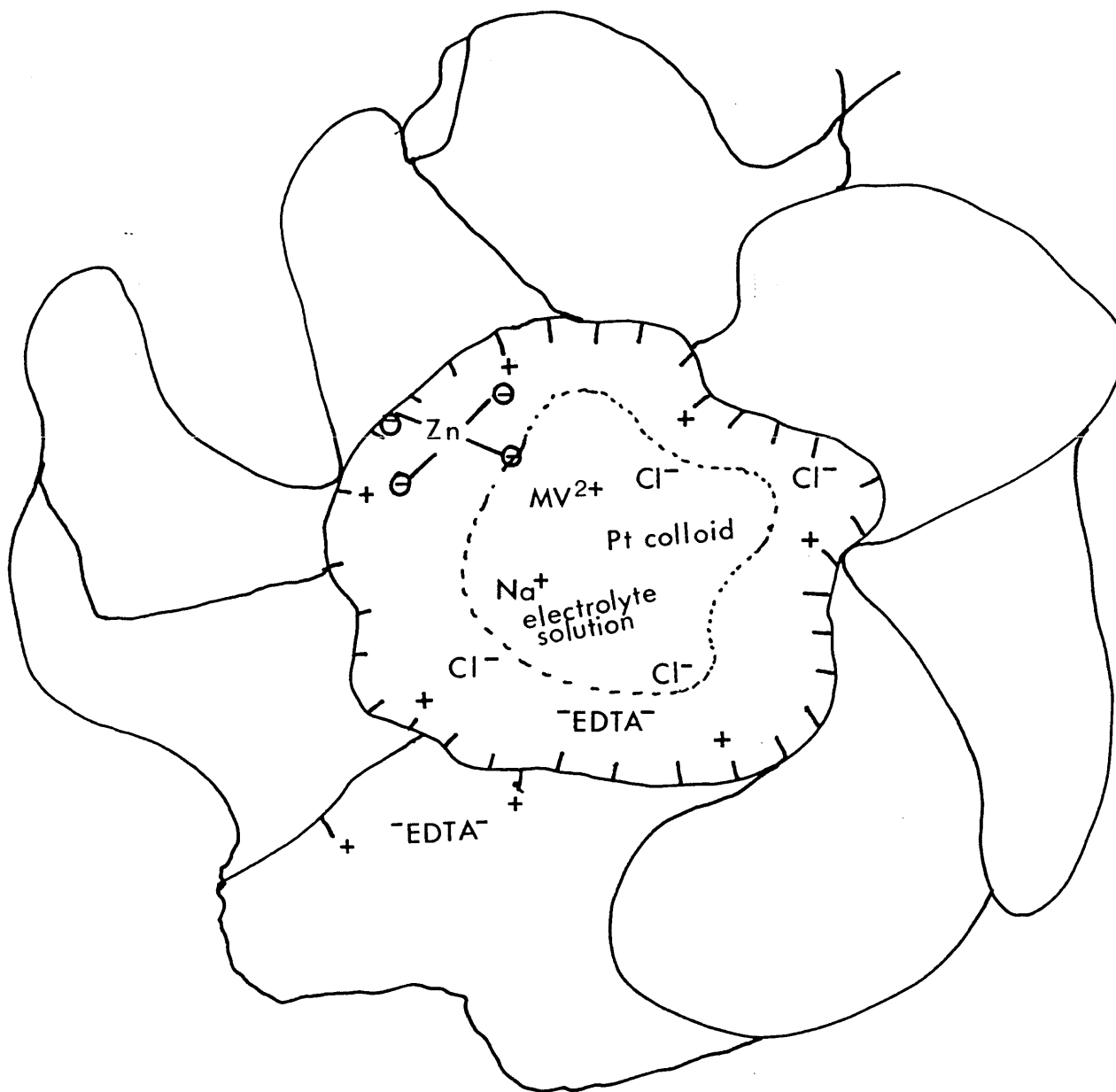


FIG.3.10  
Model of tangled up web of polymer.

domains and hence we are effectively reducing the concentration of reactants within each domain. Reducing the concentration reduces the amount of product i.e.  $H_2$ . It is assumed that reactivity between neighbouring domains is negligible. An alternative explanation could be that increasing polymer concentration deactivates the platinum colloid catalyst.

### 3.20 Triplet state data on the above system

The systems investigated were:

1.  $ZnTSPP^{4-} + EDTA^{2-} + MV^{2+}$
2.  $ZnTSPP^{4-} + EDTA^{2-} + MV^{2+} + PVP$ .

The decay curves obtained for the two systems are shown in Figs. 3.11a and 3.11b respectively.

In general there is a decrease in half life for both systems with increasing energy or alternatively with triplet concentration. This suggests that the decay is second order and would be consistent with quenching by  $MV^{2+}$ . The decay profile for system 1 is remarkably different from 2. Two different decays appear to be taking place. There is first a rapid decay with  $t_{\frac{1}{2}} = 0.3ms$ , presumably due to free triplet and then a slower decay probably associated with porphyrin cation and  $MV^{2+}$  complex. In the presence of PVP however, the pure triplet is completely quenched and only one decay is observed.

### 3.21 Irradiation experiments on the systems in 3.20

Figures 3.12a and 3.12b respectively show how systems 1 and 2 react to irradiation. Both systems were purged

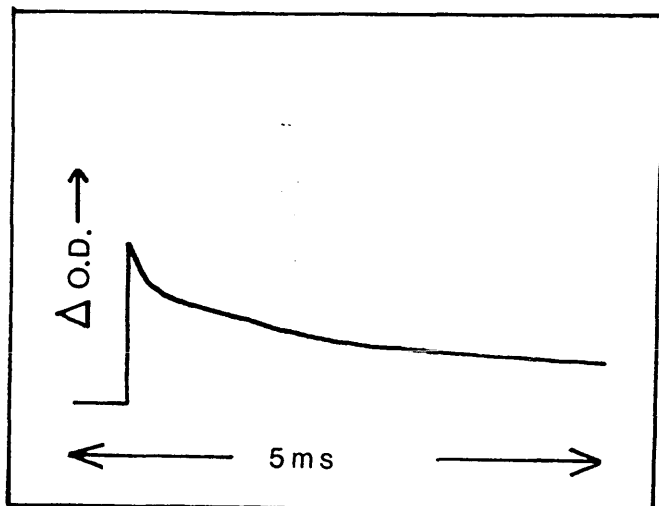


FIG.3.11a  
Triplet decay of ZnTSPP  
in the absense of PVP.

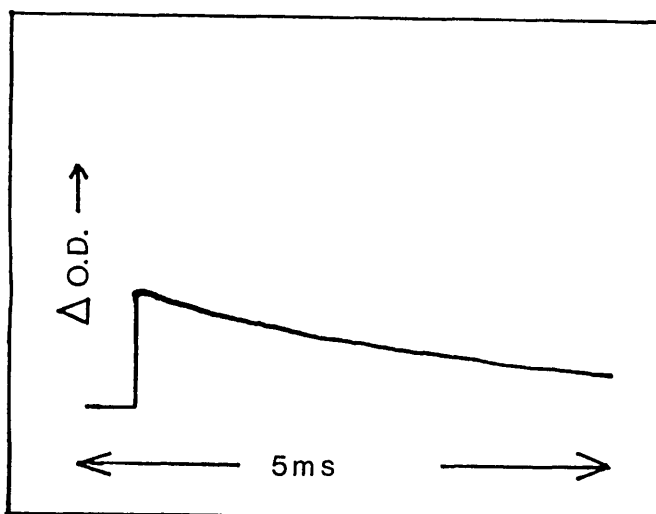


FIG.3.11b  
Triplet decay of ZnTSPP  
in the presence of PVP.

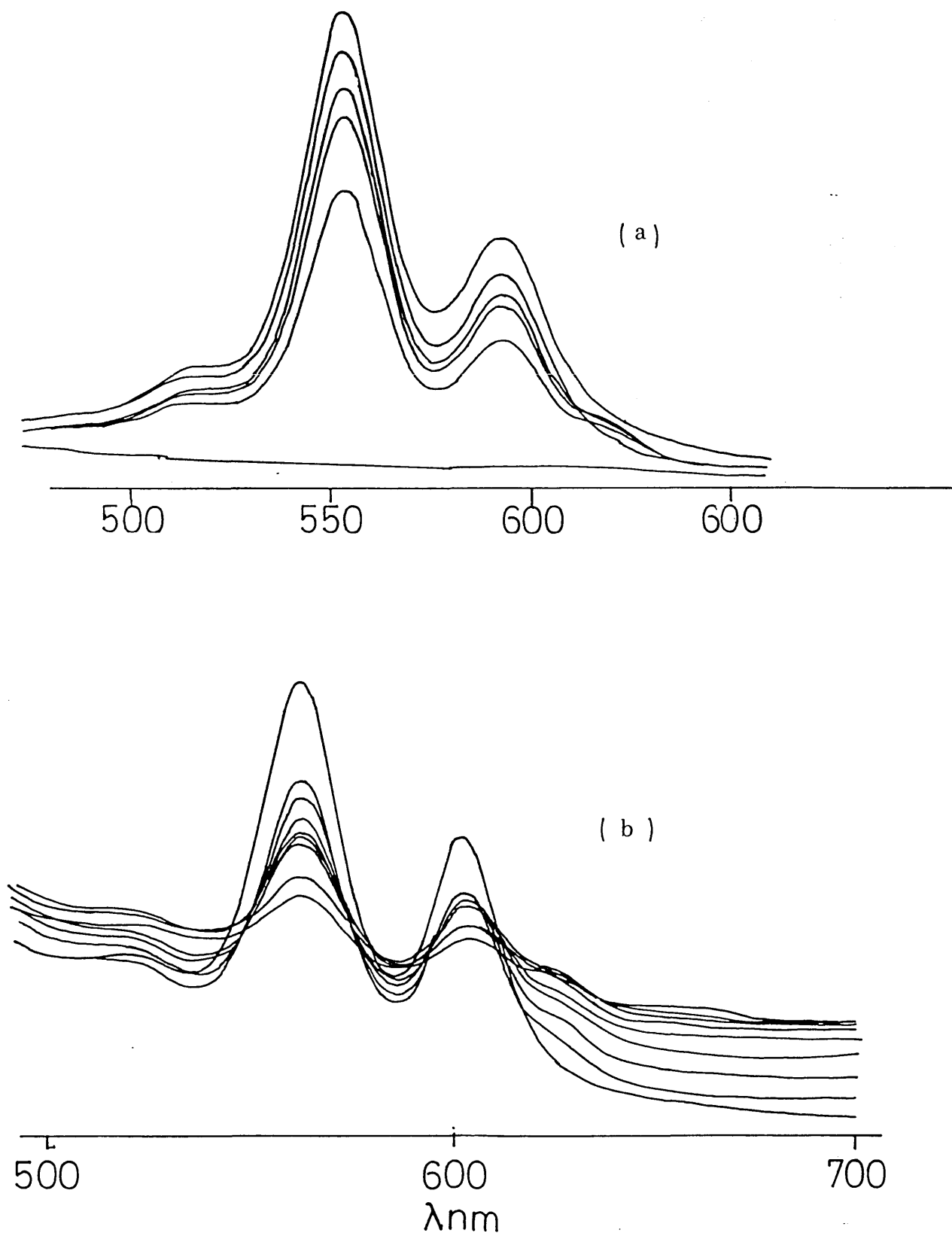


**FIG.3.12**

a) Steady state irradiation of ZnTSPP in solution together with EDTA and methyl viologen  
b) as well as PVP.

for 15 mins prior to irradiation. System 1 shows that bleaching of the porphyrin occurs on irradiation. In system 2 on the other hand reduction of porphyrins to bacterioporphyrin occurs as indicated by the shoulder appearing in the spectrum at ~610nm and also at 460nm. Such observations could indicate that hydrogen production in system 2 when platinum is also present could be generated via the reduced porphyrin.

### 3.22 Zinc porphyrin in Microheterogenous Environment

#### Introduction

In vivo systems are all made up of cells which are separated from one another by a cell membrane. In the Sanger and Nicholson [106] model the membrane consists of a fluidy matrix or lipid which is supported by proteins, thus giving the matrix a mosaic appearance. In photosynthesis most of the pigments involved in the electron transfer process are situated in the cell membrane. The previous sections have attempted to show how groups in the protein might influence the photochemistry of the porphyrins by forming axial ligands. In order to get a full picture therefore of how the membrane influences porphyrins it is necessary to model the lipid matrix too and this has been best achieved by using microheterogenous environments such as micelles.

### 3.23 Examples of microheterogenous environments

Figure 3.13 shows various examples of such media. Micelles are surfactant assemblies that form spontaneously

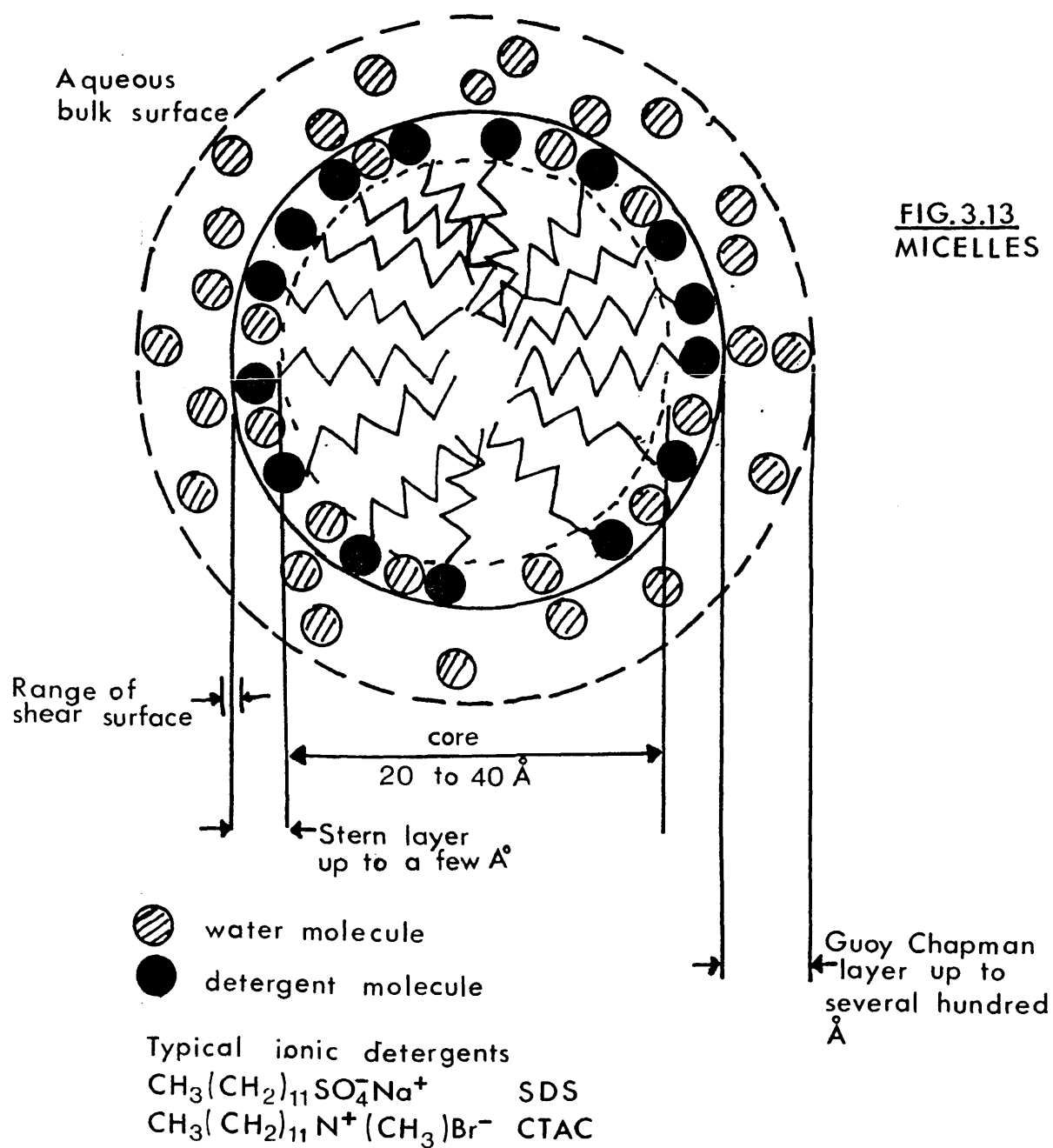
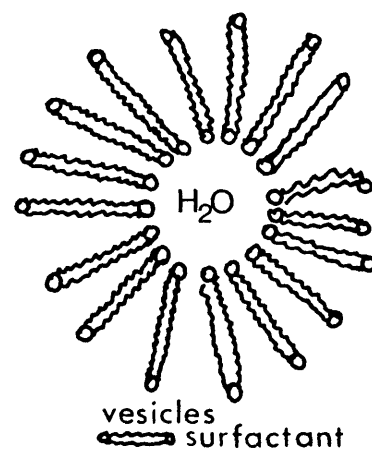
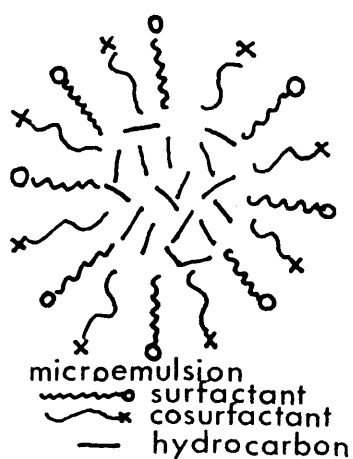
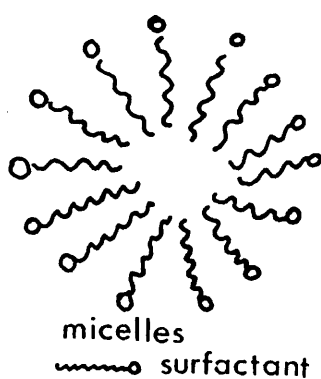


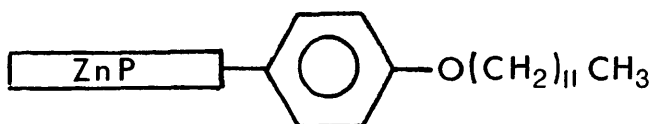
FIG.3.13  
MICELLES



in aqueous solution above a critical concentration (usually  $5 \times 10^{-3} \text{M}$ ). An important feature of micellar solutions is their microheterogeneous character. The apolar interior of the aggregates is distinguished from the aqueous phase through its hydrocarbon-like character allowing for the solubilization of hydrophobic species. Of unusual importance for light energy conversion is the electrical double layer formed around ionic micelles. This gives rise to surface potentials frequently exceeding 150mV. This charged lipid water interface provides in many instances a microscopic barrier for the prevention of back electron transfer. In the presence of borate ( $5 \times 10^{-3} \text{M}$ ) media are stable over several days but the addition of high concentrations of electrolyte (0.1M) causes turbidity. The diameters of the microemulsions and vesicles were found to be 18 and 60nm respectively by light scattering experiments.

### 3.24 Behaviour of Porphyrin in above media.

A variety of porphyrins are discussed in the ensuing section but discussion will open with the most familiar porphyrin so far i.e. Zinc Porphyrin (ZnP). In order to facilitate insertion within the micelle a surfactant ZnP was synthesised by A. Harriman as shown below:



The preparation of the micelle solutions and insertion of porphyrin is discussed in the experimental chapter. Figure 3.14 shows the absorption spectra of the above porphyrin in the various media.

The spectrum is greatly distorted in the NaLS and DAC systems. The Soret band is broadened indicating that the porphyrin is aggregated [107]. In DAC the great reduction in the Soret suggests that the electronic transition is forbidden. When the experiments are repeated using a free base porphyrin ( $H_2P$ ) the absorption spectra show the same characteristics as with the Zn surfactant porphyrin though the Q bands are not so distorted. The uncorrected fluorescence spectra of the Zn surfactant porphyrin systems are shown in Fig.3.15. No fluorescence could be obtained for the DAC system and the spectrum on NaLS is again vastly distorted and quenched. It is only the spectrum in Igepal that resembles the one expected from ZnP in solution. The quenching and distortion in emulsion is probably due to NaLS surfactant present in this particular emulsion. Again when  $H_2P$  was used in place of ZnP, the same phenomena were observed though in this case there was no quenching in emulsion and the quenching in DAC was not so drastic.

Flash photolysis was also used to measure the lifetimes of these systems. The data are tabulated below together with the fluorescent quantum yields  $\phi_F$ .

Figures 3.14 Absorption, & 3.15 fluorescence spectra of surfactant ZnP dissolved in vesicles (—), neutral micelles (---) and negatively-charged micelles (···).

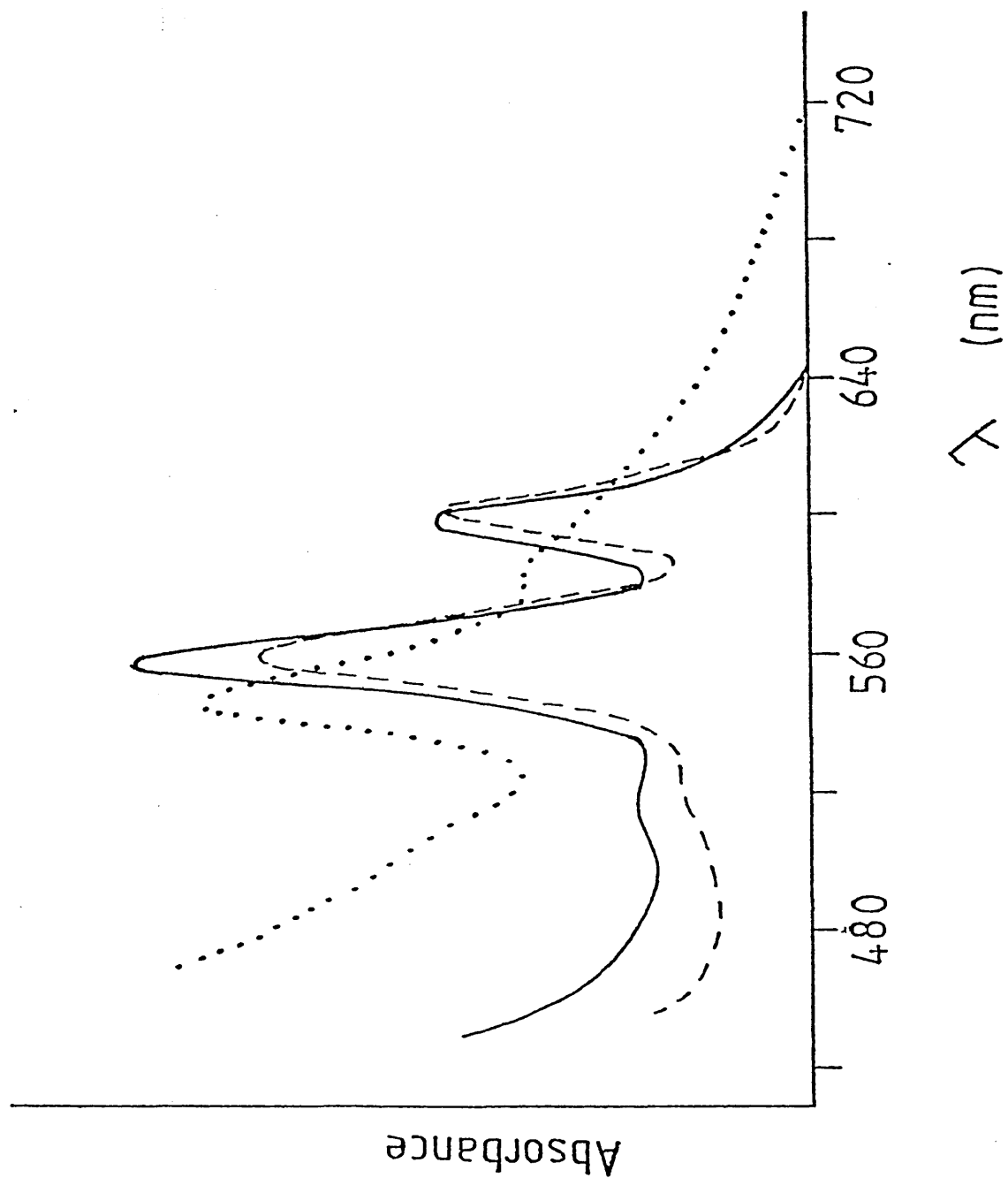


FIG.3.14

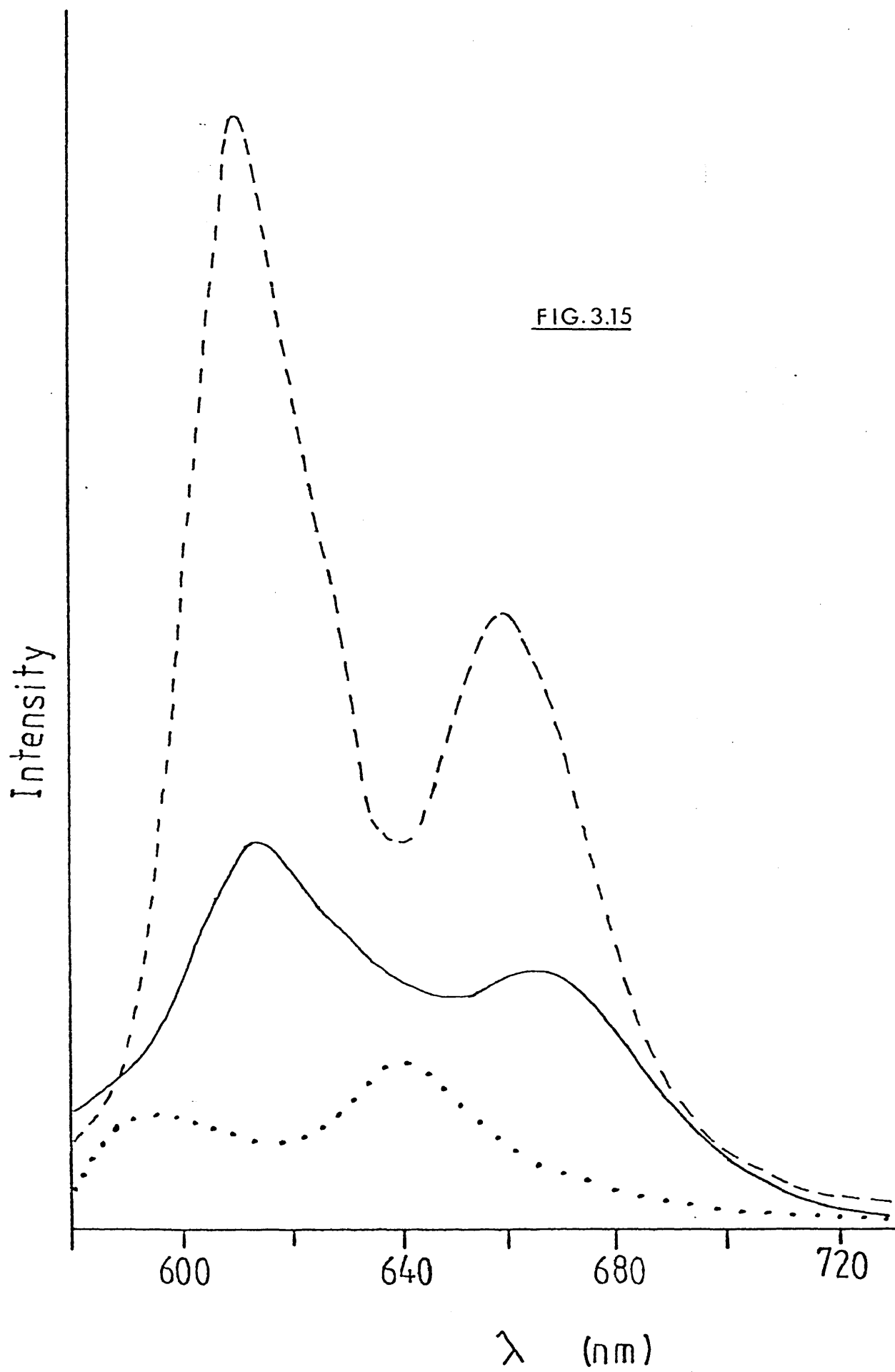


Figure 3.16 Absorption spectral profile showing formation of zinc chlorin upon irradiation of the ZnP/MnP dimer in oil/water microemulsion in the presence of EDTA ( $10^{-2}$  mol dm $^{-3}$ ) at pH 9.4.

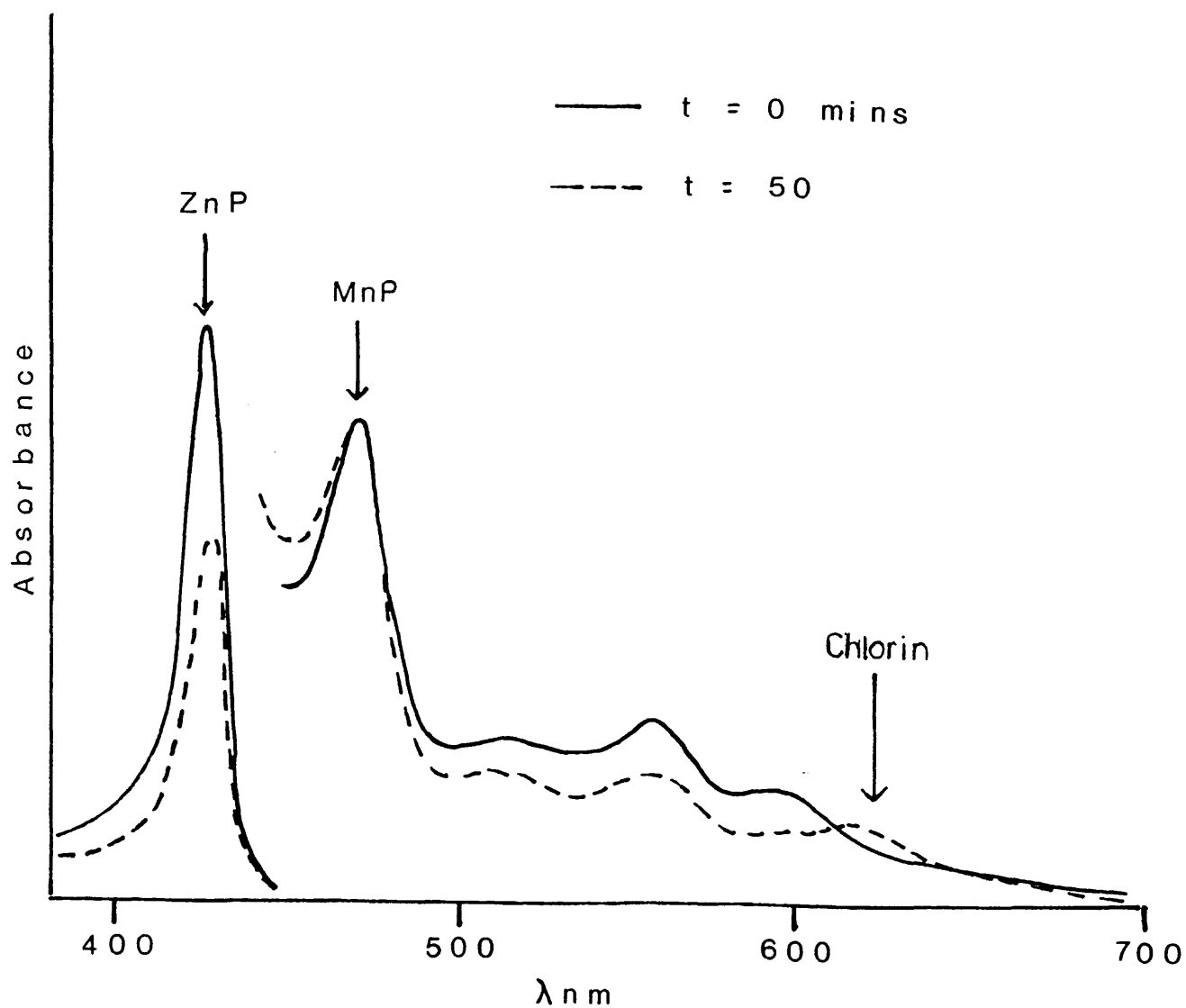


TABLE 3.5

| <u>Medium</u> | <u><math>\phi_F</math></u> | <u><math>\tau_T</math>(ms)</u> |
|---------------|----------------------------|--------------------------------|
| Benzene       | 0.04                       | 1.12                           |
| Igepal        | ~0.04                      | 7.4                            |
| NaLS          | ~0.01                      | 2.6                            |
| DAC           | ~0.01                      | 0.79                           |
| Emulsion      | ~0.02                      | 3.4                            |

Therefore inserting the porphyrin in neutral micelles or an emulsion results in a large increase in  $\tau_T$ . Thus such media are useful if a long lifetime is required e.g. in electron transfer processes. The results suggest that the excited singlet state of the porphyrin is more influenced by the nature of the interface than the triplet state. The most useful medium appears to be the neutral micelle as it gives the largest  $\tau_T$  and causes the least aggregation. However it does not allow water soluble segments to be bound at the interface and consequently has no advantage over aqueous solution. The microemulsion seems to offer the best all round environment since it gives a long  $\tau_T$  and facilitates binding of positively charged reactants at the interface. Increasing the potential by moving on to negatively or positively-charged micelles causes a severe drop in  $\tau_T$  and  $\phi_F$  and aggregation is enhanced. The use of phospholipid vesicles provides a similar environment to the emulsion ( $\tau_T = 3.2$ ,  $\phi_F = 0.03$ ) although the nature of the vesicle is more complex and several binding sites can be identified.

Of great importance for establishing a possible mechanism of electron transfer across a membrane is knowledge about the localisation of electronically excited porphyrin molecules in the lipid bilayer, because in principle there are possibilities of both their uniform distribution along the membrane thickness or their preferential localisation near the boundary surface. Work done by Parmon et al [108] using spin labels suggests that ZnTPP locates preferentially near the boundary surfaces of the bilayer. This observation supports the slightly different fluorescent results obtained with H<sub>2</sub>P and ZnP in micelles. It appears that the ZnP is more influenced by the surface potential than the H<sub>2</sub>P and there could possibly be some interaction of the charged headgroups with the Zn atom in the porphyrin. After all it was pointed out in section 3.9 that anions such as Cl<sup>-</sup> and F<sup>-</sup> formed strong axial ligands with ZnP. However complexation with the headgroups is not the only factor responsible for the observed changes in the photophysical properties since H<sub>2</sub>P showed similar characteristics as ZnP in absorption and  $\tau_T$ .

Association of metalloporphyrin with the interface appears to favour intermolecular porphyrin reactions as is apparent from the spectral changes and quenching. Aggregation is facilitated at very low concentrations. The normal consequence of such interactions is enhanced internal conversion [108] resulting in lower triplet yield. However only a fraction of the porphyrin molecules

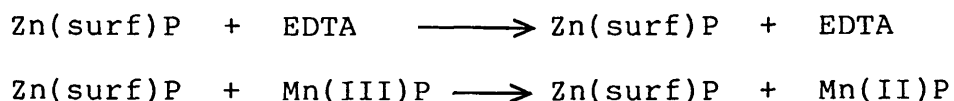
will exist as aggregates and the remainder should undergo inter system crossing to the triplet. The longer intrinsic lifetime of the triplet state permits long range electron transfer reactions to occur so that porphyrin molecules spaced too far apart to undergo singlet exciton state reactions might still be subjected to such reactions in the triplet. Thus triplet lifetimes of adsorbed porphyrins should be reduced compared to aqueous media, but when incorporated into a micelle, clustering is not so evident and hence longer  $\tau_T$  are observed except in highly charged environments.

### 3.25 Photoredox reactions sensitised by ZnP in micelles

Previous work has shown that water insoluble Mn(II) porphyrins can be solubilised in micellar and micro-heterogeneous media [109] without affecting their spectroscopic properties. It is known that the oxygen evolving active site in photosystem II comprises four manganese ions. Thus the study of manganese ions and manganese porphyrins has been, and still is, of great interest [110,111]. Irradiation of Mn(III) porphyrins in aqueous solution at pH8 containing an electron donor (e.g. EDTA, OH<sup>-</sup>) results in formation of the corresponding Mn(II) porphyrin [112]. However, because the excited

state lifetimes of the paramagnetic Mn(III) porphyrins are extremely short ( $\tau_T \sim 20\text{ns}$ ) intermolecular photoreduction requires high concentrations of donor and the quantum yields are very low (typically of the order of  $10^{-5}$ ). With diamagnetic metalloporphyrins, on the other hand, the long triplet lifetime ( $\tau_T \sim 1\text{ms}$ ) facilitates photoreduction at low concentration of donor and the quantum yields can be high.

The present work has shown that when a zinc porphyrin is dispersed in a neutral or slightly negatively charged micelle, its triplet lifetime in solution is increased significantly. In addition, results also suggested that the porphyrin positioned itself close to the surface of the micelle. Such observations lend support to the idea of using zinc porphyrins in micelles as intermediates in the photoreduction of Mn(III) porphyrins. The following scheme was envisaged:-



A positively charged manganese porphyrin (Mn(III)TMPYP) was used whilst the Zn(surf)P was dispersed in a micro-emulsion. However the quantum yield for formation of Mn(II) porphyrin was very low ( $10^{-4}$ ). This is most probably due to inefficient quenching of the ZnP triplet excited state by EDTA, which is repelled by the interface. Despite the long lifetime of the triplet state in

microheterogeneous media, the potential barrier at the interface is sufficiently strong to inhibit quenching by EDTA and the triplet lifetime remains almost unaffected by high concentrations of EDTA. Prolonged irradiation does result in some photoreduction but the observed product was the chlorin of the Zn(surf) porphyrin rather than the Mn(II) porphyrin. To account for this phenomenon it is necessary to consider that the ZnP resides in the microheterogeneous medium near to the interface but on the organic side. This would explain the extremely poor quenching with EDTA. However, upon reduction the  $\pi$ -radical anion of the porphyrin is formed [113] and, being negatively charged, it might be expelled somewhat from the organic phase. This would expose the  $\pi$ -radical anion to the aqueous solution where it can collect a second electron (from an  $\text{EDTA}^+$  radical) to form the chlorin. Partial expulsion of the  $\pi$ -radical anion would inhibit reduction of a Mn(III) porphyrin held within the organic phase of the micelle. Even when the Mn(III) porphyrin was attached directly to the surfactant zinc porphyrin via a medium length alkoxy chain the preferred reduction product was still the zinc chlorin and no Mn(II) porphyrin could be observed (Fig.3.16).

### 3.26 Conclusions

Water insoluble porphyrins are very sensitive to the surfactant medium in which they are inserted. Neutral micelles enhance the triplet lifetime whereas the reverse is true for charged micelles.

The previous chapter was mainly concerned with using zinc metalloporphyrins (ZnP) as photosensitisers. In this chapter we shall discuss the possible use of free-base porphyrin both as a sensitiser and also as a fluorescent probe for biological systems.

First impressions suggest that the free base is a promising system. For a start it absorbs a greater fraction of the solar spectrum than ZnP. Also it absorbs further into the red which is where most of the sun's intensity lies. Then it has a high quantum yield for fluorescence ( $\phi_F$ ) which makes it attractive as a model for light harvesting and also as a fluorescent label. The redox potentials for oxidation and reduction are also reasonable and finally the free base is easy to synthesise [143] and can be bought commercially in a pure state.

#### 4.2 Photophysics of H<sub>2</sub> TPP

Fig. 4.1 shows the absorption spectrum of H<sub>2</sub>TPP whilst table 4.1 lists the extinction coefficients together with the oscillator strengths. The symmetry is D<sub>2h</sub> as opposed to D<sub>4h</sub> in metalloporphyrins. In D<sub>2h</sub> symmetry the Q<sub>x</sub> and Q<sub>y</sub> transitions of the porphyrin are no longer degenerate and this accounts for the four Q bands in the free base spectrum. The oscillator strengths for the transition can be calculated from the following equation:

$$f = \frac{4\epsilon_0 \ln 10 mc^2}{e^2 L} \int \epsilon \, d\nu$$

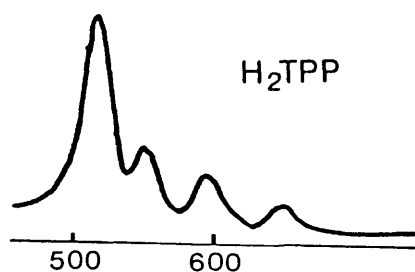


FIG. 4.1. a. Ground state  
absorption spectrum

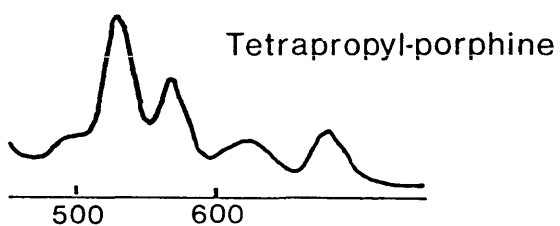


FIG. 4.1. b. "

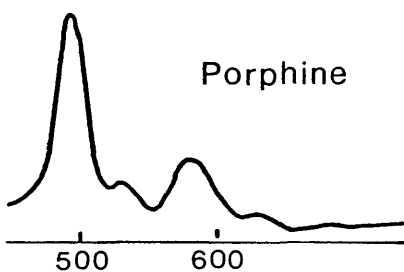


FIG. 4.1. c. "

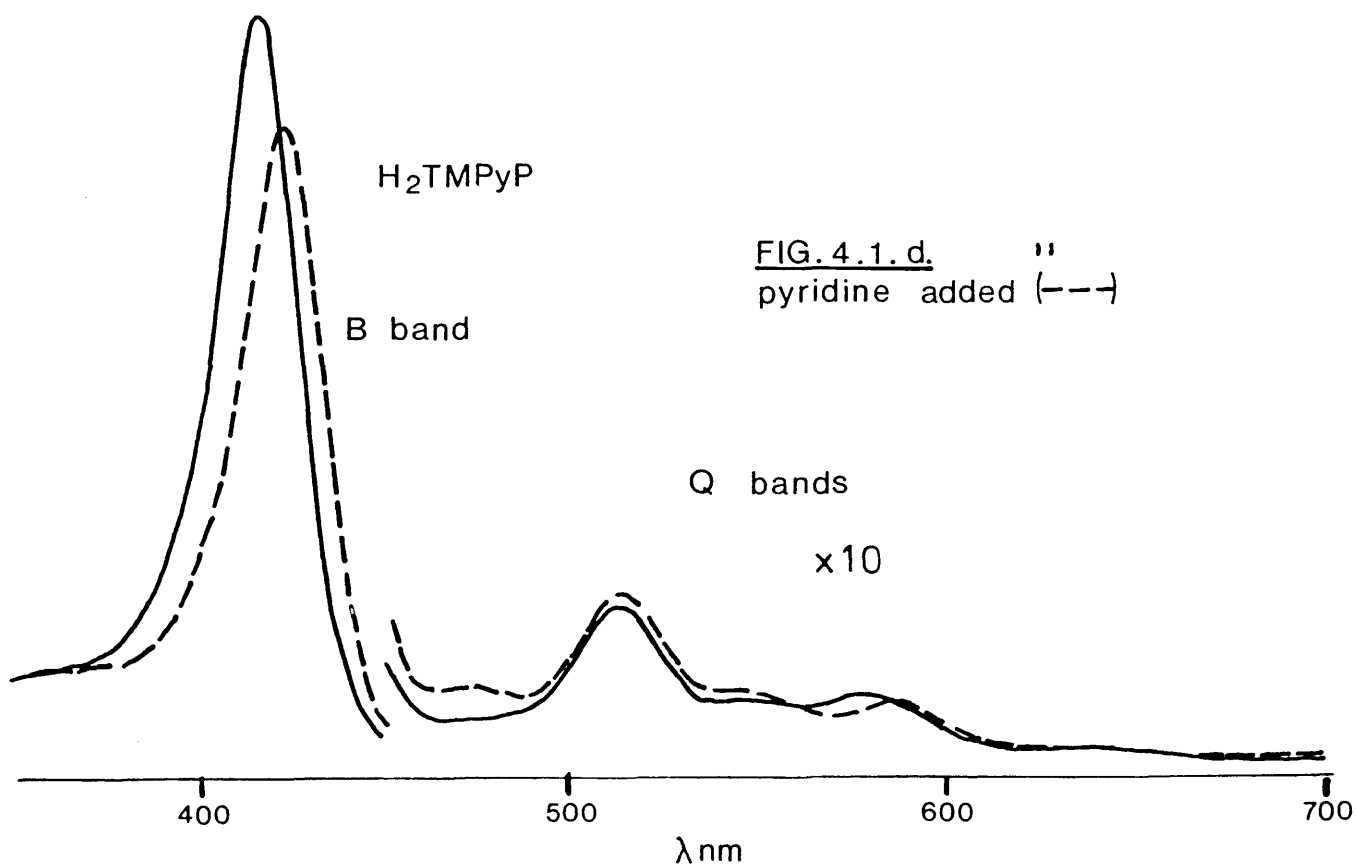


FIG. 4.1. d. " pyridine added (---)

where  $\int \epsilon dv$  is the area under the absorption band, using the decadic extinction coefficient and the constant preceeding the integral has the value  $4.32 \times 10^{-9} \text{ moldm}^{-3} \text{ cm}^2$ . The table below lists the  $f$  values for the transitions in H<sub>2</sub>TPP and is a measure of the transition probability.

TABLE 4.1

| nm          | $\epsilon$         | $f$    |
|-------------|--------------------|--------|
| 420nm       | $4.15 \times 10^5$ | 1.59   |
| 515 + 555nm | 18.822 & 7748      | 0.0976 |
| 592 + 647nm | 5277 & 3538        | 0.0224 |

The singlet lifetime ( $\tau_s$ ) of H<sub>2</sub>TPP is ca. 10 ns which is longer than eg. ZnP's 2 ns. As pointed out in the introduction this is due to the heavy atom effect.

In the case of the triplet state, the lifetime is similar to ZnP but the yield ( $\phi_T = 0.72$ ) and the triplet energy ( $E_T = 1.1\text{eV}$ ) are lower. Because of the lower triplet energy this implies a larger non-radiative rate constant from the triplet state which explains why the  $\tau_T$  of H<sub>2</sub>P and ZnP are similar. A transient absorption spectrum of the triplet state is shown in Fig. 4.2.

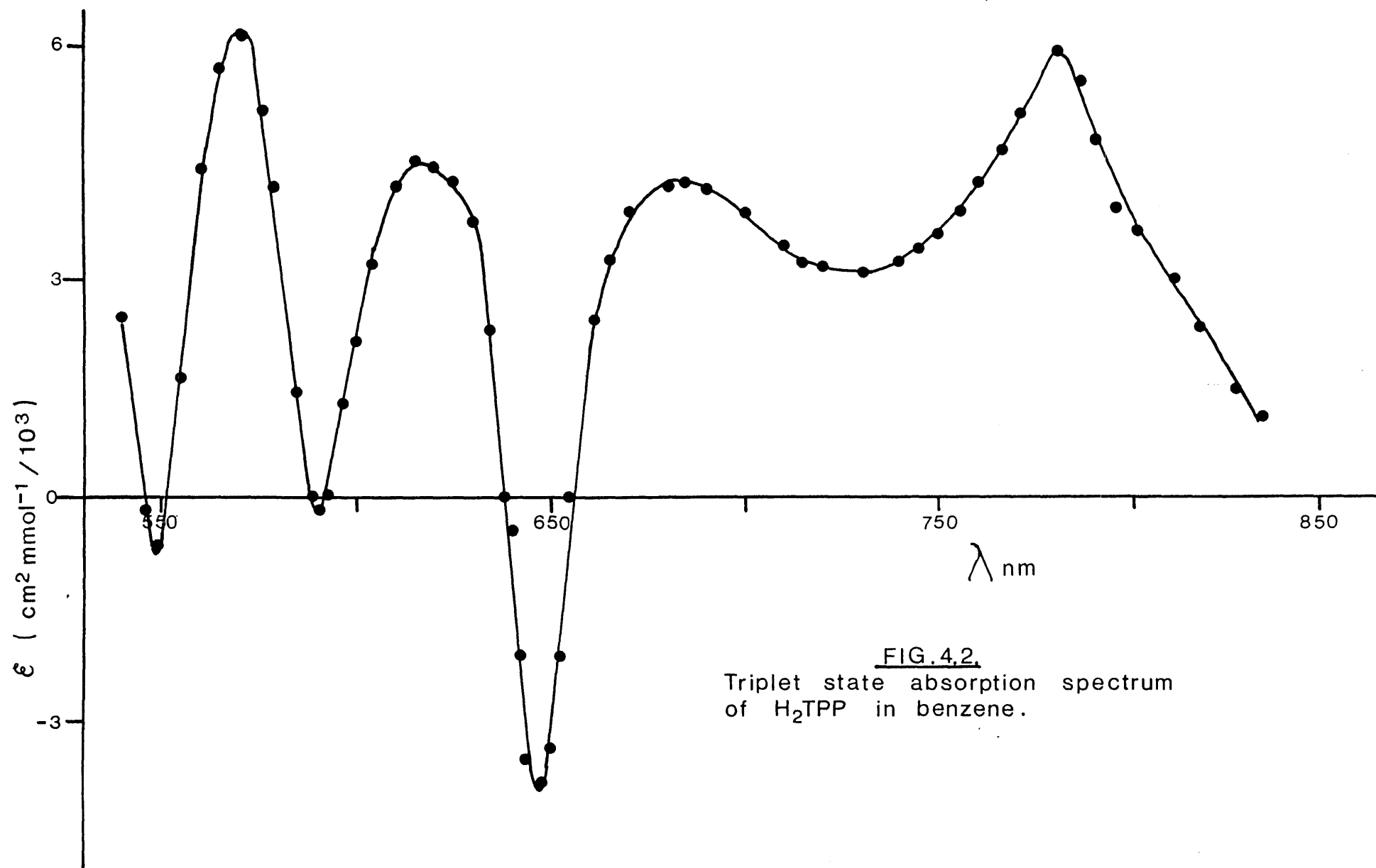
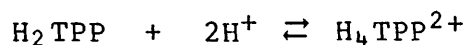


FIG.4.2.  
Triplet state absorption spectrum  
of H<sub>2</sub>TPP in benzene.

### 4.3 Stability

H<sub>2</sub>TPP is soluble in many organic solvents and is quite stable in solution over a period of a few weeks. However at pH ~4 it becomes protonated [135].



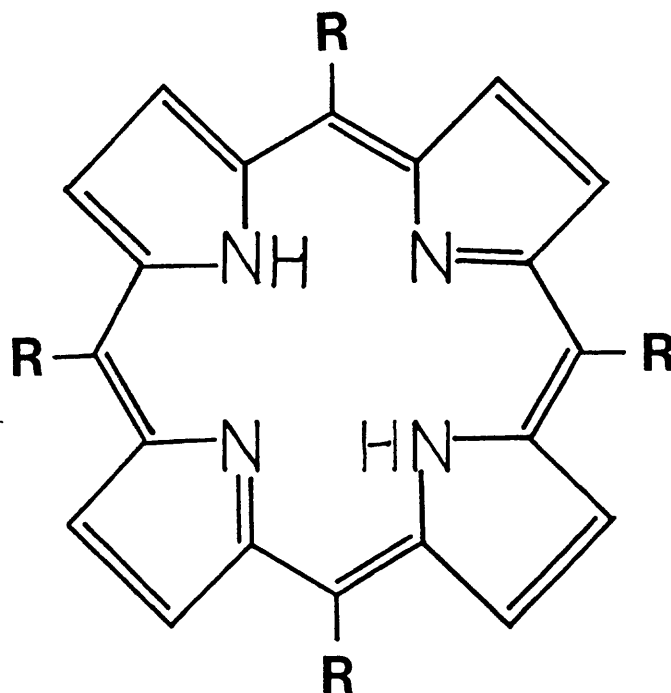
The absorption and fluorescence spectrum is

considerably more into the red than H<sub>2</sub>TPP. However both the  $\tau_S$  and  $\tau_T$  are very short lived and hence the diacid is not very suitable for our purposes. In most cases it is more convenient to do chemistry in aqueous solution. Luckily, however, water soluble porphyrins can readily be synthesised. Thus one can have negatively charged substituents as in H<sub>2</sub>TSPP or positive ones, e.g. H<sub>2</sub>TMPyP. The corresponding metallo-porphyrins have found prominent use as photosensitizers in solar-energy storage devices based upon the photodissociation of water [116,117,121-123].

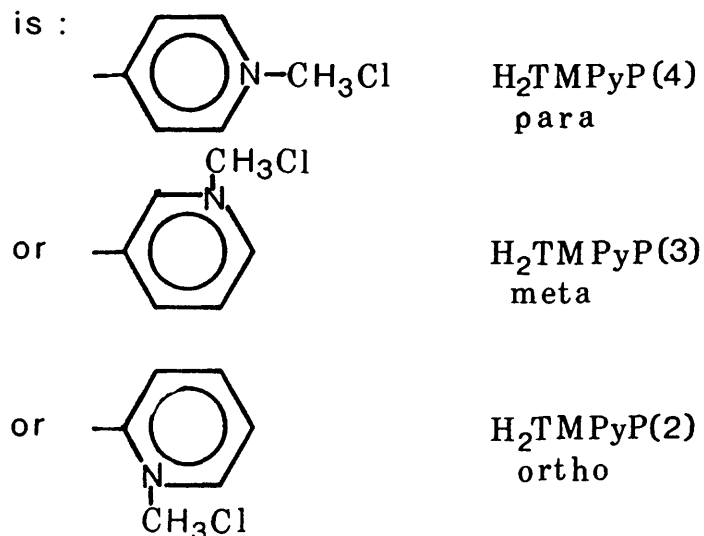
In the biological field some of the positively charged porphyrins have been used to intercalate with DNA. The type of complex formed between the porphyrin and nucleic acids depends on both the type of porphyrin used and the composition of neighbouring base pairs on the DNA [124-126]. The medical field is also interested in these types of porphyrins for use in cancer therapy [127].

#### 4.4. The Systems Studied

This chapter describes some interesting photochemistry of free base tetramethyl pyridyl porphyrin synthesised by A. Harriman. Compounds having negatively charged substituents on the porphyrin ring were not considered because of their high tendency to aggregate [118,119] thus reducing their photosensitising abilities. Besides, most cell membranes are negatively charged and thus a positively charged porphyrin is more appropriate. The porphyrins studied are shown below:



where R is :



## 4.5 Results and Discussion

### Absorption Spectra

The absorption spectra of all three isomers are similar and appear as Fig. 4.1d. The spectrum is etio-type as one would expect of a symmetric porphyrin but the  $Q_y(0-0)$  band has a larger extinction coefficient than the  $Q_x(0-1)$  band and in this respect resembles the spectrum of porphine (Fig. 4.1c). If these spectra are compared to those of TPP and tetrapropyl porphine (Fig. 4.1a and 4.1b) then a correlation is shown to exist between the positions and relative intensities of the absorption bands and the nature of the side chains on the macrocycle. The spectra suggest that different substituents will affect different changes in the  $\pi$  electron density of the macrocycle [129]. It would therefore appear that adding to the  $\pi$  electron density of the porphyrin ring leads to spectra such as 1a and 1b. In the case of TMPyP the pyridyl groups do not seem to cause much of a change when compared to the porphine spectrum and therefore one could tentatively suggest that the  $\pi$  orbitals of the porphyrin cycle and pyridyl substituents hardly have any influence on each other. Addition of pyridine reduces and shifts the Soret Band and the  $Q_x$  bands whilst the  $Q_y$  bands are not shifted. A similar observation was noted by Kano et al. [130] on addition of MeOH. This is in contrast to energy observations of the  $Q_x$  and  $Q_y$  bands as related to substituent changes where a prominent feature is that the  $Q_y$  band moves at

about twice the rate of the  $Q_x$  band [131]. In one theory free base formation is explained as a cyclic polyene perturbation. It predicts that the lowest porphyrin transition i.e. the  $Q_x$  bands, is polarized parallel to the H-H axis. If this is the case then a possible explanation of the  $Q_x$  band shift on addition of pyridine or MeOH is that H-bonding might be taking place with the pyrrole hydrogens.

### Fluorescence Spectra

The fluorescence spectra obtained for the three isomers are shown in Fig. 4.3. Contrary to their absorption spectra the steady state emission is significantly different, especially in the para isomer. At  $10^{-6}M$  the spectrum is broad and structureless with a maximum at about 730nm and a poorly defined shoulder at about 680nm. Diluting the solution to about  $10^{-8}M$  leads to a marked change in spectral profile (4.3d), which is typical of free base porphyrin. This behaviour of the para isomer has also been noted by other authors [131,132] and the former ascribed the broad spectrum to a stacked dimer species. However their spectra are in poor agreement with the ones reported here as they were not corrected. Changing the counterion ( $Cl^-$ ,  $I^-$ ,  $SO_4^{2-}$  or tosylate) had no effect upon the fluorescence spectra of either monomer or dimer and there was good correlation between the corrected excitation spectrum and the ground-state absorption spectrum.

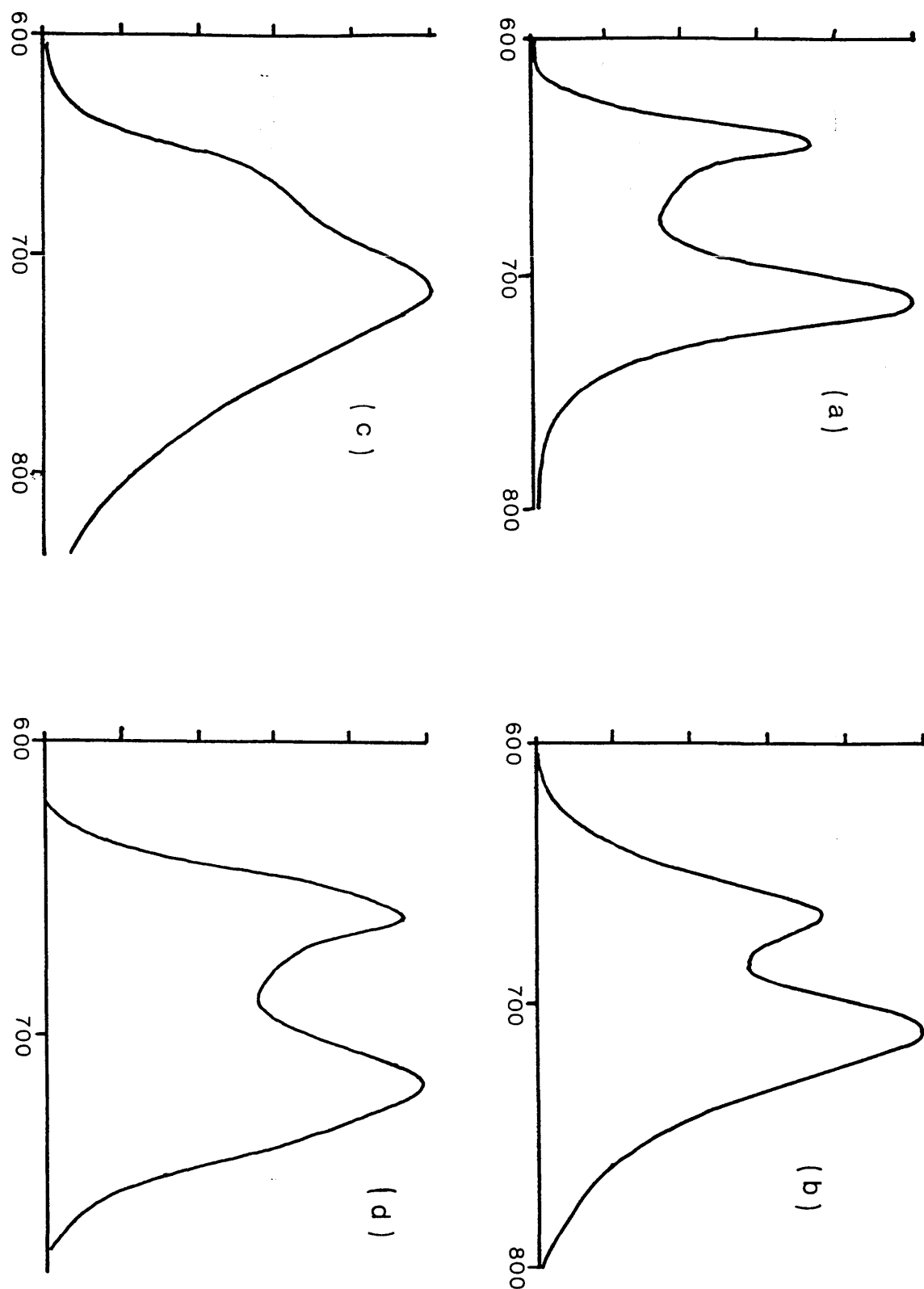
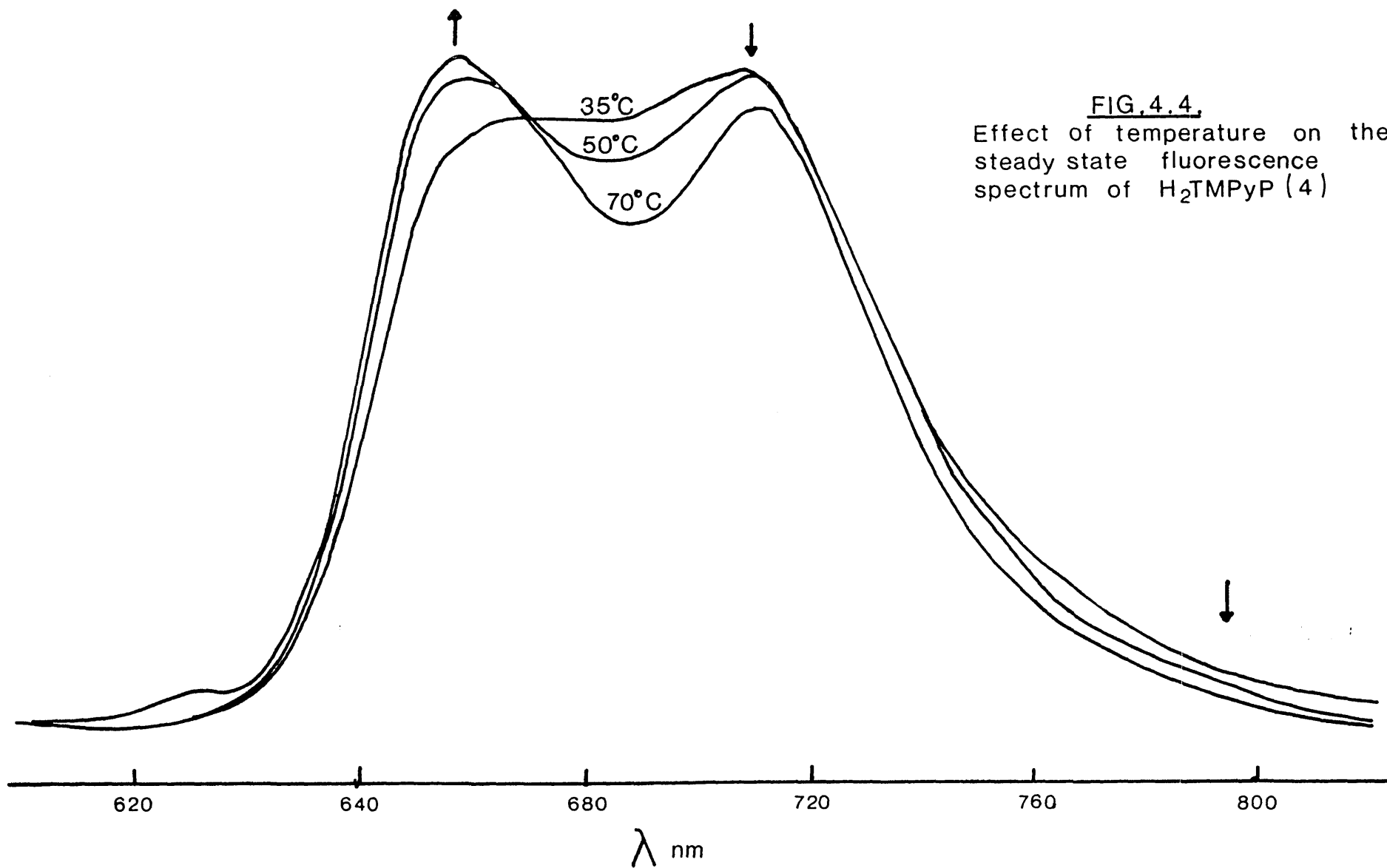


**Fig. 4.3**

Steady-state fluorescence spectra of: (a)  $\text{H}_2\text{TMPyP}(2)$ ; (b)  $\text{H}_2\text{TMPyP}(3)$ ; (c)  $\text{H}_2\text{TMPyP}(4)$  and (d) infinitely diluted ( $10^{-8} \text{ mol dm}^{-3}$  as opposed to  $10^{-6} \text{ mol dm}^{-3}$ )  $\text{H}_2\text{TMPyP}(\quad)$  in aqueous solution

The dimer fluorescence readily breaks down to the monomer if it is adsorbed onto a surface such as that of colloidal  $\text{TiO}_2$  or SDS micelles. Addition of pyridine which is known to break down metalloporphyrin dimers [133] also works for the free base. The mechanism for monomer formation in this instance is not quite clear, but it nevertheless is a genuine effect and warrants more research. Increasing the temperature to  $75^\circ\text{C}$  brings about a progressive increase in the concentration of monomer as monitored by means of fluorescence spectroscopy (Fig.4.4). Finally, increasing the ionic strengths of the medium by addition of KCl (1M) to a very dilute solution of  $\text{H}_2\text{TMPyP}(4)$  ( $10^{-8}\text{M}$ ) causes dimerisation.

Most of the accounts dealing with aggregation of porphyrins [118,119] have failed to accept  $\text{H}_2\text{TMPyP}^{4+}$  as a dimer on the basis of a Beer-Lambert plot. Thus compounds such as TCPP and TSPP<sub>3</sub> and other negatively charged porphyrins were shown to have appreciable deviation from Beer's law over a concentration range of  $6 \times 10^{-7}\text{M}$  to  $9 \times 10^{-6}\text{M}$ , whilst the positively charged porphyrins did not. The conclusion from these studies was that anionic porphyrins, apart from TPPS<sub>4</sub>, aggregated in water whilst the cationic ones did not. An explanation for this phenomenon was that the positive centres on the periphery cause the delocalised  $\pi$  electron cloud to be more diffuse over the surface of the molecule whereas negative centres pushed electron density into the porphyrin.



On the basis of the data obtained from fluorescence spectroscopy it was decided to repeat the Beer law plot over a much larger concentration range. The result is shown in Fig. 4.5. Cells of large path length were used in order to get to the very low concentrations whilst small path lengths (0.1cm) were used for the high concentrations. As seen the plot is linear over most of the concentration range, but it is curved at the lower end. The curvature is very subtle and only realised if plotted carefully. The behaviour is consistent with very efficient dimerization and clearly shows that the dimer is the dominant species at concentrations above  $10^{-6}\text{M}$  and below that an equilibrium between the dimer and monomer exists. However we were unable to observe a system with only monomer species present.

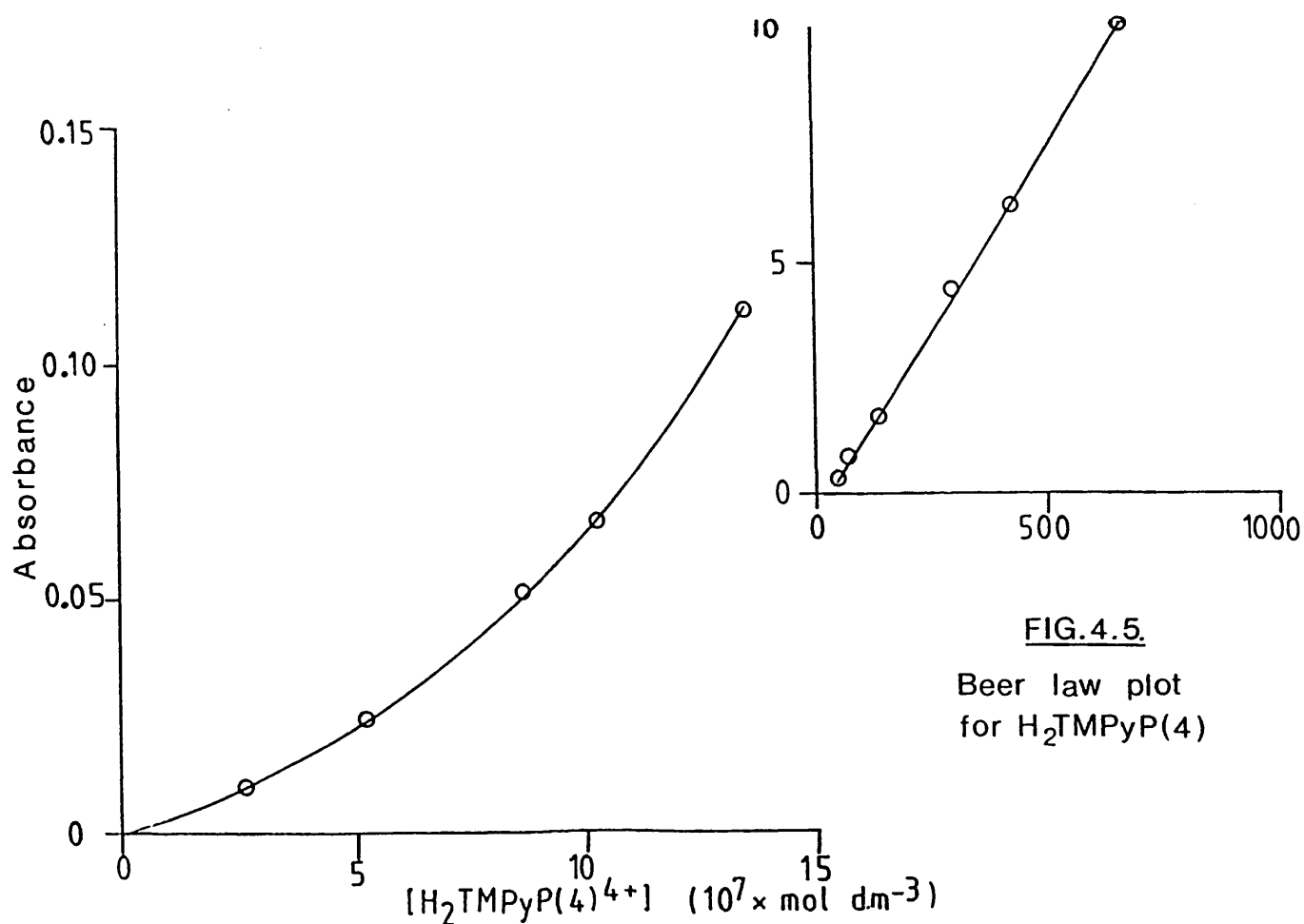
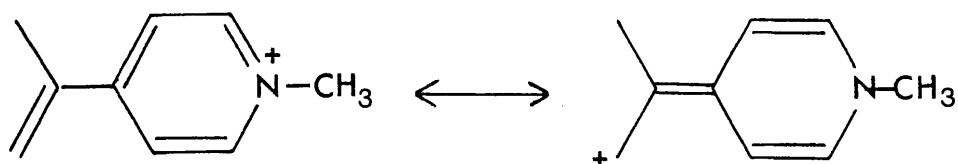


**FIG.4.5.**  
Beer law plot  
for  $\text{H}_2\text{TMPyP(4)}$

At the lowest concentration studied the Soret band was shifted about  $1.5\text{nm} \rightarrow 2.0\text{nm}$  relative to that found at  $10^{-5}\text{M}$  and a similar trend was observed in the respective excitation spectra. The slight red shift on dimerization suggests that exciton coupling in the dimer is minimal [134], a possible consequence of electron repulsion between the two charged porphyrins. The linear relationship of the Beer's plot above  $10^{-6}\text{M}$  implies that association is restricted just to dimerization rather than higher order aggregation. For the ortho and meta isomers there is no evidence for dimerization and both the five-coordinated zinc chelate ( $\text{ZnTMPyP}(4)$ ), and the conjugate diacid ( $\text{H}_4\text{TMPyP}(4)$ ) [135] exhibit only monomeric species at concentrations below  $10^{-4}\text{M}$ . Thus of the compounds studied, only  $\text{H}_2\text{TMPyP}(4)$  shows evidence of dimerization.

This suggests that the dimer has a stacked face to face orientation with the two porphyrin rings held about  $1\text{nm}$  apart (this distance being compatible with the B band shift of  $2\text{ nm}$ ). The reason for the facile ability of the para isomer, but not the ortho and meta isomers, to aggregate must be due to a unique property of  $\text{H}_2\text{TMPyP}(4)$ . That property is the ability of the pyridyl groups to participate in direct conjugation with the porphyrin ring [136] as shown below:



Evidence for direct conjugation comes from electrochemistry where a single 2-electron reduction wave rather than two one electron reduction waves (as is the case for all other porphyrins investigated) implies direct conjugation. Only two other examples of direct conjugation have been published so far. These are tetrakis(p-hydroxyphenyl) porphyrins together with their metal complexes [137,138] and tetra-para-substituted (TPP) Fe(III) [139]. The meta isomer can only delocalize its positive charge around the pyridyl ring and hence cannot enter into direct conjugation. Whilst in principle the ortho substituent could push charge into the ring, this is prevented in practice because of steric hindrance; from X-ray crystallographic structure determinations  $\beta$ -pyrrole and orthophenyl protons are constrained to being out of the porphyrin plane most of the time [140]. However Wolberg [141] suggested that nearly co-planar positions, which are necessary for resonance transfer of substituent effects, can be achieved in solution. The fact that phenyl rings rotate with activation energies of 11-17KCal/mol [142] indicates that they are in the porphyrin plane for some fraction of time. Thus the dimerization of the para isomer is related to the fact that steric hindrance is not a problem and the molecule is suitably adapted for resonance isomerisation.

One of the interesting results of this work is that the fluorescent properties of the dimer are almost identical with those of the monomer (Table 4.2), and in fact the fluorescent yield is greater.

TABLE 4.2

| Compound                | Species | $\phi_F^a$ | $\tau^b$<br>(ns) | $\tau^c$<br>(ns) | $\tau^d$<br>(ns) |
|-------------------------|---------|------------|------------------|------------------|------------------|
| H <sub>2</sub> TMPyP(2) | Monomer | 0.082      | 10.4             | 13.8             | -                |
| H <sub>2</sub> TMPyP(3) | Monomer | 0.057      | 5.3              | 7.9              | -                |
| H <sub>2</sub> TMPyP(4) | Monomer | 0.048      | 3.7              | -                | -                |
| H <sub>2</sub> TMPyP(4) | Dimer   | 0.056      | 6.1              | 6.0              | 4.1              |

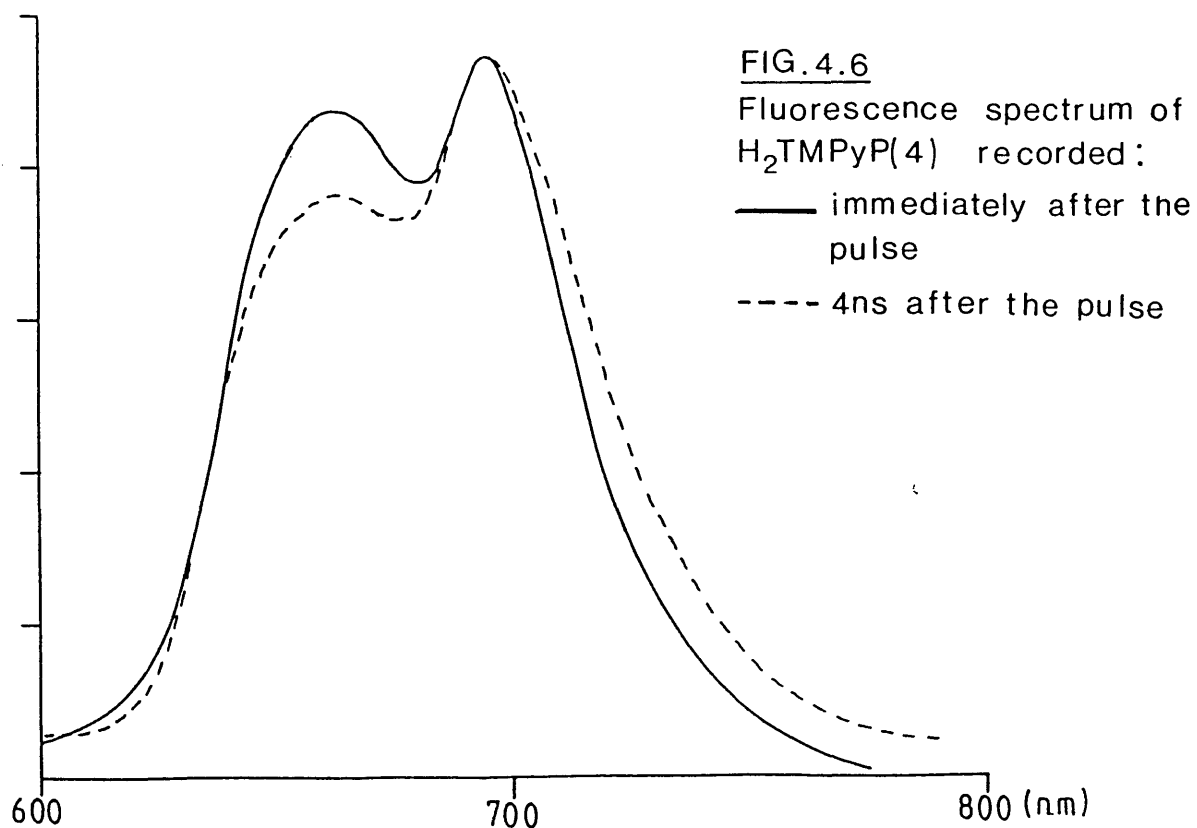
a  $\pm$  5%, b  $\pm$  1ns (this work)

b  $\pm$  1ns (this work)

c From ref. 132

d From ref. 130

The time-resolved fluorescence decay is shown in Fig. 4.6 and supports the steady state data. The fluorescence spectrum recorded immediately after the pulse is somewhat blue-shifted relative to that recorded 4 ns after the

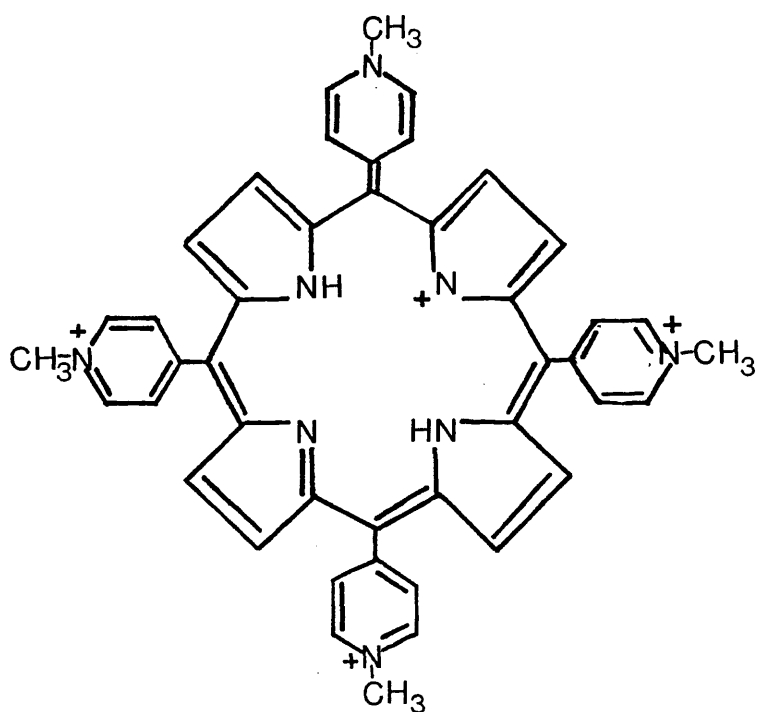


pulse. Thus the dimer appears to possess the larger lifetime. The results are not surprising in view of the fact that exciton coupling is minimal in the dimer. In fact the dimer appears to be more fluorescent than the monomer. This is in conflict with usual reports of fluorescent quenching in most other dimer systems such as ZnTSPP<sup>4-</sup> and sulphonated Zinc phthalocyanine where the reduced fluorescence has been put down to increased non-radiative decay due to internal conversion. In the case of H<sub>2</sub>TMPyP(4) however, where the exciton coupling is minimal, this is not the case.

#### 4.6 Conclusions

Spectroscopic evidence for efficient dimerization of H<sub>2</sub>TMPyP(4) in aqueous solution has been firmly established. The other isomeric H<sub>2</sub>TMPyP<sup>4+</sup> compounds together with the non planar chelates and diacids do not dimerize in aqueous solution at concentrations below 10<sup>-4</sup> mol dm<sup>-3</sup>. In addition the dimerization of H<sub>2</sub>TMPyP(4) does not really affect its fluorescent properties, although the dimer spectrum is markedly different from that of the monomer. Suggestions to explain the willingness of dimerization in this compound have been forthcoming. Almost certainly the ability of the molecule to become planar via direct conjugation is the primary explanation. Another reason put forth by Kano et al. [130] is that electrostatic repulsion is reduced when the positive charges are delocalised into the porphyrin ring. However

I do not fully agree with the latter reason as pushing positive charge into the ring generally tends to increase repulsion. An alternative speculative theory for the distribution of charge could be that the positive charge is not just delocalised to the methine bridges but can also extend to the pyrrole nitrogens as shown below:-



. The structure would also lend support to the fact that the pK<sub>a</sub> is a low 1.4. If the pyrrole nitrogens have positive charges then protonation would be more difficult. The low pK<sub>a</sub> of the ortho compound is not so readily explained but it might be due to steric hindrance by the counter ions which are almost certainly counteracting the positively charged pyridinium groups at low pH's.

The findings of this study therefore show that the use of  $\text{H}_2\text{TMPyP}(4)$  has its problems as a photosensitiser for photosynthetic models and is not to be recommended as a fluorescent label for DNA and other biological materials.

CHAPTER V  
COVALENTLY LINKED PORPHYRIN DIMERS

## 5.1 Introduction

The terms 'donor' and 'acceptor' are familiar expressions used in the description of both energy and electron transfer processes. Very frequently the acceptors are also referred to as 'traps'. As highlighted in Chapter I the efficiency of such processes is highly dependent on the mutual orientation of both the donor and the acceptor molecules. The most successful system for the efficient conversion of solar energy into useful products via a sequence of energy transfer and electron transfer steps is the green leaf. The realisation that nature relies upon closely-spaced metalloporphyrins with a high degree of directionality to perform the primary processes of photosynthesis has stimulated a lot of interest in the design and construction of model systems [144,145]. These primary processes take place in the reaction centre where magnesium dihydroporphyrin systems are involved in the transfer of energy which is ultimately trapped by a (bacterio) chlorophyll dimer [146]. The excited state dimer is the primary electron donor and it rapidly transfers an electron to a (bacterio) pheophytin or a monomer chlorophyll molecule held in close proximity.

In solution porphyrins adopt a random orientation with respect to one another. In order to introduce some directionality into the system many different metalloporphyrin dimers have been synthesised and generally the porphyrin rings are separated by covalent

linkages [147,148]. The type of porphyrin dimers that have been studied so far in vitro can be classed into four groups: 1) the simplest are the  $\mu$ -oxo bridged species where an oxygen atom links the two porphyrin rings via their central metal ions. Such species are important for  $\text{Fe}^{\text{III}}$ , [149],  $\text{Sc}^{\text{III}}$  [150] and  $\text{Al}^{\text{III}}$  [151] and generally the fluorescence is quenched relative to the monomer [151]. 2) Polar solvent molecules can be used to bridge  $\text{Mg}^{\text{II}}$  porphyrins, [152,153] forming structures closely akin to those of the light harvesting chlorophylls in photosynthetic organisms. 3) The third important class of compounds concerns the cofacial dimer [154,157]. Here efficient energy [158] and electron transfer [159,161] have been observed from the singlet excited state of one of the metalloporphyrins. Such compounds also appear to have applications for oxygen reduction [162]. 4) Finally, metalloporphyrin dimers linked by a single flexible hydrocarbon chain have been synthesised [81,82] and they are the type of dimers discussed in this chapter. Many such dimers have been prepared and it is relatively easy to insert different metal ions into the two porphyrin rings to produce mixed metal dimers. As in the previous class of compounds, both energy [163,165] and electron transfer [161,82] have been described. Thus, with a zinc/free-base dimer [164] singlet energy transfer occurs from  $\text{Zn}^{\text{II}}$  porphyrin to the free-base porphyrin with high efficiency, whereas triplet energy transfer has been

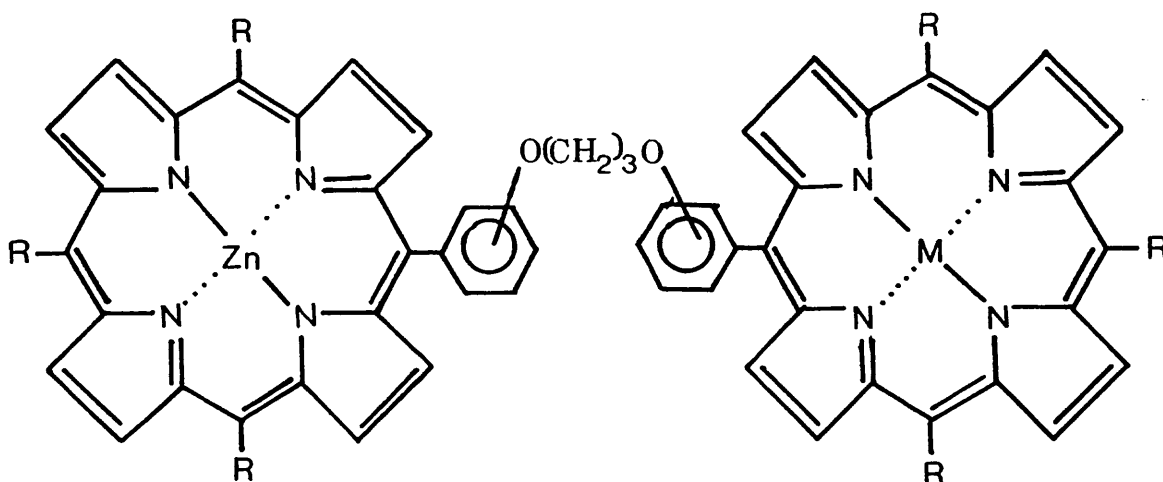
observed from  $\text{Zn}^{\text{II}}$  porphyrins to covalently linked  $\text{Cu}^{\text{II}}$  porphyrins [163,165]. Electron transfer has been shown to occur for  $\text{Mg}^{\text{II}}$ /free-base porphyrin dimers in polar solvents when the dimer has a closed conformation [161].

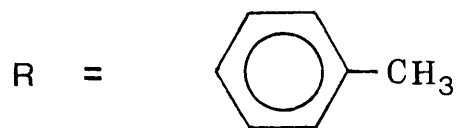
This chapter is divided into two parts. The first describes the fluorescent properties of a series of  $\text{Zn}^{\text{II}}$ /metal ion porphyrin dimers in which the two porphyrin moieties are bridged by a short, flexible chain whilst the latter part of this chapter is concerned with energy transfer in a  $\text{Zn}^{\text{II}}$ /free base porphyrin dimer. The aim of this chapter is to model the primary processes of photosynthesis that is the events occurring before electron transfer along the electrochemical gradient in the Z scheme takes place. The modelling of the latter processes will be described in the following and final chapter.

## Part I Zinc/mixed metal dimers

### 5.2 Results

The porphyrins used for this work are of the type shown below:



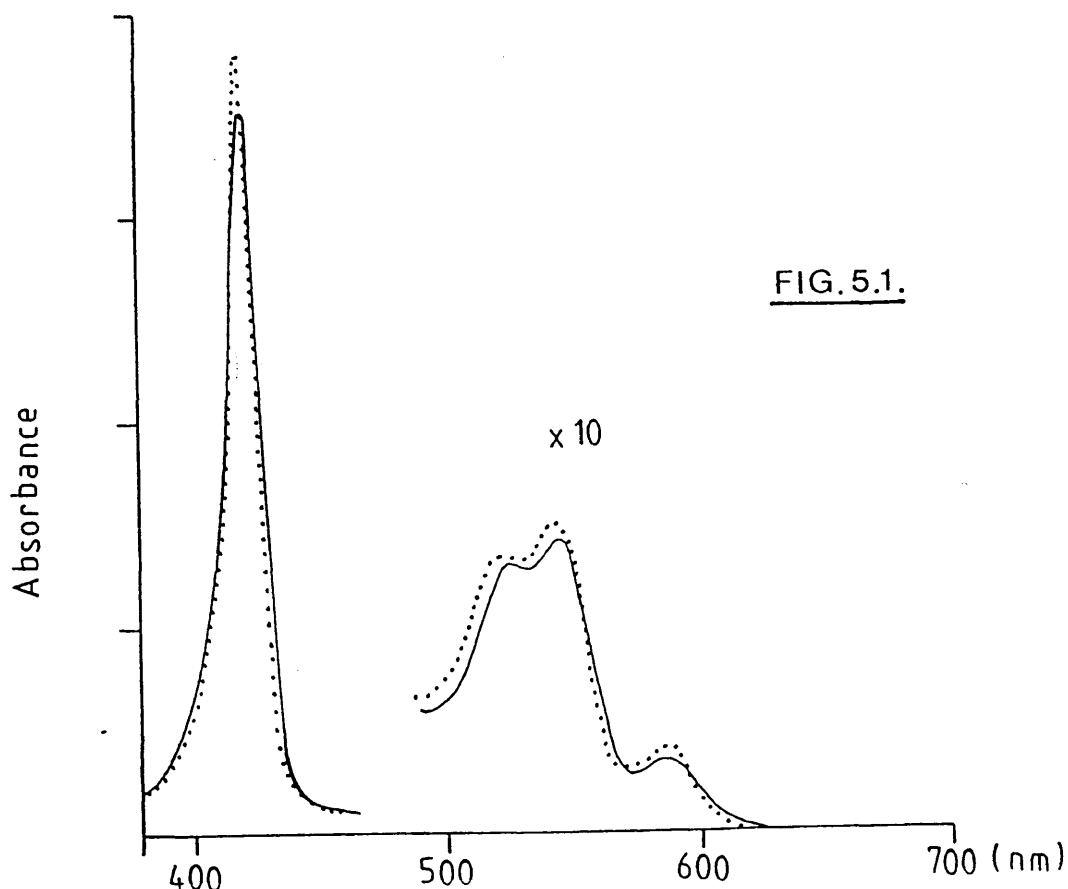


All of the dimers were linked in the para-para position of the phenyl ring apart from the Zn/Mn dimer where 3 dimer isomers were synthesised with the link in either the ortho- or para-position.

The absorption spectra of all the compounds can be explained in terms of a superposition of the absorption spectra of the individual porphyrins concerned. Thus for example Fig. 5.1 compares the absorption spectrum of the Zn/Ni dimer with an equimolar mixture of ZnTPP and NiTPP in benzene. No significant broadening of the B bands is observed from which it is concluded that exciton coupling in the dimers is small [166].

This suggests that the porphyrin rings are not held in close proximity and hence are unlikely to be closely stacked.

The fluorescence measurements of the systems considered are greatly simplified by the practically non-existent luminescence of all the porphyrins with the



Absorption spectra recorded in dilute benzene solution for a 1/1 molar mixture of ZnTPP + NiTPP (····) and the pZn/pNi dimer (—).

exception of zinc porphyrin [66,67]. Thus the consequence of attaching another porphyrin to the zinc porphyrin can simply be observed by monitoring the effect it has on the luminescence properties of that porphyrin. The reason for the lack of fluorescence from the other porphyrins is due to their very short singlet lifetimes which can be attributed to the heavy atom effect (see Chapter 1) and the paramagnetic nature of some metal ions such as FeIII, CuII and MnIII. Fig. 5.2 shows the fluorescent spectra recorded for the various dimers in benzene solution (excitation wavelength 558nm). In all cases maxima at 600 and 660nm typical of zinc porphyrin were observed, independent of excitation wavelength.

Slight differences in the ratios of the two peaks were noted, especially for the ortho substituted  $Zn^{II}$  porphyrin. For dimers containing  $Fe^{III}$  and  $Mn^{III}$  porphyrins it is possible that the spectra are distorted by an inner filter effect since these porphyrins absorb quite intensely at 600-630nm and therefore can reabsorb any fluorescence emitted in this region.

The fluorescence excitation spectra [72,167] were in poor agreement with the ground state absorption spectra of the dimers. Essentially the spectra obtained are equivalent to the ground state absorption spectrum of zinc porphyrin thus indicating that only light absorbed directly by the  $Zn^{II}$  porphyrin led to fluorescence. This effect is shown in Fig. 5.3 which compares excitation and absorption spectra recorded for ZnTPP, pZn/pNi and pZn/pMn

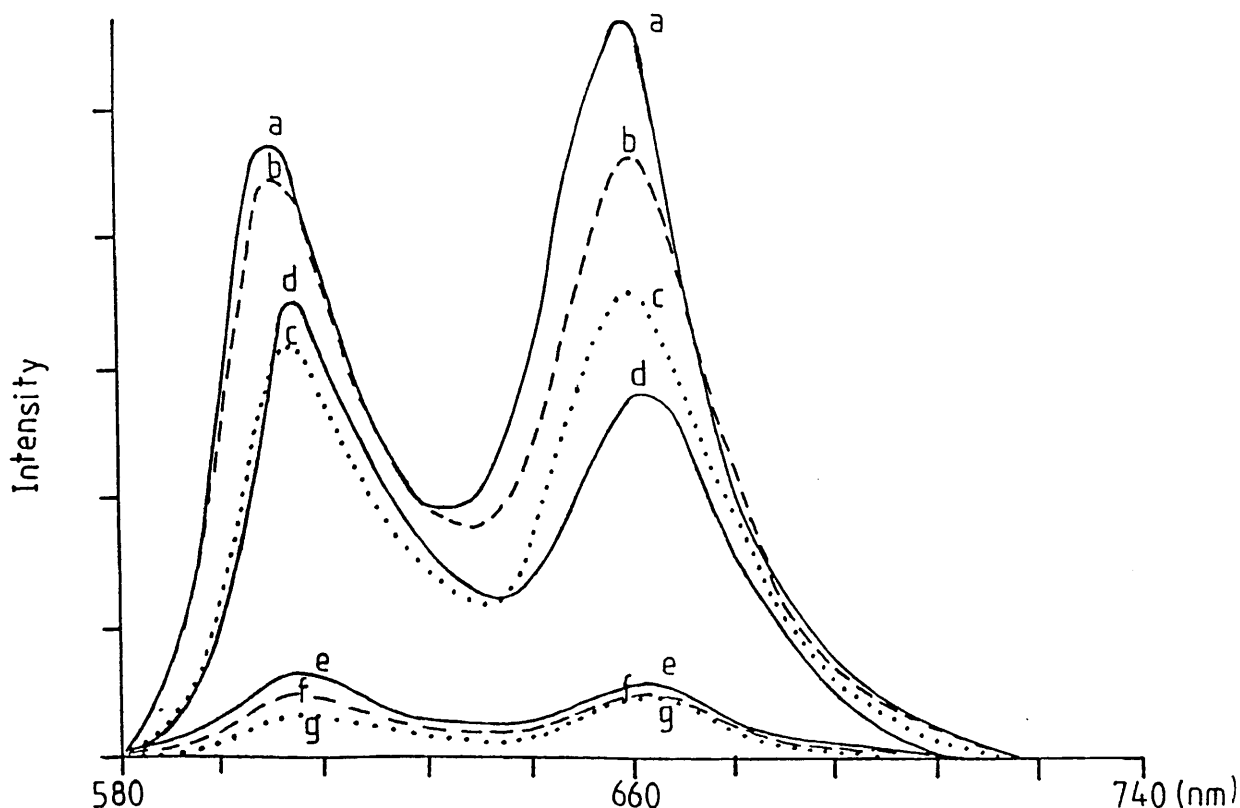


**FIG. 5.2.**

Fluorescence spectra recorded for the various metalloporphyrins in dilute benzene solution (excitation wavelength 558nm);  
 (a) ZnTPP (b) oZn/oMn (c) pZn/pNi (d) pZn/oMn (e) pZn/pCu  
 (f) pZn/pFe and (g) pZn/pMn.

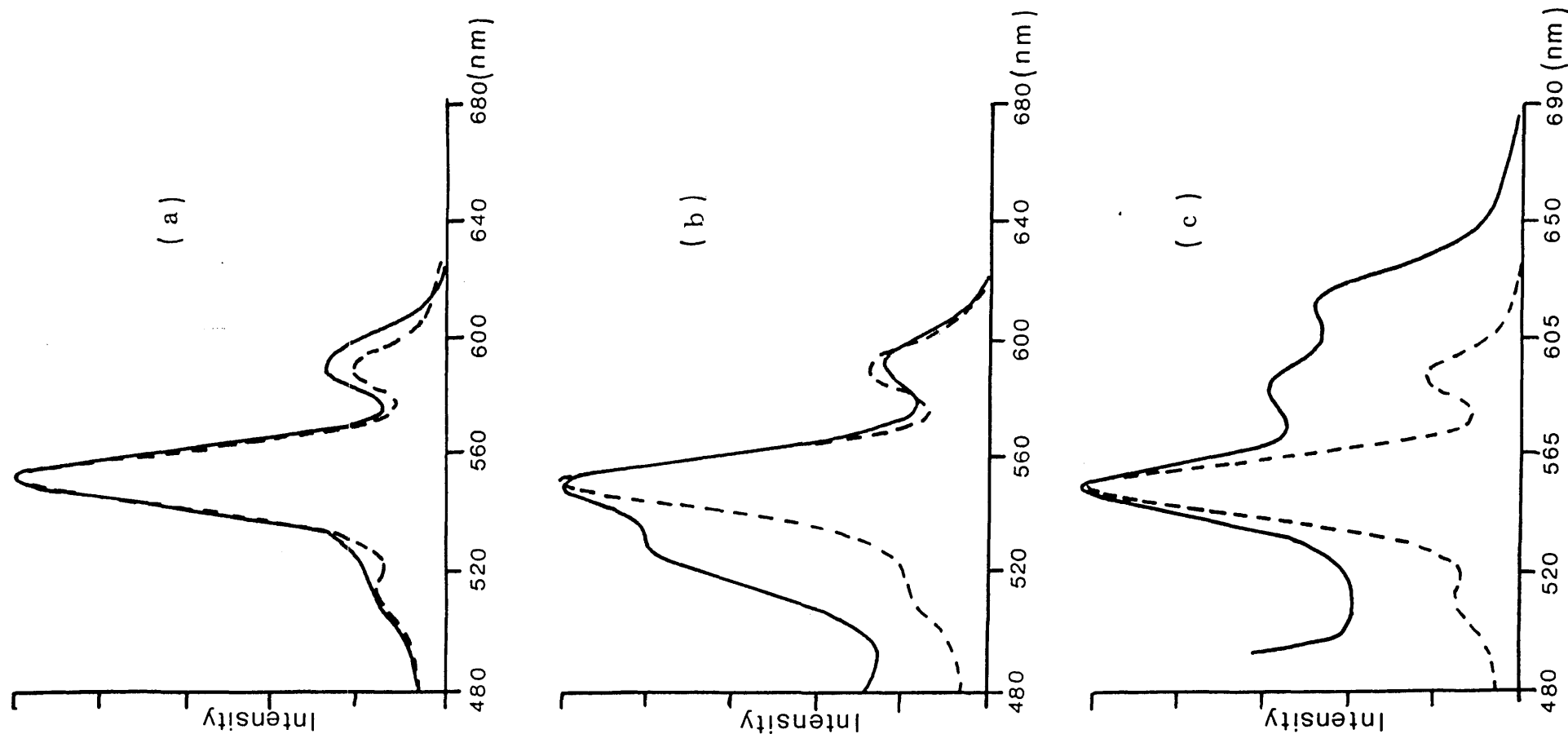


FIG.5.3.

Comparison of the ground state absorption spectra (—) and the corrected excitation spectra (---) recorded in dilute benzene solution; (a) ZnTPP (b) pZn/pNi and (c) pZn/pMn. The spectra have been normalised to the absorption centred around 555nm.

in benzene solution. For ZnTPP, the excitation and absorption spectra match very well throughout the entire visible region. However, for the mixed metal dimers it is clear that light absorbed by the second metalloporphyrin is not transferred to the  $Zn^{II}$  porphyrin.

At 558nm excitation, most of the incident light is absorbed by the  $Zn^{II}$  porphyrin, but a small fraction is also claimed by the other metalloporphyrin. Consequently, since we do not observe energy transfer to the  $Zn^{II}$  porphyrin, it is necessary to correct any fluorescence quantum yields obtained, so that they take into account the partitioning of the incident light.

Table 5.1 lists the uncorrected quantum yields ( $\phi_F^{UNC}$ ) and the corresponding values calculated on the basis of the amount of light incident upon the  $Zn^{II}$  porphyrin ( $\phi_F^{COR}$ ). These latter values were derived by removing the  $Zn^{II}$  ions with trifluoroacetic acid, as suggested by Schwartz et al. [163]. The singlet lifetimes ( $\tau_S$ ) of the dimers, also given in Table 5.1 were recorded by the single photon counting technique. The measurements were carried out in both a non-polar solvent (benzene) and a more polar solvent (DMF). Because of the practically non-existent fluorescence from the pZn/pCu, pZn/pFe and pZn/pMn dimers it was necessary to use long counting times to try and maximise the signal-to-noise ratio to enable the analysis of the data. In these cases, the derived  $\tau_S$  values are rough estimates only.

TABLE 5.1

| dimer   | $\phi_F^{\text{UNC}}$ | $\phi_F^{\text{COR}}$ | $\tau_s/\text{ns}$ | $\tau_s^a/\text{ns}$ | $\tau_T$          | $\phi_T$ |
|---------|-----------------------|-----------------------|--------------------|----------------------|-------------------|----------|
| ZnTPP   | 0.0300                | 0.0300                | 2.00               | 2.00                 | 1.2ms             | 0.90     |
| pZn/pNi | 0.0234                | 0.0266                | 1.25               | 1.36                 | 380 $\mu\text{s}$ | 0.93     |
| pZn/pCu | 0.0106                | 0.0160                | -                  | -                    | 30ns              | -        |
| pZn/pFe | 0.0033                | 0.0035                | 0.05               | 0.05                 | 20ns              | -        |
| pZn/pMn | 0.0024                | 0.0034                | 0.05               | 0.05                 | 20ns              | -        |
| pZn/oMn | 0.0181                | 0.0270                | 1.61               | 1.72                 | 550 $\mu\text{s}$ | 0.93     |
| oZn/oMn | 0.0283                | 0.313                 | 1.75               | 1.95                 | 600 $\mu\text{s}$ | 0.94     |

a in DMF

Photophysical properties of the metalloporphyrin dimers measured in dilute benzene solution.

Flash photolysis was used to record the triplet-triplet absorption spectrum [66] of ZnTPP in outgassed benzene solution (Fig. 5.4) and the triplet lifetime ( $\tau_T$ ) is 1.2ms at room temperature. The mixed-metal dimers showed almost identical triplet absorption spectra and are very similar to that for ZnTPP. The spectra obtained for pZn/pNi and pZn/oMn are also shown on Fig. 5.4. In dilute benzene solution, the triplet lifetimes of the dimers were somewhat shorter than that found with ZnTPP under identical conditions (Table 5.1). For the pZn/pCu dimer, the measured  $\tau_T$  value is close to the time resolution of the instrument and accurate lifetimes could not be determined for pZn/pFe and pZn/pMn. For the longer-lived triplets, quantum yields for formation of the

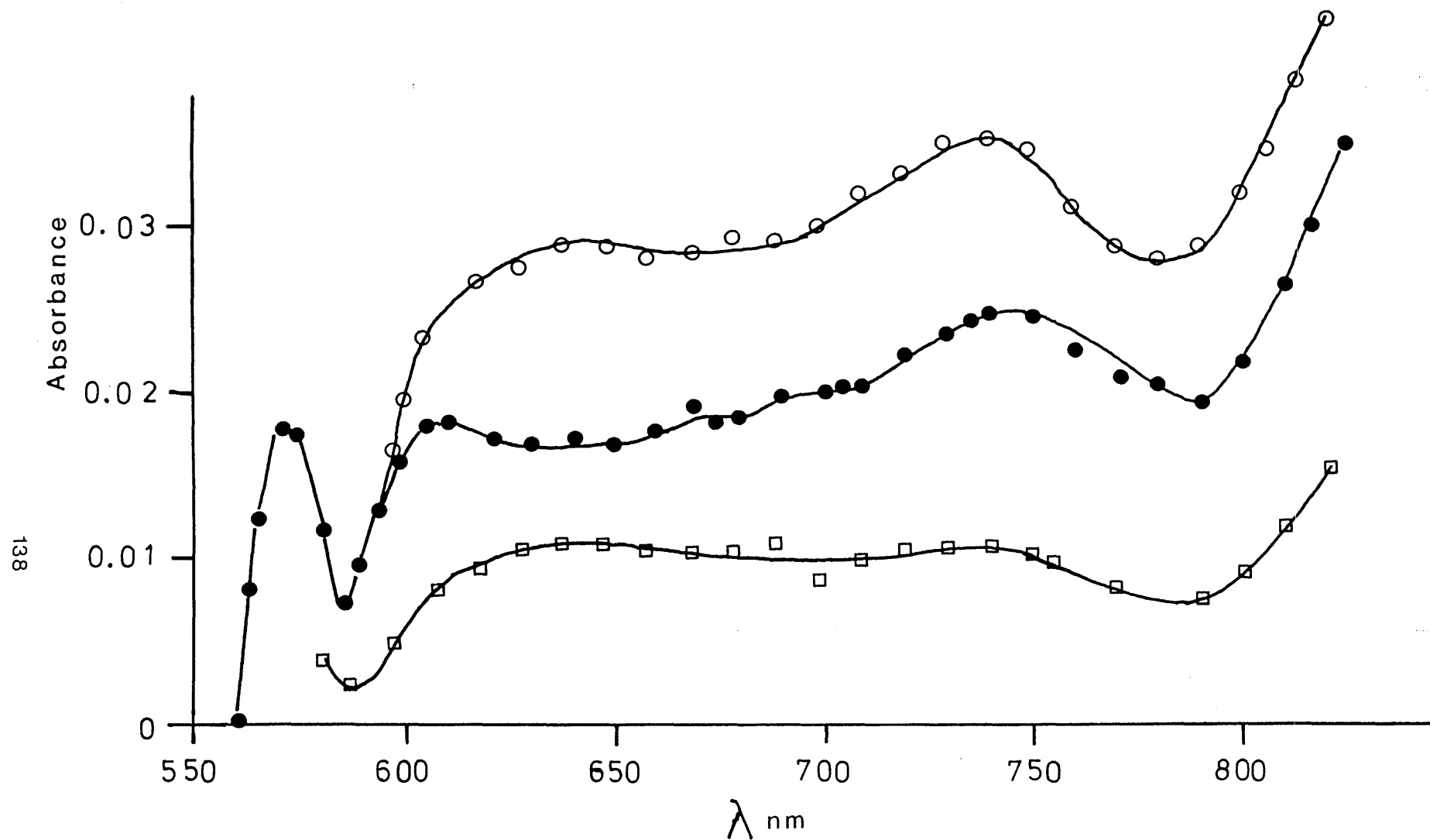


FIG. 5.4.

Triplet absorption spectra recorded for the various metalloporphyrins in outgassed benzene solution (a) ZnTPP (●—●—●); (b) pZn/pNi (□—□—□) and (c) pZn/oMn (○—○—○).

triplet state ( $\phi_T$ ) were measured at 470 and 680nm assuming that all the compounds had the same molar extinction coefficient [168] for the triplet excited state. The extinction coefficients used were  $\epsilon_{470} = 7.1 \times 10^4$  and  $\epsilon_{680} = 4.5 \times 10^3 \text{ cm}^2 \text{ mol}^{-1}$ .

### 5.3 Discussion

#### Excited-State Quenching

Of the metalloporphyrins used in this work, only  $\text{Zn}^{II}$  porphyrins fluoresce in fluid solution at room temperature and only  $\text{Zn}^{II}$  ( $\tau_T = 1.2\text{ms}$ ) and  $\text{Cu}^{II}$  ( $\tau_T = 25\text{ns}$ ) porphyrins have triplet excited states sufficiently long lived to be detected by the equipment used in this study. The other metalloporphyrins possess very short-lived excited states [66,67]. Hence the observed fluorescence and triplet absorption spectra can be assigned entirely to the  $\text{Zn}^{II}$  porphyrin. From the fluorescence excitation spectra one can conclude there is no singlet excitation energy transfer from the other metalloporphyrin to the covalently linked  $\text{Zn}^{II}$  porphyrin. Similar conclusions have been reached before for Zn/Cu and Zn/Ni porphyrin dimers [163,164].

After correction for partitioning of the incident light, it is seen that fluorescence from the  $\text{Zn}^{II}$  porphyrin in the dimer is quenched relative to ZnTPP (Table 5.1). The extent of quenching ( $Q$ ) can be expressed by

$$Q = \left( 1 - \frac{\phi_F^{\text{COR}}}{\phi_F^{\text{O}}} \right) \times 100\%$$

where  $\phi_F^O$  is the fluorescence quantum yield of ZnTPP. As shown in Table 5.2 the quenching depends markedly upon the nature of the central metal ion (Table 5.2). For the pZn/p-metal ion dimers, fluorescence quenching increases along the series  $Ni < Cu < Fe \approx Mn$  and the singlet excited-state lifetimes recorded in benzene and DMF parallel this quenching trend. It is also clear that for the Zn/Mn dimers the site of attachment of the covalent linkage affects the magnitude of fluorescence quenching (Table 5.2). Although the chain length remains constant throughout the series, fluorescence quenching in the oZn/oMn dimer is unimportant. Some quenching is noted for the pZn/oMn dimer, but in the pZn/pMn dimer, it is very pronounced. As will be seen later, this effect is connected with the geometry of the various dimers and it seems that the various conformers do not equilibrate within the singlet excited state lifetime.

From the singlet excited state lifetimes in benzene, the rate constant for quenching the  $Zn^{11}$  porphyrin fluorescence by the second metalloporphyrin ( $k_Q^S$ ) can be calculated from:

$$k_Q^S = (1/\tau_S - 1/\tau_S^O)$$

where  $1/\tau_S^O$  is the singlet lifetime of ZnTPP. The calculated values are collected in table 5.2 and it is seen that quenching by  $Mn^{111}$  and  $Fe^{111}$  porphyrins is extremely efficient in the p/p dimers.

Table 5.2  
Quenching rate constants for the various  
metalloporphyrin dimers in dilute benzene solution

| dimer   | $k_Q^S/s^{-1}$    | $k_Q^T/s^{-1}$    |
|---------|-------------------|-------------------|
| oZn/oMn | $7.0 \times 10^7$ | $8.4 \times 10^2$ |
| pZn/oMn | $1.2 \times 10^8$ | $1.0 \times 10^3$ |
| pZn/pNi | $3.0 \times 10^8$ | $1.8 \times 10^3$ |
| pZn/pCu | -                 | $3.3 \times 10^7$ |
| pZn/pFe | $10^9$            | $10^8$            |
| pZn/pMn | $10^9$            | $10^8$            |

Where measurements were possible, the  $\phi_T$  values (table 5.1) show that fluorescence quenching leads to slightly enhanced triplet state formation. Thus excluding the pZn/pFe and pZn/pMn dimers, the presence of the second metalloporphyrin enhances intersystem-crossing to the triplet state of the  $Zn^{II}$  porphyrin. As with the singlet excited state, the triplet state of the  $Zn^{II}$  porphyrin in the dimers is quenched with respect to ZnTPP. The calculated values of  $k_Q^T$  are collected in table 5.2 and it is clear that they mirror the corresponding  $k_Q^S$  values

suggesting that the same quenching is operable in both cases. However, the observed  $K_Q^T$  values spread over four orders of magnitude for the p/p dimers and there is a tremendous difference in  $\tau_T$  for the various Zn/Mn isomers.

Work carried out much earlier by Schwartz et al. [163] showed that the triplet lifetime of a  $Zn^{11}$  porphyrin in rigid glass at 77K was slightly shortened by the presence of a covalently linked  $Cu^{11}$  porphyrin. However, under such conditions the observed quenching effect was small and highly dependent upon the nature of the linkage [163]. Slightly more efficient quenching was noted for a Zn/Co porphyrin dimer under identical conditions. More recently, Mialocq et al. reported  $\tau_T$  values of 415, 210 and 395ns respectively for  $\underline{o}Zn/\underline{o}Cu$ ,  $\underline{o}Zn/\underline{p}Cu$  and  $\underline{p}Zn/\underline{o}Cu$  porphyrin dimers in toluene solution at room temperature. These lifetimes correspond to  $K_Q^T$  values in the range  $(2.4-4.8) \times 10^6 s^{-1}$ . Comparison with table 5.2 shows the enhanced quenching effect characteristic of the p/p dimers and it is clear that the structures of the p/p isomers greatly facilitate deactivation of the  $Zn^{11}$  porphyrin excited states.

From the triplet absorption spectra, there is no sign of the  $Cu^{11}$  porphyrin excited state in the pZn/pCu dimer so that its lifetime must be reduced to less than 15ns. Similar findings have been reported for the other Zn/Cu isomers [165]. Since partitioning of the incident light

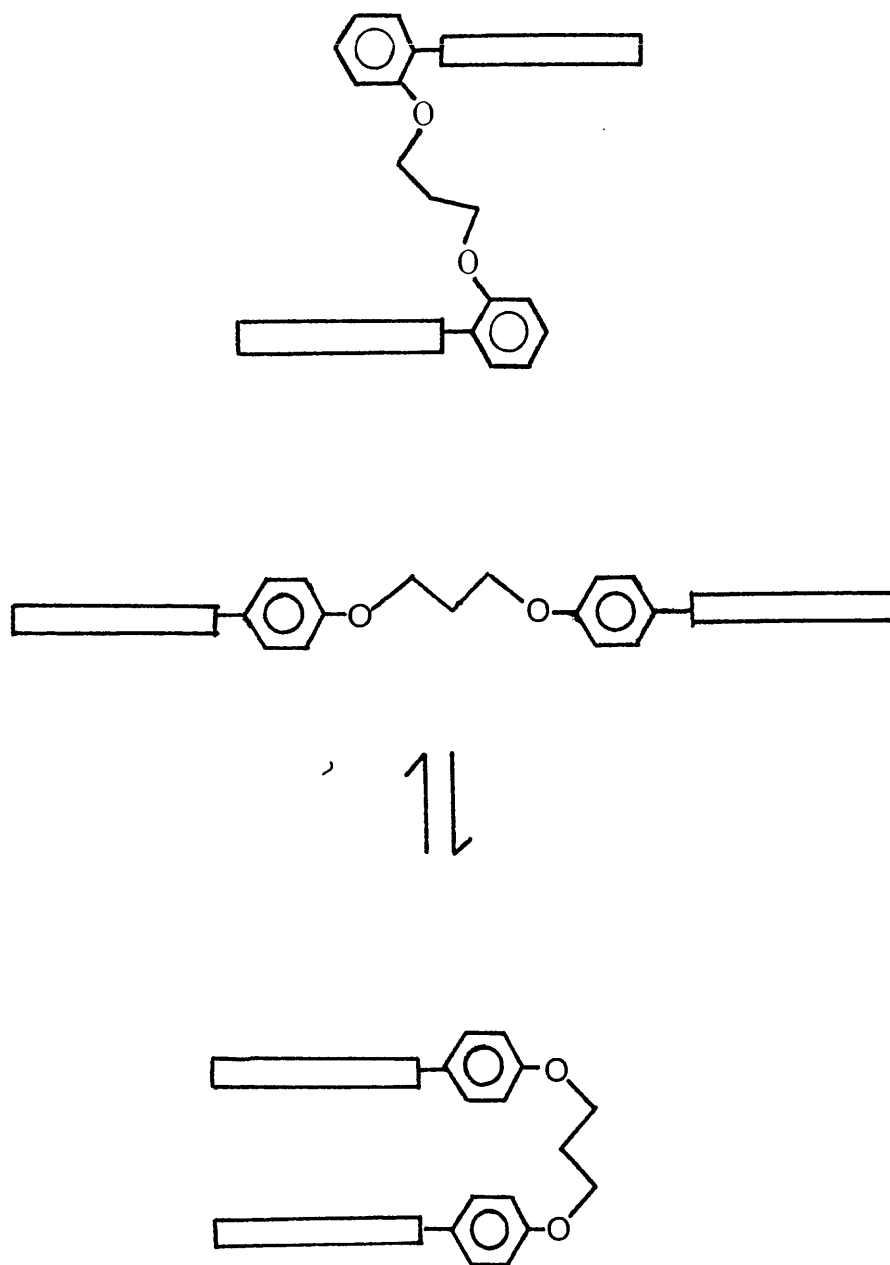
at 530nm is in favour of the  $\text{Cu}^{\text{II}}$  porphyrin and in monomeric species the triplet state is formed with unit efficiency ( $\phi_{\text{T}}=1$ ), it appears that  $\text{Zn}^{\text{II}}$  porphyrins are efficient quenchers for  $\text{Cu}^{\text{II}}$  porphyrin triplet excited states.

### 5.3a CONFORMATIONS

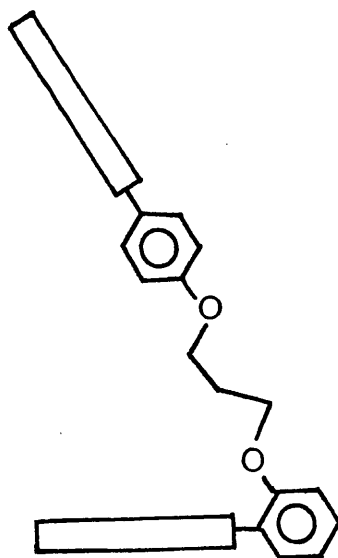
At this stage the reason for the vast difference in behaviour of the Zn/Mn isomers has to be delved into a bit deeper. The substituent effect is not sufficient to explain the results. An example of a substituent effect is discussed in Chapter VI.

In fact the results observed here can be interpreted in terms of the conformations adopted by the three systems in solution. From proton n.m.r. studies the geometries of analogues to our system have been deduced [165]. It is now known that o/o isomers adopt a Z-shaped configuration and remain in such form over a wide temperature range. This "Z"-shaped structure is less favourable to the overlap of the wavefunctions of the two moieties and hence also to energy transfer. The other isomers seem to show a more closed configuration in which the two porphyrin rings come into closer contact. Space filling models show that there is considerable steric hindrance towards forming cofacial arrangements for all the dimers and the open forms look to be more stable. However, detailed n.m.r. studies [31] have shown that exchange between open and closed forms occurs faster than the n.m.r. timescale for

the p/p isomer. Results have concluded that the p/p isomer exists in solution primarily in an open form whilst the closed form of the o/o isomer is most unlikely [169].



The o/o isomer seems to exist in fluid solution in a configuration in which the two porphyrin rings are perpendicular to each other [169], but rotation around the para linkage is fairly easy and a cofacial structure can be adopted. Thus, in non-polar solvents the o/o isomer seems to prefer the open Z structure, whereas the p/p isomer should be considered as an equilibrium between open and closed forms. The p/p isomer is somewhere between the other two and it seems to prefer the perpendicular form



Obviously, the nature of the central metal ion will exert some influence on the average conformation of the dimer in solution. This is especially true for the Fe and Mn porphyrins, which have an axially bound chloride ion. Our results show that the p/p isomer is a much more effective

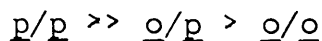
quencher than either the o/o or p/p isomers. Whatever the quenching mechanism, the efficiency of fluorescence quenching should increase as the distance separating the two porphyrin rings decreases. The closed forms of the dimers should show high quenching efficiencies whereas the open forms are expected to exhibit little quenching. Thus, this work supports the idea that the p/p isomer is able to form a relatively closed conformation whilst the o/o isomer does not favour such a structure [169]. It is of interest to note that introduction of a single ortho linkage into the dimer results in a drastic drop in the quenching efficiency. Presumably this is due to adoption of the perpendicular structure in which the porphyrin rings are held some distance apart.

#### 5.4 Quenching Mechanisms

The presence of the second metalloporphyrin quenches both singlet and triplet excited states of the  $Zn^{II}$  porphyrin in benzene solution. Although the actual quenching rate constants differ enormously, the same trend is observed for singlet and triplet quenching in the dimers



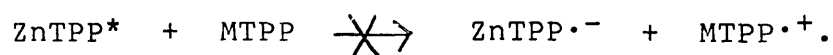
and



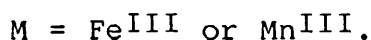
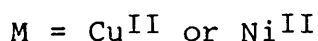
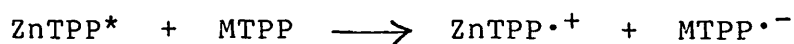
Such findings suggest that the same quenching mechanism is responsible for singlet and triplet quenching effects. In fact, several different mechanisms need to be considered including electron transfer, energy transfer and spin-orbit coupling effects due to heavy atoms and/or paramagnetic ions. All the quenchers contain heavy atoms and, except for  $\text{Ni}^{II}$ , the central metal ions are paramagnetic so that there will be some spin-orbit coupling perturbations in all cases. Quenching of  $\pi\pi^*$  excited states by paramagnetic and heavy metal ions is well known [170,171] and the paramagnetic effect can be extremely pronounced. This can be demonstrated by comparing the excited singlet and triplet lifetimes of ZnTPP ( $\tau_S=2.0\text{ns}$ ,  $\tau_T=1.2\text{ms}$ ) and CuTPP ( $\tau_S=10\text{ps}$ ,  $\tau_T=25\text{ns}$ ). However, spin-orbit coupling effects are important only when the perturber and quencher orbitals overlap and this requirement essentially restricts such quenching effects to the p/p dimers. Effective overlap of the  $\text{Zn}^{II}$  porphyrin  $\pi$  system with the d-orbitals on the central metal ion on the second porphyrin is possible only in the closed forms of the dimers and, even here, it might not be very pronounced. Hence, spin-orbit coupling effects associated with the central metal ion of the second porphyrin are probably quite weak, especially for the axially coordinated Fe and Mn porphyrins.

Photoinduced electron transfer is known to occur in mixed metal porphyrin dimers in polar solvents [159-161]. For the dimers studied here there was no spectral evidence

to show the involvement of charge transfer intermediates (redox ions or exciplexes) in either benzene or DMF solutions. However, it is possible that electron transfer makes some contribution towards the overall quenching mechanism. Consideration of the redox potentials [172] measured for various monomeric TPP complexes and the excited state energy levels determined [66] for ZnTPP concludes that in no case can the excited singlet or triplet state of ZnTPP oxidise the other metalloporphyrin:



With the singlet excited state of ZnTPP, reduction of the other metalloporphyrin can occur with standard free energy changes of -13.5, -15.4, -96.5 and -107.1 kJmol<sup>-1</sup>, respectively for M = Cu<sup>II</sup>, Ni<sup>II</sup>, Fe<sup>III</sup> and Mn<sup>III</sup>.



The ZnTPP triplet excited state can reduce only Fe<sup>III</sup> ( $\Delta G^\circ = -52.1$  kJmol<sup>-1</sup>) and Mn<sup>III</sup> ( $\Delta G^\circ = -62.7$  kJmol<sup>-1</sup>) porphyrins. Thus, electron transfer cannot be responsible for quenching the triplet excited state of the Zn<sup>II</sup> porphyrin by Ni<sup>II</sup> or Cu<sup>II</sup> porphyrins, but in all other cases it might contribute towards the observed quenching.

The rate constant for electron transfer ( $k_{el}$ ) depends strongly upon the edge to edge distance ( $r$ ) separating the two porphyrin rings [173].

$$k_{el} = \nu \exp(-ar)$$

where the frequency factor  $\nu$  has a limiting value of  $10^{13} \text{ s}^{-1}$  and the constant  $a$  is ca.  $0.88 \text{ \AA}^{-1}$ . The derivation of this equation was described in Chapter I. Thus the conformations adopted by the various dimers will exhibit quite different rate constants for electron-transfer quenching, even though  $\Delta G^0$  remains constant. For the Zn/Mn dimers, electron transfer should be efficient in the p/p isomer but the larger separation distances should preclude electron transfer in the o/p and the o/o isomers.

Flash photolysis studies have shown that net electron transfer does not occur in benzene solution, at least on the ns timescale. However, it is possible that short lived ion pairs are formed. Singlet ion pairs can decay either to ground state reactants or to triplet excited states whilst decay of triplet ion pairs should form the ground state reactants. Thus in benzene solution, electron transfer quenching can result in enhanced non-radiative deactivation of the excited state.

Absorption spectroscopy shows that the lowest  $\pi\pi^*$  singlet excited states of the various metalloporphyrins lie close in energy. The energy levels for NiII

$(E_S = 214 \text{ kJmol}^{-1})$  and  $\text{Cu}^{\text{II}}$  ( $E_S = 207 \text{ kJmol}^{-1}$ ) are situated above that of  $\text{Zn}^{\text{II}}$  ( $E_S = 198 \text{ kJmol}^{-1}$ ) whilst  $\text{Mn}^{\text{III}}$  ( $E_S = 194 \text{ kJmol}^{-1}$ ) and  $\text{Fe}^{\text{III}}$  ( $E_S = 187 \text{ kJmol}^{-1}$ ) lie at slightly lower energy. The triplet energy of ZnTPP, as derived from low-temperature phosphorescence, is  $153 \text{ kJmol}^{-1}$  but no luminescence or spin forbidden  $S_0 \rightarrow T_1$  absorption bands can be observed for NiTPP. The remaining metalloporphyrins show complicated triplet manifolds due to interactions between the unpaired d-electrons and the porphyrin  $\pi\pi^*$  triplet state [174] and it is difficult to assign triplet levels with any real accuracy. Absorption spectroscopy shows the lowest triplet levels of  $\text{Mn}^{\text{III}}$ TPP and  $\text{Fe}^{\text{III}}$ TPP to be at 153 and 150  $\text{kJmol}^{-1}$ , respectively. Low temperature luminescence from CuTPP is very broad [66] probably due to overlapping bands, with a maximum at 760nm. This places the triplet level at  $157 \text{ kJmol}^{-1}$ , but the real value might be as low as  $150 \text{ kJmol}^{-1}$ . In addition, there will be low energy dd states associated with the central metal ions which might act as energy acceptors. This is especially important for NiTPP [175].

Thus, singlet excitation energy transfer could occur from  $\text{Zn}^{\text{II}}$  porphyrins to both  $\text{Mn}^{\text{III}}$  and  $\text{Fe}^{\text{III}}$  porphyrins. The most probable mechanism [163] is dipole-dipole coupling for which the rate constant ( $k_{\text{en}}$ ) is strongly dependent upon distance:

$$k_{\text{en}} \propto 1/r^6$$

where  $r$  = separation distance between the two porphyrins. Exchange coupling is also possible. Therefore we can say that energy transfer is probable for the pZn/pMn isomer, but not so likely for the o/p and o/o isomers, where the average separation distance is larger. Singlet energy transfer might be expected to occur from Ni<sup>II</sup> and Cu<sup>II</sup> porphyrins to Zn<sup>II</sup> porphyrins, but the very short singlet state lifetimes ( $\tau_s < 10\text{ps}$ ) precludes this from happening. The presence of low lying dd states in Ni<sup>II</sup> porphyrins could facilitate inefficient energy transfer from the  $\pi\pi^*$  singlet excited state of the Zn<sup>II</sup> porphyrin.

With the possible exception of Ni<sup>II</sup> porphyrins, the triplet levels are all closely situated in energy and they should be in thermal equilibrium. The lowest energy tripmultiplet states of Cu<sup>II</sup>, Mn<sup>III</sup> and Fe<sup>III</sup> porphyrins can be populated from the lowest  $\pi\pi^*$  excited triplet state of the Zn<sup>II</sup> porphyrin. Since the tripmultiplet states are all short lived, energy transfer will lead to a large decrease in the lifetime of the Zn<sup>II</sup> porphyrin. For the triplet manifold, dipole-dipole energy transfer is too slow to compete with the inherent non radiative decay [163] but triplet energy transfer can occur via exchange coupling. In this mechanism, energy transfer occurs only for reactants in close proximity, and it will be insignificant for the o/o and o/p isomers.

In most cases studied, the presence of the second metalloporphyrin results in some quenching of the Zn<sup>II</sup> porphyrin fluorescence. The efficiency and mechanism for

the fluorescence quenching process depends markedly upon the geometry of the dimers, and efficient quenching is observed only where there exists the possibility of orbital overlap between the two porphyrin rings. Where measurements have been possible, fluorescence quenching results in enhanced triplet-state formation but this might be the result of spin-orbit coupling perturbations or electron transfer mechanisms. For the  $\text{pZn/pFe}$  and  $\text{pZn/pMn}$  dimers, quenching of the  $\text{Zn}^{11}$  porphyrin fluorescence might involve singlet energy transfer to the second metalloporphyrin via a dipole-dipole mechanism. The close overlap of the donor and acceptor levels might render this process quite efficient, although electron transfer is also possible in these systems. Similar difficulties exist in assigning the nature of the triplet quenching process. Electron transfer almost certainly contributes towards the quenching observed in the  $\text{pZn/pMn}$  and  $\text{pZn/pFe}$  dimers, but the redox products have not been detected. Triplet energy transfer via exchange coupling is possible in all cases and it is probably the dominant quenching process although spin-orbit coupling perturbations cannot be ignored.

## 5.5 Conclusions

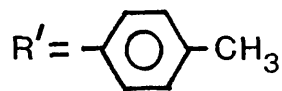
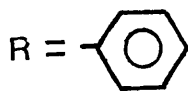
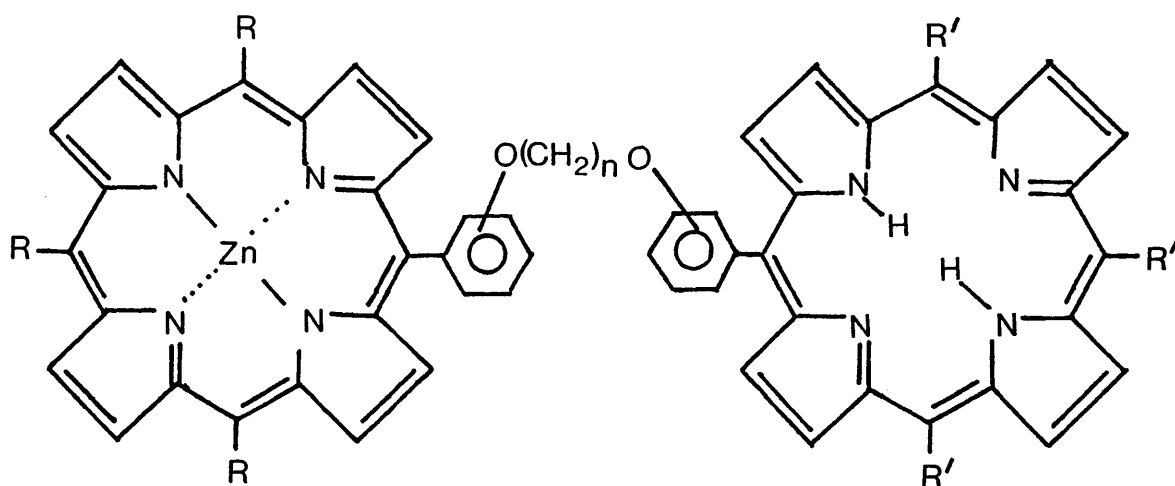
In my opinion the dimers described in this chapter are good models for the quenching processes that take place between the pigment molecules in the photosynthetic reactions centre. In particular the  $\text{Zn/Mn}$  porphyrin

isomers help illustrate how quenching mechanisms can be switched on and off by a simple change in conformation. In vivo the chlorophylls are attached to protein systems which can control and change the conformation of pigment molecules relative to one another simply by folding and unfolding via e.g. hydrogen bond breakage. Thus plants appear to have attained the state of the art for maximising forward energy and electron transfer and minimising the back process i.e. whilst a face-to-face configuration is beneficial for the forward processes it also encourages the back processes. The next breakthrough in porphyrin synthesis will come with the design of a porphyrin dimer which can change conformation from being face-to-face to perpendicular or linear on transfer of energy or an electron.

## PART II

### 5.6 Zinc/Free Base Dimers

The first part of this chapter was concerned with a variety of Zn/mixed metal dimers and their respective photophysics. An insight into the difference that the site of attachment of the covalent linkage makes to the photophysics observed was gained. The work is now extended to consider the effect of the length of the connecting chain on both singlet and triplet energy transfer processes. The study uses Zn/free base porphyrin dimers of the type shown below:



where  $n = 2, 3, 4, \text{ or } 6$ .

For the  $n=2$  Zn/H<sub>2</sub> porphyrin dimer the connecting chain was attached at the ORTHO positions of the two phenyl rings. For all the other dimers the connecting chain was attached at the two PARA positions.

All the work describing the singlet excited state processes has been recorded by Ralph Brookfield [177] but I have found it necessary to include some of his work in this chapter as it is closely related to events taking place in the triplet state.

The main quenching mechanism in ZnP attached to a free base porphyrin is that of energy transfer. As shown in Chapter I, Fig. 1, the free base absorption spectrum overlaps the zinc porphyrin fluorescence spectrum. Indeed efficient singlet energy in such compounds has already been described in the literature [163,145,176]. It was found that the efficiency of energy transfer from the excited singlet state of the ZnP to the H<sub>2</sub>P was greater than 85% and that assuming a random orientation, the average rate constant for intramolecular energy transfer was  $1.9 \times 10^9 \text{ s}^{-1}$ . A later study [176], in which the relative orientation of the two porphyrin rings was varied, also found efficient energy transfer (ca. 84%) from ZnP to H<sub>2</sub>P. Where the connecting chain is kept short [158], energy transfer can approach 100%.

## Results and Discussion

### 5.7 Steady State Absorption and Fluorescence

In dilute benzene solution the various Zn/H<sub>2</sub> porphyrin dimers exhibit absorption spectra that are

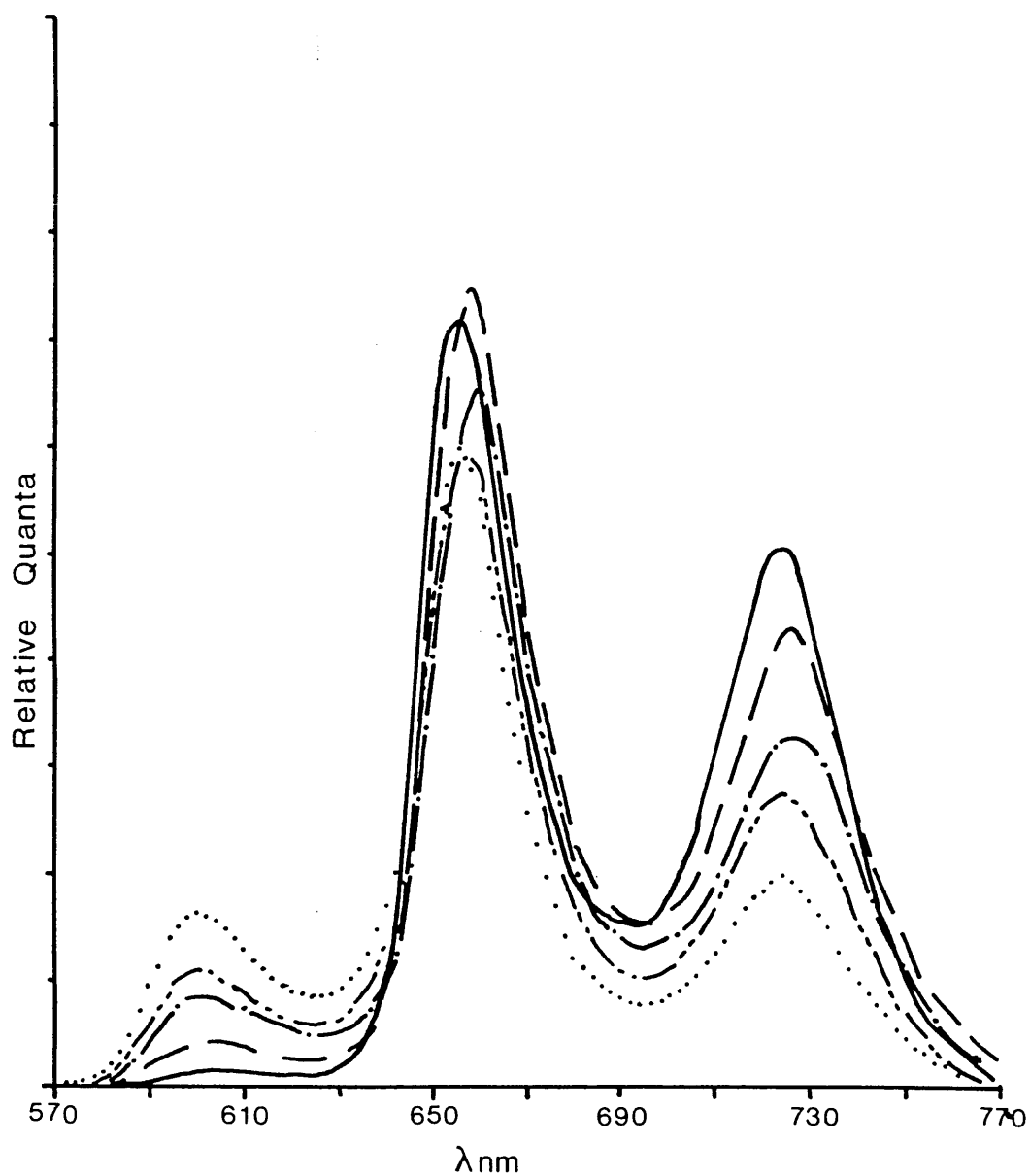
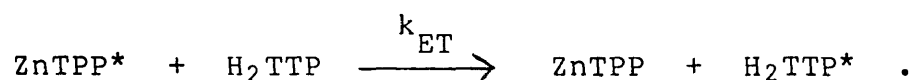


FIG.5.5.

Steady state fluorescence spectra recorded in dilute benzene solution (excitation wavelength 550nm) for a 1/1 molar mixture of ZnTPP + H<sub>2</sub>TPP (.....) and for the Zn/H<sub>2</sub> porphyrin dimers; n = 2 (—), n = 3 (---), n = 4 (-.-), n = 6 (-.-.-).

similar to that of the 1/1 molar mixture of ZnTPP+H<sub>2</sub>TTP. A close examination however shows that the molar extinction coefficients of the dimers are only ca. 60-75% of the corresponding bands in the mixture of monomers and in addition the B-bands of the dimers are slightly red-shifted by about 2-4nm. [177]. For the n=2 dimer the B band was clearly split in dilute DMF solution indicating that exciton coupling was taking place. These observations in the absorption spectra are consistent with other examples in the literature [178,179,81]. With a gable porphyrin dimer [158], it has been shown that the B-band is split into two compounds, similar to that found for the n=2 dimer in DMF.

There is considerable overlap between the room temperature fluorescence emitted by ZnTPP and the ground state absorption spectrum of H<sub>2</sub>TTP indicating that excitation energy transfer should be extremely efficient



ZnTPP fluoresces at 605nm and 660nm whilst H<sub>2</sub>TTP fluoresces at 660nm and 720nm. Thus singlet energy transfer has been shown to occur in the dimer systems by monitoring the decrease in fluorescence associated with the ZnTPP component (i.e. 605nm) and the corresponding increased emission of the H<sub>2</sub>TTP component at 720nm. The spectra are shown in Fig.5.5 and they can be used to determine energy transfer efficiencies ( $\phi_{\text{ET}}$ ):

$$\phi_{ET} = (1 - I_D^{605} / I_M^{605}) \times 100\%$$

where  $I_D^{605}$  refers to the fluorescence intensity at 605nm for the Zn/H<sub>2</sub> porphyrin dimer and  $I_M^{605}$  is the corresponding value for the 1/1 molar mixture of monomers. The calculated values are found in Table 5.3 and are seen to be highly dependent upon the length of the connecting chain. The n=2 dimer shows nearly quantitative energy transfer (94%) whereas for the n=6 dimer,  $\phi_{ET}$  is only 48%. Strangely the n=4 dimer gives a lower value than the n=6 compound suggesting that there is an optimum chain length for keeping the two porphyrin rings separated by the maximum distance.

The values of  $\phi_{ET}$  can then be used to calculate the average rate constants for intramolecular energy transfer ( $k_{ET}$ ):

$$\phi_{ET} = k_{ET} / (k_{ET} + k_O)$$

where  $k_O$  is the reciprocal of the excited state lifetime of the corresponding Zn/Zn porphyrin dimers ( $k_O = 5.6 \times 10^8 \text{ s}^{-1}$ ). The derived values are also collected in Table 5.3 and show the same trend as the  $\phi_{ET}$  values. The  $k_{ET}$  values can in turn be used to estimate the average separation distance (R) between the ZnP and H<sub>2</sub>P units (Table 5.3):-

Table 5.3

| <u>Steady-state</u> |                    |                                                 |           | <u>Time-Resolved</u>                              |               |                                                   |               |
|---------------------|--------------------|-------------------------------------------------|-----------|---------------------------------------------------|---------------|---------------------------------------------------|---------------|
| n                   | $\phi_{ET}$<br>(%) | $k_{ET}$<br>(s <sup>-1</sup> /10 <sup>8</sup> ) | R<br>(nm) | $k_{ET}^a$<br>(s <sup>-1</sup> /10 <sup>8</sup> ) | $R^a$<br>(nm) | $k_{ET}^b$<br>(s <sup>-1</sup> /10 <sup>8</sup> ) | $R^b$<br>(nm) |
| 2                   | 94                 | 88                                              | 1.52      | 78                                                | 1.55          | 94                                                | 1.50          |
| 3                   | 75                 | 17                                              | 2.00      | 53                                                | 1.65          | 53                                                | 1.65          |
| 4                   | 35                 | 3.0                                             | 2.66      | 38                                                | 1.74          | 36                                                | 1.76          |
| 6                   | 48                 | 5.2                                             | 2.43      | 17                                                | 1.99          | 14                                                | 2.06          |

Energy transfer parameters derived from steady-state fluorescence spectra in benzene and from time-resolved fluorescence decays measured at 605nm in a) benzene and b) DMF solutions.

$$k_{ET} = k_o (R_o/R)^6$$

where  $R_o = 2.4\text{nm}$ . The derived values suggest a separation of 1.5 to 2.7nm between the porphyrin rings. However these values do not tell us anything about the stereochemistry adopted by the various dimer systems, although Part 1 of this chapter suggests that the n=3 dimer is an equilibrium between open and closed forms, where the two porphyrin rings are parallel to each other. If that is the case then this could explain the high value of  $\phi_{ET}$  for the n=3 dimer compared to its homologues n=4 and n=6.

Further evidence for energy transfer comes from the fluorescent excitation spectra in Fig.5.6. The porphyrin dimers were scanned through the visible range and the fluorescence emitted at 720nm was monitored. At this wavelength only emission from the free-base porphyrin entity is expected as ZnP emits only at 605 and 660nm. The excitation spectra obtained were then overlayed on their respective ground state absorption spectra and normalised at 515nm. If the energy transfer efficiency is 100% then complete overlap of the two spectra is expected. In fact overlap is nearly complete for the n=2 dimer. The spectra for the n=3 and n=6 dimers also confirm energy transfer is taking place but the overlap here is not as satisfactory as that of the n=2 dimer. The results correlate well with the values in Table 5.3.

## 5.8 Time Resolved Measurements

Measurements performed under steady state conditions are based on average positions adopted by the various isomers and do not distinguish between rapidly equilibrating stereoisomers. For this reason time resolved measurements were undertaken. A full explanation of these measurements will be given in R. Brookfields thesis [72b]. This chapter shall only describe the results and conclusions drawn.

Decay of the ZnP fluorescence was observed at 605nm and that of the free base at 720nm. Whilst the monomer porphyrins gave good single exponential fits, the

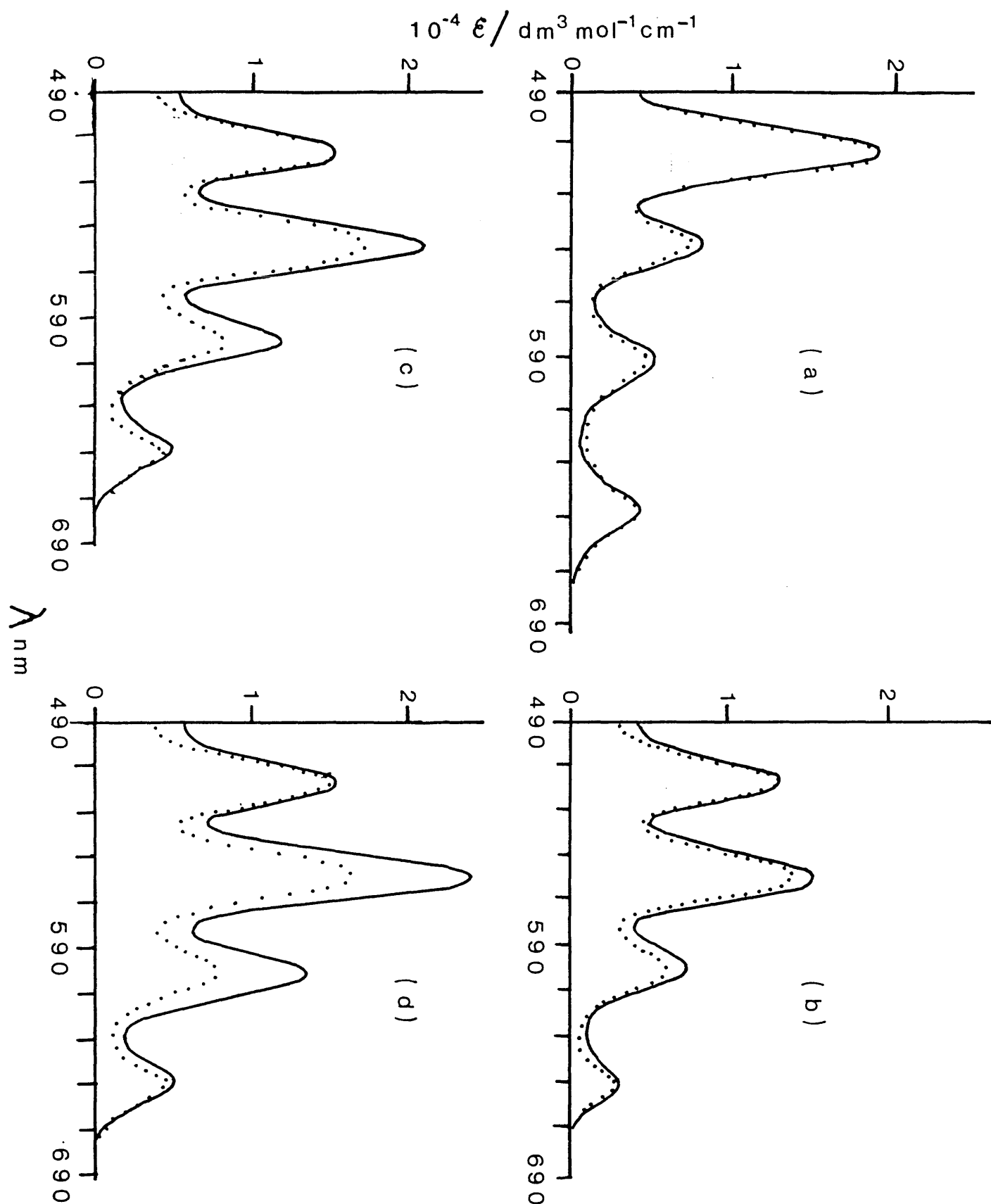


**FIG.5.6.**

Comparison of corrected excitation (emission wavelength 720nm) (.....) and ground state absorption (—) spectra recorded in dilute DMF solution; (a)  $\text{H}_2\text{TPP}$  (b)  $n=2$  (c)  $n=3$  (d)  $n=6$ . The spectra have been normalised at 514nm

covalently linked porphyrin dimers gave complex kinetics and even dual exponential fits were poor for some of the compounds. The lifetimes recorded were taken as those for the dominant processes. Table 5.4 lists the dominant lifetimes recorded at 605 and 720nm.

Table 5.4

Singlet lifetime measurements for the dominant processes at 605 and 720nm.

|                    | $\tau_s/\text{ns}$ |              |
|--------------------|--------------------|--------------|
|                    | <u>6.05nm</u>      | <u>720nm</u> |
| ZnTTP              | 2.02               | -            |
| H <sub>2</sub> TTP |                    | 10.5         |
| n=2                | 0.12               | 11.2         |
| n=3                | 0.17               | 10.5         |
| n=4                | 0.23               | 10.6         |
| n=6                | 0.45               | 10.4         |

The ZnP emission for the dimers appeared to contain two processes that could be approximated to decays of 100-520 ps which were dependent upon chain length (see table 5.4) and ca. 2ns which was independent of chain length. This latter value cannot be satisfactorily explained though some of it could be due to impurity or artefacts in instrumentation. An exciplex type [180] intermediate can also be ruled out as the same behaviour

was observed in polar solvents. Finally reverse energy transfer from the H<sub>2</sub>P unit is also unfavourable as the energy difference between singlet states of ZnP to H<sub>2</sub>P is 19kJ mol<sup>-1</sup>.

The data can be explained in terms of the different conformations which might be present in solution. Equilibration might not take place within the singlet lifetimes and thus only favourable conformations such as closed forms will lead to efficient fluorescence quenching whilst for the open forms it is relatively inefficient. In the case of n=2 dimer the connecting chain is so short that it ensures close proximity of the porphyrin rings even in a "Z" shaped conformation and this accounts for its efficient quenching. Another set of quenching rate constants for intramolecular energy transfer can be calculated from the lifetime data via the expression:

$$k_{ET} = \frac{1}{\tau} - \frac{1}{\tau_0}$$

where  $1/\tau_0 = 5.6 \times 10^8 \text{ s}^{-1}$  and  $\tau$  = the singlet lifetime of the dimer. The derived values (Table 5.3) were then used to determine the average separation distance (R) as explained before. No apparent solvent dependence was observed. Furthermore the R values derived for the n=2 dimer are in excellent agreement with those obtained previously from steady state measurements. However for the other dimers agreements of the R values from the two sets of data are poor. If we assume the quenching we

observe occurs when maximum overlap between the two porphyrins is established, then the R values obtained refer to the closed porphyrin conformation. Since the R values increase with increasing chain length, it appears that the dimers do not form closely-packed conformations but instead exist as slowly-equilibrating extended and partially-closed forms [169].

### 5.9 Triplet State Processes

Absorption spectra recorded for the triplet excited states of ZnTPP and H<sub>2</sub>TPP have been available for a very long time [168]. Transient difference spectra recorded in outgassed benzene solution (Fig.5.7) using conventional flash photolysis show several important features. For H<sub>2</sub>TTP there are isosbestic points at 588, 592, 638 and 654nm, an absorption peak at 780nm and a sharp bleaching at 645nm. With ZnTPP the isosbestic point is at 560nm and there are absorption peaks at 745 and 840nm. Triplet state lifetimes of ZnTPP and H<sub>2</sub>TTP in outgassed benzene are 1.25 and 1.35ms respectively. From ns flash photolysis studies the quantum yields for formation of the triplet excited state were found to be 0.90 and 0.72 for ZnTPP and H<sub>2</sub>TTP respectively. Low temperature phosphorescence studies [66] have located the triplet energies of ZnTPP and H<sub>2</sub>TTP to be 150 and 138 kJ mol<sup>-1</sup> respectively. Thus from the triplet energy gap the equilibrium constant for triplet energy transfer



will be 625.

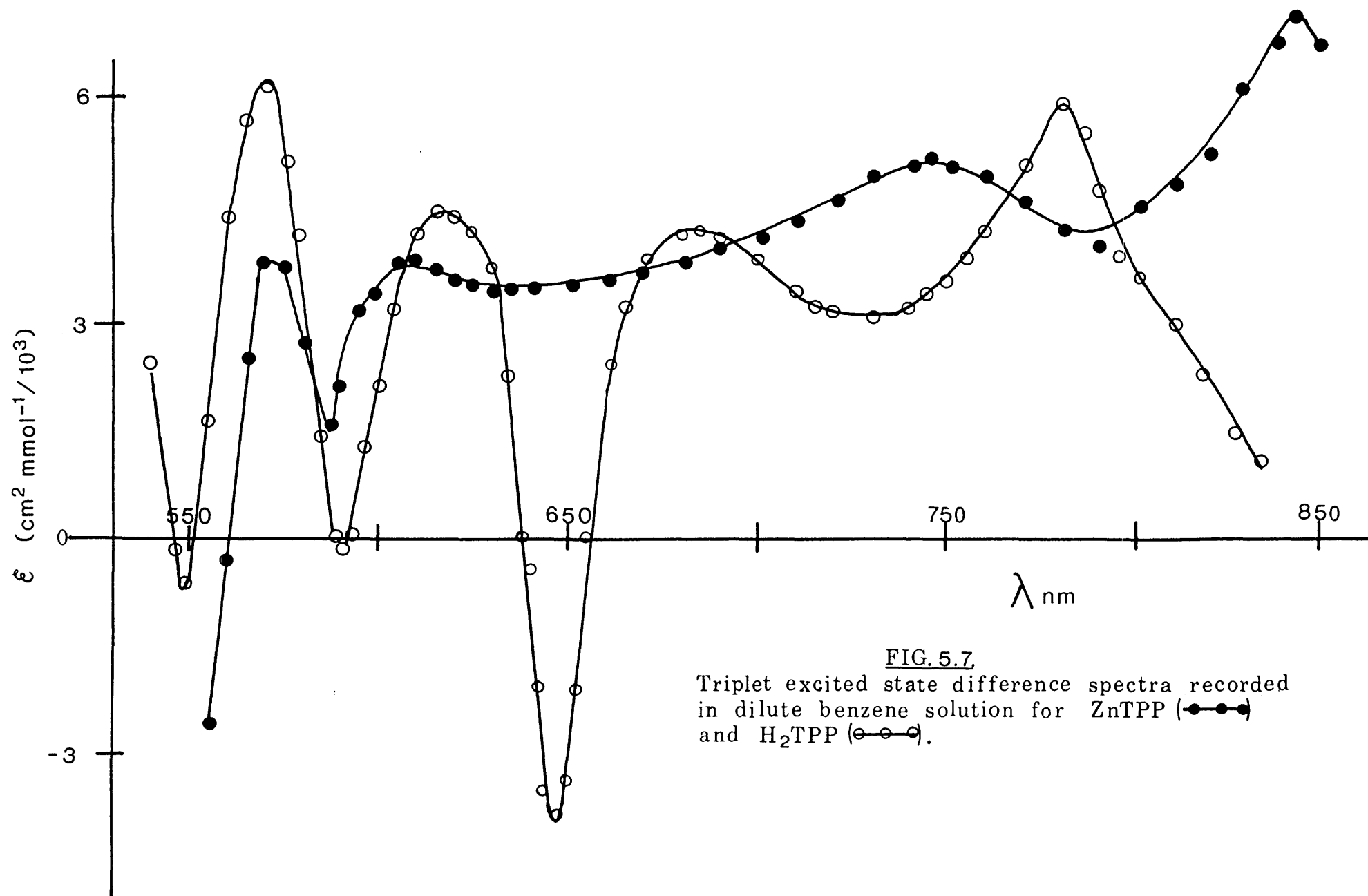


**FIG. 5.7**  
Triplet excited state difference spectra recorded  
in dilute benzene solution for ZnTPP (●—●) and H<sub>2</sub>TPP (○—○).

Triplet absorption spectra recorded for the various Zn/H<sub>2</sub> porphyrin dimers in outgassed solution (Fig.5.8) are similar to those in Fig.5.7. For the n=2 dimer in both benzene and DMF solutions, the triplet spectra correspond to those recorded for H<sub>2</sub>TTP under identical conditions. The clear isosbestic points observed at 586, 592, 636 and 652nm in benzene solution together with the sharp bleaching at 645nm and the general profile show that only the H<sub>2</sub>P unit contributes to the observed spectra. Even at times 50ns after the excitation flash, the ZnP triplet state is not seen. Decay of the transient absorption occurred by mixed kinetics giving an approximate lifetime ( $\tau_T$ ) of 0.77ms. No redox ion products could be detected in either solvent and the spectral profile did not change with time.

The other Zn/H<sub>2</sub> porphyrin dimers gave mixed triplet absorption spectra (Fig. 5.8). At 560nm, where the ZnP\* has an isosbestic point, the concentration of H<sub>2</sub>P\* can be determined and compared to the concentration of ZnP\* as determined at 590nm. Such determinations gave the percentage ZnP\* in the total triplet population to be 0, 22, 35 and 29% respectively for the n=2, 3, 4 and 6. Again the spectral profiles did not appear to change significantly with time and no redox ion intermediates were found in benzene or DMF solutions. Decay profiles always gave mixed kinetics with typical  $\tau_t$  values around 0.45ms in benzene. It is quite normal [168] to observe mixed kinetic profiles for decay of porphyrin triplet

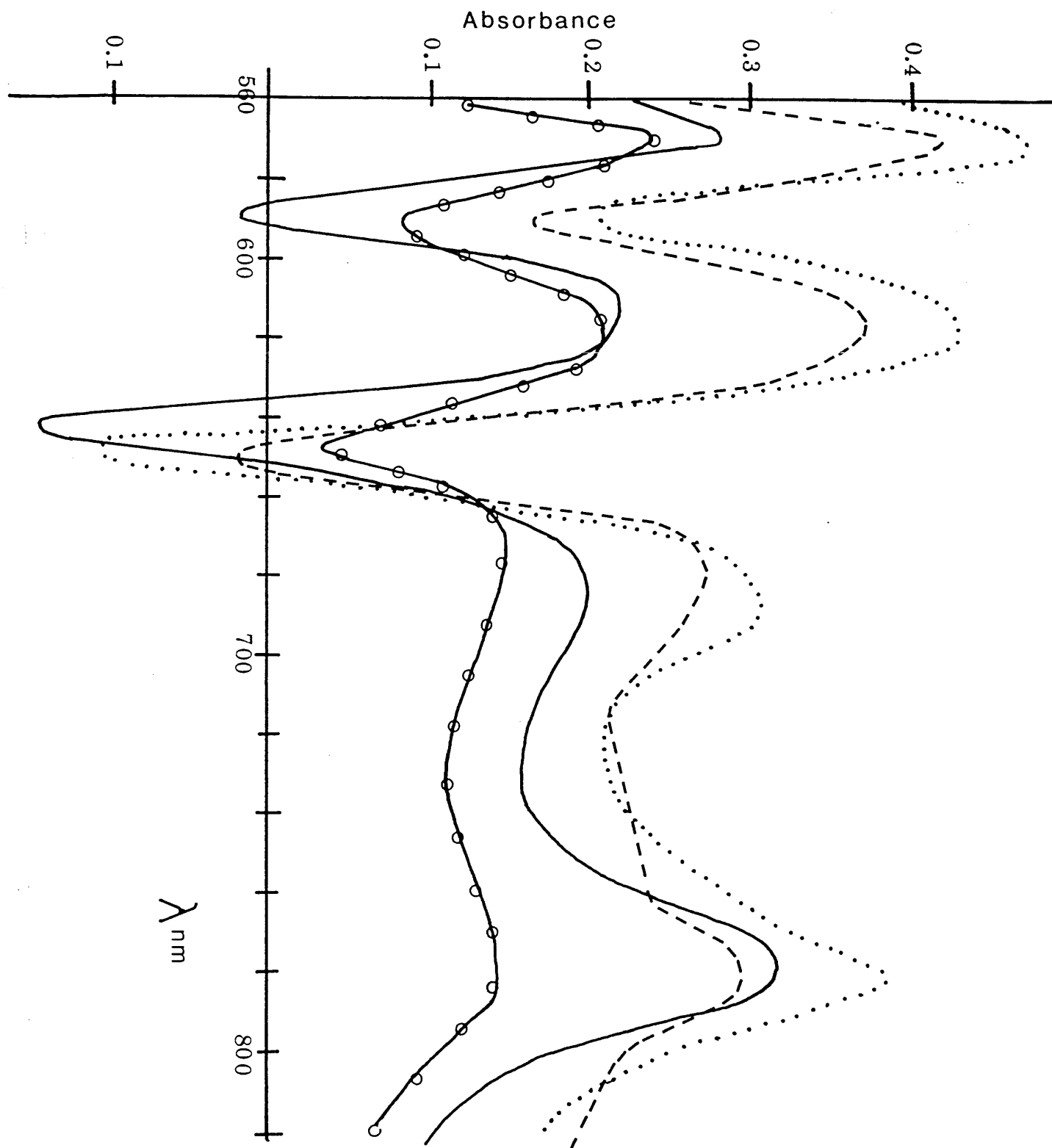


FIG. 5.8.

Triplet excited state difference spectra recorded in outgassed benzene solution for the various  $\text{Zn}/\text{H}_2$  porphyrin dimers;  $n=2$  (—),  $n=3$  (.....),  $n=4$  (○—○) and  $n=6$  (---).

excited states in fluid solution because of triplet/triplet annihilation. Even so, the lifetimes observed for the Zn/H<sub>2</sub> dimers are shorter than those measured for the corresponding monomers. This suggests that there is some exciton coupling effect which perturbs the excited triplet state.

Excitation of the Zn/H<sub>2</sub> porphyrin dimers with visible light (>500nm) results in formation of both ZnP and H<sub>2</sub>P excited singlet states. Integration of the monomer absorption spectra shows that about 40% of the incident photons are absorbed directly by the H<sub>2</sub>P unit. Of the 60% that go to the ZnP moiety some will be transferred to the H<sub>2</sub>P unit ( $\phi_{ET}$ ). The residual ZnP excited singlet state molecules will decay via radiative and nonradiative processes from which the ZnP excited triplet state will be formed with a quantum efficiency of 90%. Consequently, the percentage ZnP triplet of the total triplet population ( $\phi_{Zn}^T$ ) expected under such conditions can be expressed in the form

$$\phi_{Zn}^T = (1 - \phi_{ET}) \times 0.9 \times 0.6$$

assuming that reverse energy transfer is negligible.

From the  $\phi_{ET}$  values given in Table 5.3,  $\phi_{Zn}^T$  values of 3, 13, 35 and 28% respectively for n=2,3,4 and 6 can be

calculated. Considering the experimental limitations, these values are in very good agreement with the experimentally derived values. Such findings suggest that triplet energy transfer from ZnP to H<sub>2</sub>P is unimportant in the Zn/H<sub>2</sub> porphyrin dimers despite the favourable energy level positioning.

Triplet energy transfer normally takes place via exchange coupling, which occurs over short distances only [168]. For efficient exchange, it is necessary that the relevant orbitals overlap significantly. In fact, the geometric requirements for efficient triplet energy transfer are much more stringent than those involved in Forster singlet energy transfer because of the distance dependence [181]. Any Zn/H<sub>2</sub> porphyrin dimer that has the necessary conformation for efficient triplet energy transfer will also exhibit rapid singlet energy transfer. Such conformations will show high  $k_{ET}$  values and, consequently, they do not favour formation of the triplet excited state of the ZnP unit. These realisations support our failure to observe triplet energy transfer within the Zn/H<sub>2</sub> dimers.

## CHAPTER VI

### ELECTRON TRANSFER PROCESSES IN PORPHYRIN DERIVATIVES

## 6.1 Introduction

An introduction to the primary electron transfer processes in photosynthesis was given in Chapter I, together with a brief description of some model systems. Most of the model systems used to date have made extensive use of quinones [181-184] due to the importance these intermediates have in the natural process. However in in vivo processes quinones are unstable with respect to reduction and it is difficult to avoid hydroquinone impurities. To overcome this problem, viologens have been employed.

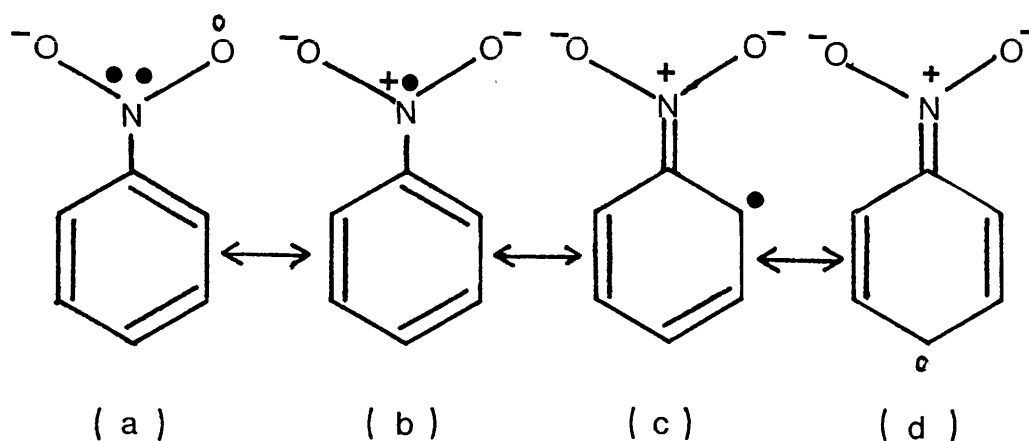
In this chapter where we are working with organic systems we have used nitro aromatic compounds and silver complexes as electron acceptors.

Following the discussions raised in the introduction it is clear that the long lived triplet excited state of the porphyrin favours bimolecular electron transfer. The very short singlet lifetime is not advantageous to bimolecular reactions and necessitates either 1) high concentration of quencher or 2) covalent binding. Both approaches are considered for the two systems studied here.

## 6.2 Nitro-Aromatics

Many different porphyrins, including chlorophyll, have been shown to undergo quenching by nitroaromatics [185-187]. Nitroaromatics are not easily reduced but they undergo a well defined one electron reduction to form the

radical anion [188-190]. In fact the e.s.r. spectra of these radicals are well documented in the literature and can be drawn as four canonical forms:



Coupling constants ( $\alpha$ ) for the various groups on the radical can be calculated and these are proportional to the electron density of that group. The  $\alpha$  values for the  $\text{NO}_2$  group ( $\alpha_{\text{N}}$ ) have been shown to depend on the type of substitution on the benzene ring and also on the solvent. Thus, for example, electron withdrawing substituents tend to reduce  $\alpha_{\text{N}}$  whilst the opposite is true for electron donating groups. The  $\alpha_{\text{N}}$  values are also greater in solvents of high dielectric constant such as water and correspond to an increased contribution to the hybrid of canonical form (b) i.e. a form which would be favoured in a hydrogen bonding or polarising medium. In fact

formation of the anion is irreversible in water because of rapid protonation.

Table 6.1 gives  $\alpha$  values for two nitroaromatic compounds which shall also be discussed in the ensuing pages.

Table 6.1

|                | $\alpha_N$ | $\alpha_{2-H}$ | $\alpha_{3-H}$ | $\alpha_{5-H}$ | $\alpha_{6-H}$ | $\alpha_{CH_3}$ |
|----------------|------------|----------------|----------------|----------------|----------------|-----------------|
| p-Nitrotoluene | 10.79      | 3.39           | 1.11           | 1.11           | 3.39           | 3.98            |
| p-Nitroanisoie | 11.57      | 3.43           | 1.11           | 1.11           | 3.43           | 0.30            |

Typical reduction potentials are about -1.3V vs SCE i.e. quite low which makes them difficult to reduce but at the same time it means it can store most of the photon energy. In the green plant practically all of the energy is stored in the first step.

The use of nitroaromatics as electron acceptors with porphyrins is investigated in three stages. First, the components involved are unattached. In the next stage they are linked together via an amide linkage and finally the nitro group is directly attached to the phenyl group on the porphyrin ring thus effectively creating a nitro porphyrin.

### 6.3 The Bimolecular System

#### Quenching Characteristics of Nitrotoluene and p-nitroanisole

Both compounds quenched the singlet and triplet excited states of ZnTPP in benzene solution but the quenching pattern of the two compounds showed remarkable differences. Fig. 6.1 (a and b) shows the Stern Volmer plots for the two compounds using the same concentration range of quencher. Thus whilst the plot obtained with nitrotoluene is linear over the concentration range considered, that of nitroanisole shows negative deviation from the linearity. A plot of rate constants for triplet decay versus quencher concentration again shows differences between the two systems, as shown in Fig. 6.2a and b. The plot in Fig. 6.1a yields a bimolecular quenching rate constant value ( $5 \times 10^8 \text{M}^{-1}\text{s}^{-1}$ ) that is approximately one tenth diffusion controlled. The linear Stern Volmer plot indicates that the quenching is dynamic. No sign of ground state complexation is observed.

With nitroanisole, on the other hand, the plot looks more like that expected for a titration.

### 6.4 Discussion

The absorption spectrum of ZnTPP remained unaltered on addition of the aromatic compounds and hence ground state complexation seems to be minimal. Other authors [191-193] have made similar observations using ZnOEP with a variety of weak electron acceptors, including nitro-

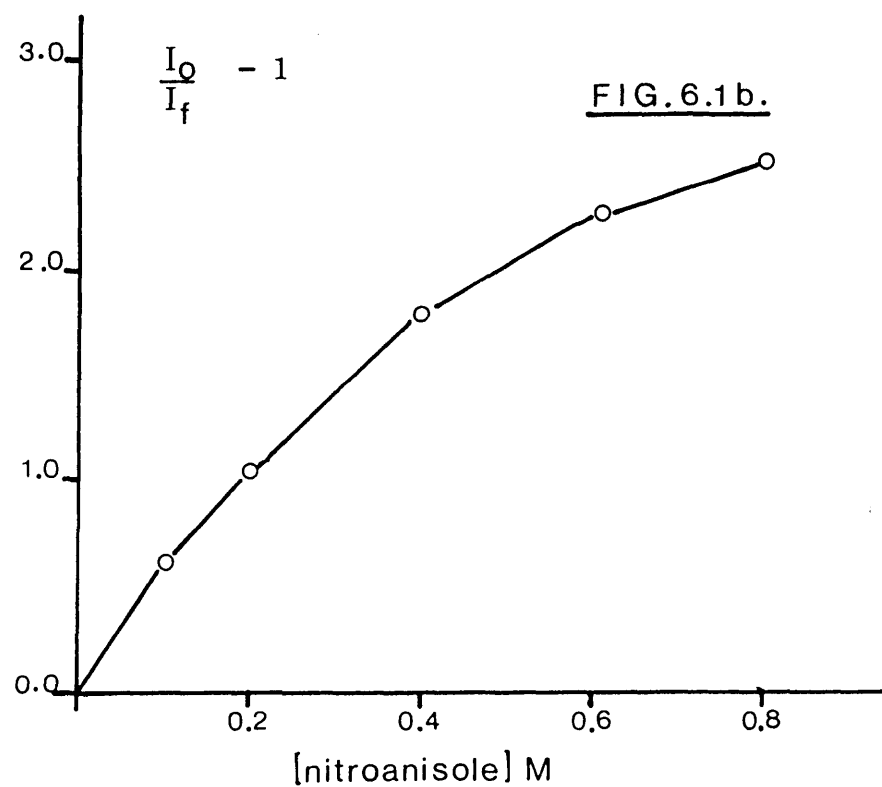
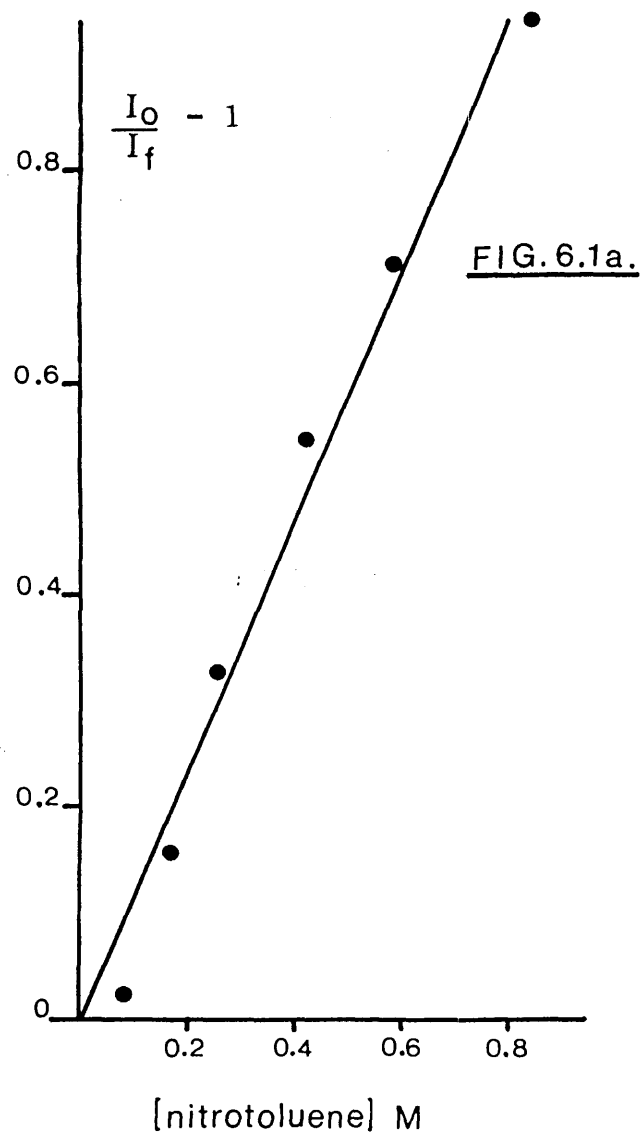


FIG 6.1. Stern-Volmer plot showing quenching of ZnTPP fluorescence by:  
 a. nitrotoluene  
 b. nitroanisole

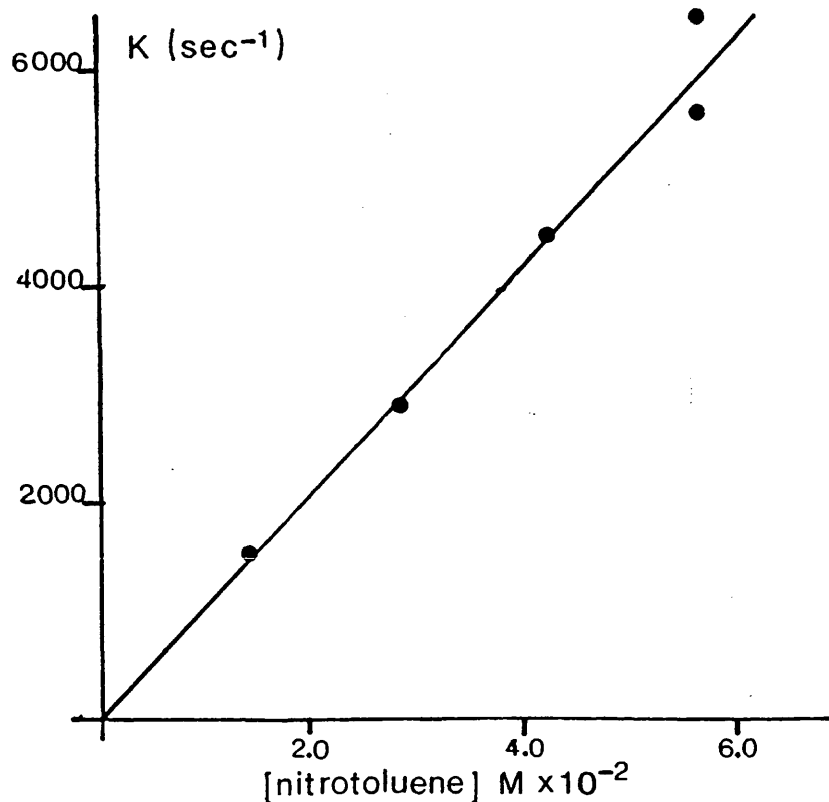


FIG. 6.2a. Quenching of ZnTPP triplet excited state by nitrotoluene

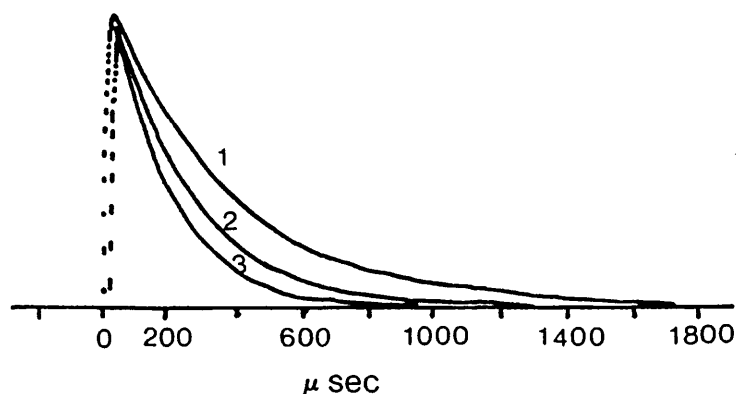


FIG. 6.2c. Triplet decay of ZnTPP ( $10^{-6}$ M) in benzene and (1)  $2.82 \times 10^{-2}$ M nitrobenzene, (2)  $4.24 \times 10^{-2}$ M nitrobenzene, (3)  $5.65 \times 10^{-2}$ M nitrobenzene.

aromatics, and have interpreted the data in terms of exciplex formation. In addition they claimed that charge separated products were observed when a more polar solvent was used. In this study, however, no such species were detected.

One explanation for the observed quenching is that electrons are pulled out of the porphyrin ring. Further

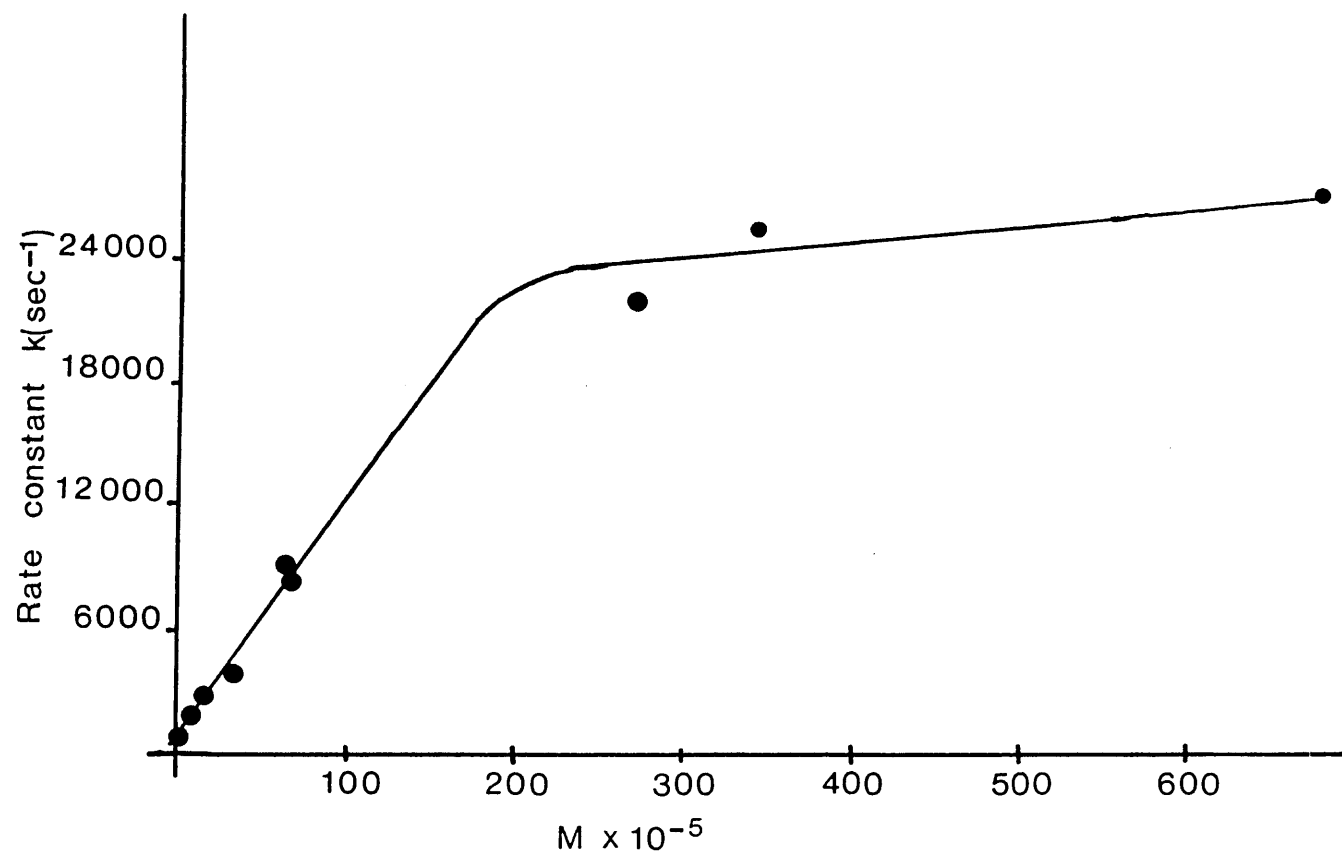
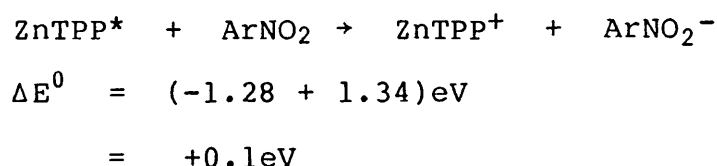


FIG. 6.2b.

Quenching of the ZnOEP triplet excited state  
by p nitroanisole in outgassed benzene solution.

on in the nitroporphyrin systems it has been shown that pulling electrons off the porphyrin leads to a decrease in fluorescence intensity. The heavy atom effect and energy transfer are not applicable to explain quenching in this instance.

The quenching rate constant ( $k_Q$ ) for nitrotoluene seems to be consistent with the modest  $\Delta G^0$  for the proposed reaction:



where  $E_{\frac{1}{2}}$  for nitrotoluene = -1.28 V vs SCE

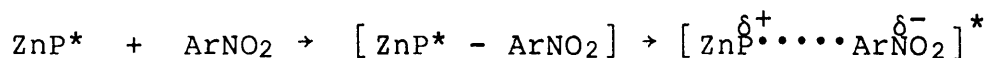
$E_{\frac{1}{2}} \text{ ZnTPP}^*/\text{ZnTPP}^{*+} = -1.34 \text{ V vs SCE}$

The small  $\Delta G^0$  ( -0.1eV) explains why the rate constant is less than diffusion controlled. A reasonable  $\Delta G^0$  ( $\sim -0.3\text{eV}$ ) is needed to overcome activation energy parameters which would accompany processes such as solvent reorganisation and charge separation. Another reason for the low  $k_Q$  with nitrotoluene is the low value for the self-exchange constant ( $k_{aa} = 2 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$ ). [194] Marcus theory predicts that the rate of an electron transfer will vary with the  $\Delta G^0$  of the system according to;

$$\begin{aligned} k_{ab} &= (k_{aa} k_{bb} k_{ab} f_{ab})^{\frac{1}{2}} \\ \text{where } f_{ab} &= \frac{(\log K_{ab})^2}{4 \log (k_{aa} k_{bb} / Z^2)} \end{aligned}$$

and  $k_{ab}$  = equilibrium constant,  $k_{bb}$  = self exchange constant for ZnTPP.

The low self exchange constant for nitrotoluene is thought to be associated with a change in shape on formation of the radical. Quenching by nitrotoluene would involve the reactants coming together and forming a caged ion pair where electron density from the porphyrin is pushed towards the nitrotoluene. This leads to excited state quenching though complete electron transfer does not occur.



With nitroanisole, on the other hand, plot 6.1b suggests that quenching depends upon complexation of nitroanisole with the porphyrin. The plot looks more like a titration and once all the porphyrin is in a complexed state the quenching observed does not change significantly with added quencher. Nitroanisole is a better electron acceptor than nitrotoluene and therefore it complexes more readily with the zinc porphyrin but it also suggests that nitroanisole must have an even worse self-exchange rate than nitrotoluene. So, although  $\Delta G^0$  is more favourable, overall there is no dynamic quenching.

The quenching process in both of the above systems involves pulling electron density off the porphyrin ring and in the case of nitroanisole the quencher is also complexed to the porphyrin. Ground state complexation is not observed.

The explanation proposed above could be clarified by excited state lifetime measurements. Unfortunately the singlet excited state lifetimes have not yet been measured but the triplet decay rates as a function of nitroanisole concentration are plotted in Fig. 6.2b and show the same trend as the steady state results. This substantiates the idea of a complex which effectively changes the quenching characteristics from being dynamic in the first instance to static as complexation proceeds.

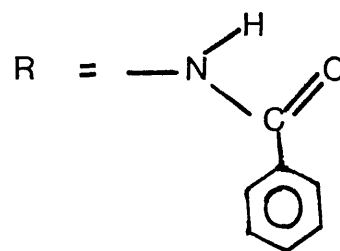
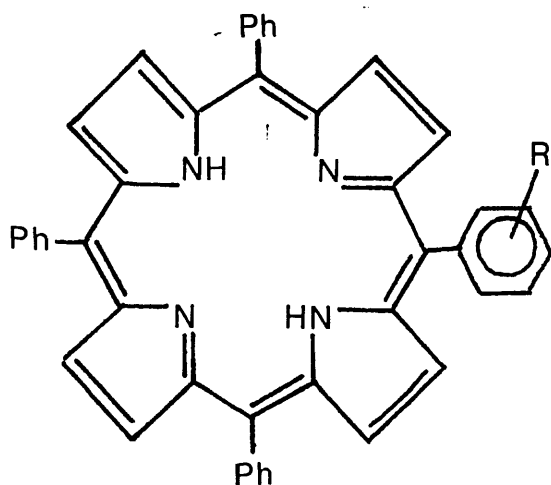
#### 6.5 Possible conformation of excited state complex

Just as conformation is very important in electron and energy transfer processes, it follows that if exciplexes are involved in intermedial stages of these processes, then they too are governed by the same conformational parameters. Indeed any charge transfer complex or collision complex that has a longer than usual lifetime might show a preference for a particular conformation. Without the use of sophisticated techniques such as e.g. NMR, what is to be described next may seem a bit like a hit and miss technique of elucidating conformational structure but it proceeds as follows:- Suppose that nitroanisole formed a weakly-bound excited state complex with ZnTPP which we have assumed is weak, and where it sits somewhere above the porphyrin ring rather than in a side by side conformation. If this is the case then it would not be able to form a complex with ZnTPP if ZnTPP happened to be complexed to something

else. In Chapter III we considered the stability constants of a few axial ligands and concluded that pyridine formed a strong ligand with ZnTPP and showed an extended triplet lifetime of 2.5ms i.e. it appeared to be complexed even in the excited state. Thus in order to test the above theory a solution containing  $\sim 10^{-3}M$  of pyridine and  $\sim 10^{-2}M$  nitroanisole together with ZnTPP was made up, outgassed and subject to flash photolysis. From Fig. 6.2b it can be seen that such a concentration of nitroanisole would produce a  $\tau_T$  0.2ms. With the added pyridine, however,  $\tau_T$  was  $\sim 2.3ms$ . Therefore it appears that pyridine has taken up the position that nitroanisole needs if it is to form an excited state complex and hence any association nitroanisole forms with ZnTPP is weaker than that which pyridine forms on ligation.

#### 6.5.1. Linked Compounds

Once it has been established that the nitro compounds quench excited state ZnTPP the next step usually is one of trying to eliminate the diffusion controlled process. This is generally achieved by linking the reactants to each other. The compounds about to be described were synthesised by Professor Guo's group in Beijing University, China and are shown below:-



Ph = Phenyl

## 6.6 Results and Discussion

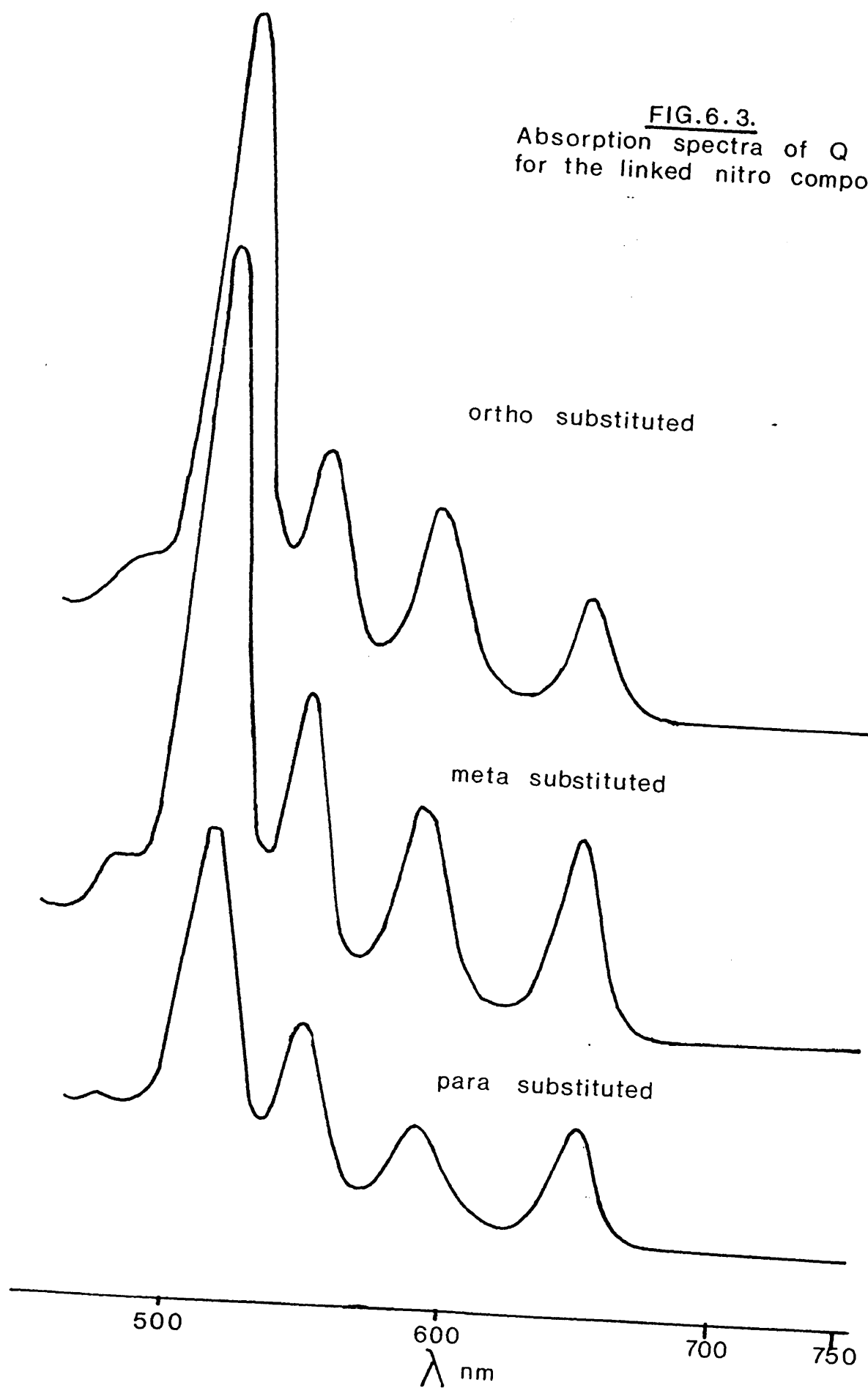
The standard used to compare the quenching and absorption characteristics of the above three isomers was H<sub>2</sub>TTP (tetratolyl porphyrin). Figs. 6.3 and 6.4 show the absorption and fluorescence spectra (normalised at 660nm) of the ortho, meta and para substituted isomers whilst the table below shows the fluorescence quantum yields.

Table 6.1b

| <u>substituent</u> | <u><math>\phi_F</math></u><br>(in benzene) |
|--------------------|--------------------------------------------|
| ortho              | 0.08                                       |
| meta               | 0.096                                      |
| para               | 0.117                                      |

As can be seen none of the isomers are significantly quenched compared to H<sub>2</sub>TTP ( $\phi_F \sim 0.11$ ). A first glance at these values might tempt one to explain the small difference in  $\phi_F$  and the trend in the quenching values para meta ortho in terms of electron transfer. However a close inspection of the absorption and fluorescence spectra suggests otherwise. Fig. 6.4 shows that the ratio of the intensity of the band at 660nm/720nm also follows the trend para > meta > ortho and corresponds to a similar pattern in the absorption spectra (Fig. 6.3) where the 640 and 597nm bands mirror the changes occurring in the fluorescence spectra. Hence the results observed can be

FIG.6.3.  
Absorption spectra of Q bands  
for the linked nitro compounds



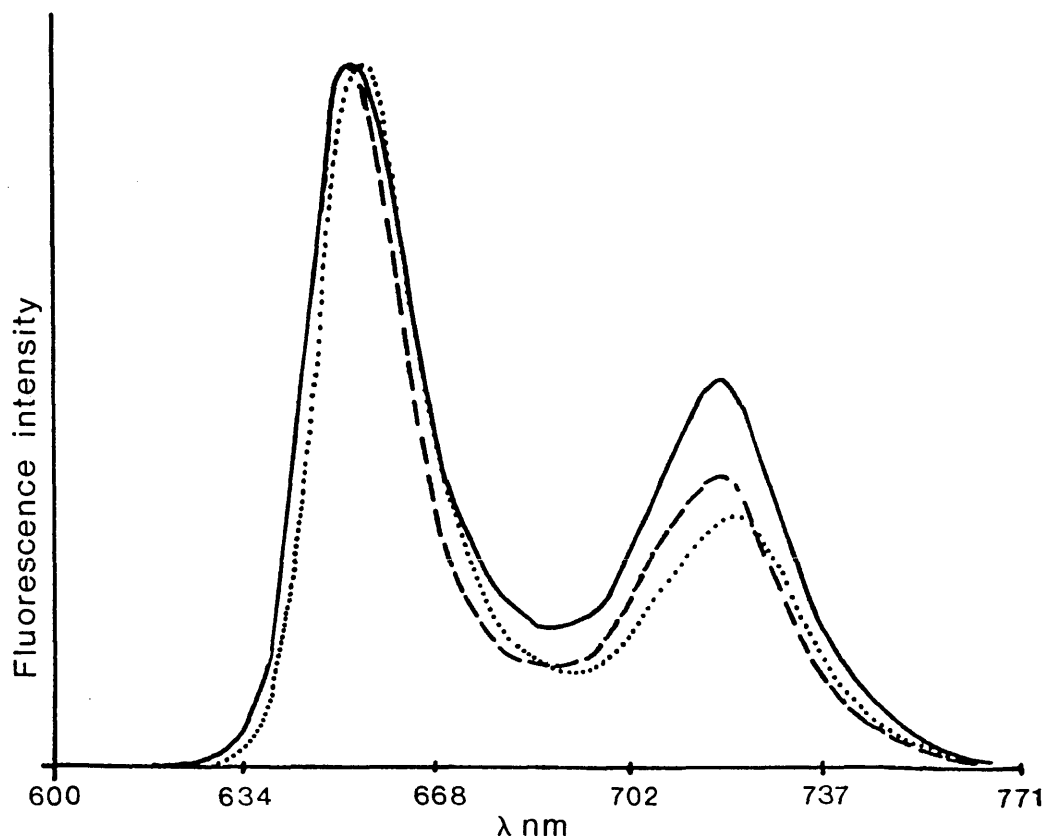


FIG.6.4.

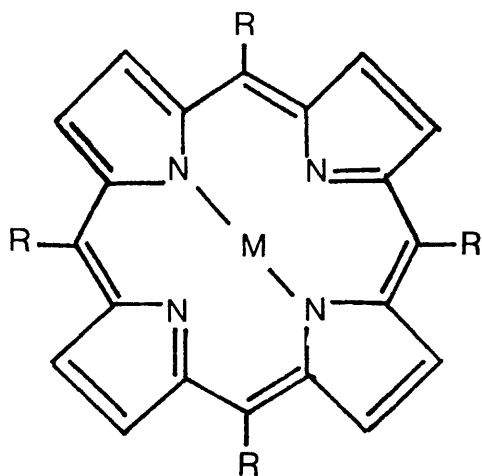
Steady state fluorescence spectrum of the linked porphyrin-nitro compounds: ortho substituted (—); meta substituted (---) and para substituted (.....).

(N.B. We do not know redox potentials but substitutions do make a change in redox potentials. Without having an available model we cannot say much about the redox potentials. It is possible that in linking through an amide we have changed  $E^0$ ).

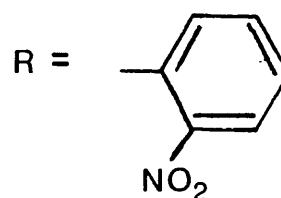
explained simply in terms of substituent effects. The 2nm red shift in the case of the para isomer could be due to electron density being pushed towards the porphyrin ring. No electron transfer products were observed in any instance i.e. neither in the ground state (cations absorb at ~680nm) nor in the excited states. The observed results do not exclude electron transfer quenching, but, in the absence of control compounds showing the relative

$\phi_F$  of o, m, p substituents we cannot take the argument too far. Synthesis of appropriate controls is in progress. Thus the linked compounds do not appear to give high quenching. This may be due to the limited conformations available to the molecule. As suggested previously quenching is most likely to occur when the nitro group can assume an axial position on the porphyrin. If this condition is not satisfied then any kind of association between porphyrin and nitro group cannot be established. The results also suggest that synthesis of a capped porphyrin-nitro compound might show more promising results.

#### 6.7 Nitro Porphyrin Systems



where  $M = \text{Zn or H}_2$



The molecules discussed in this section are of the type shown above where M can either be Zn or  $\text{H}_2$  (i.e. free base). The tetra 2-nitrophenyl porphyrins were synthesised by A. Harriman.

## 6.8 Results

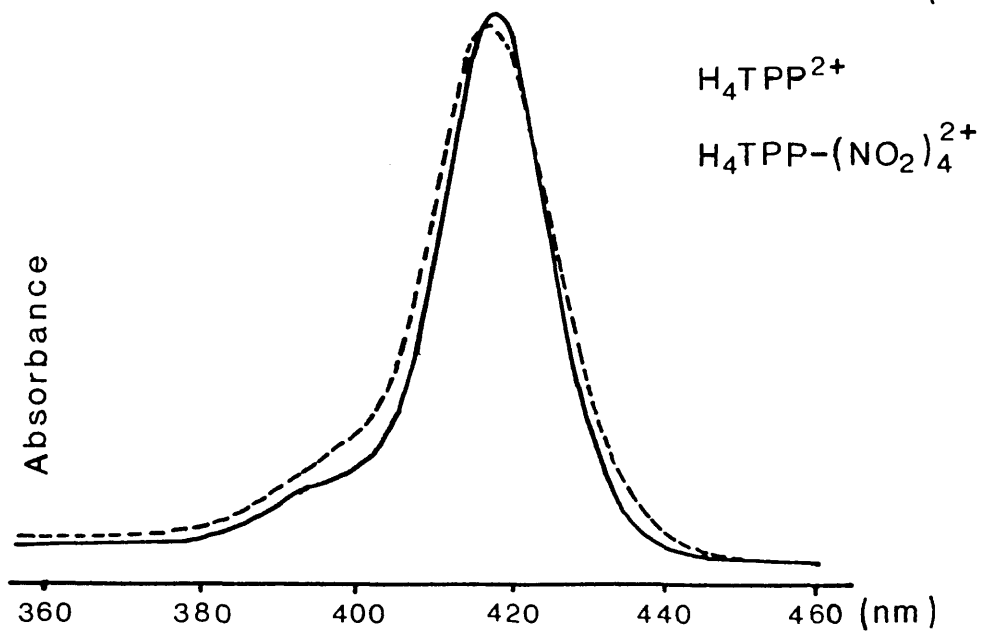
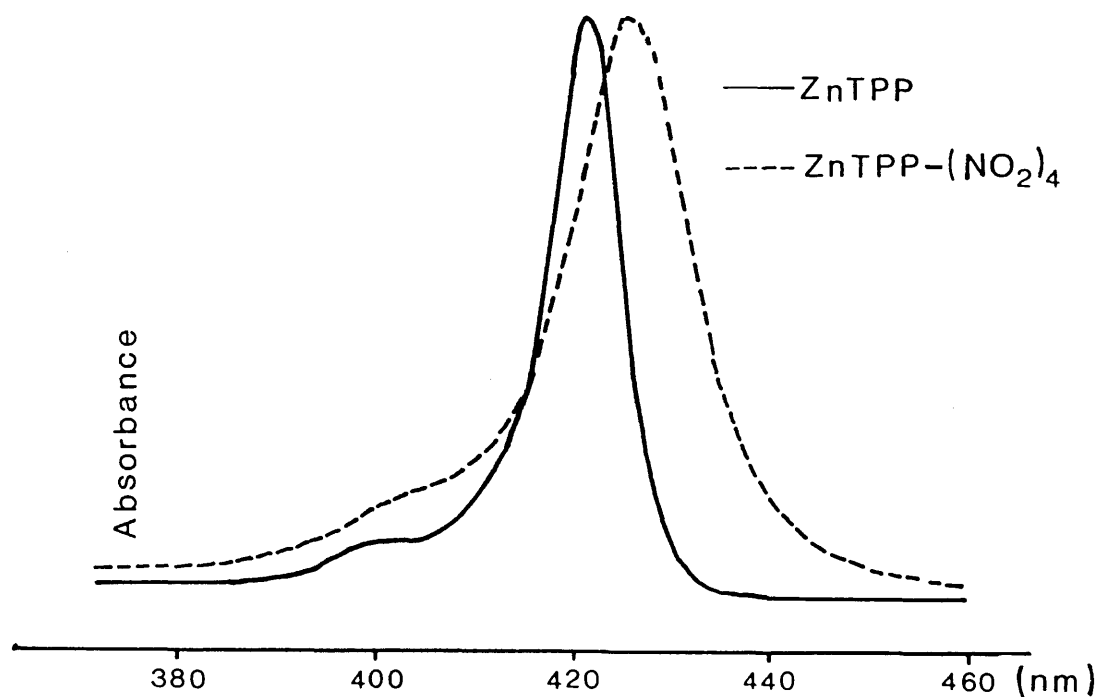
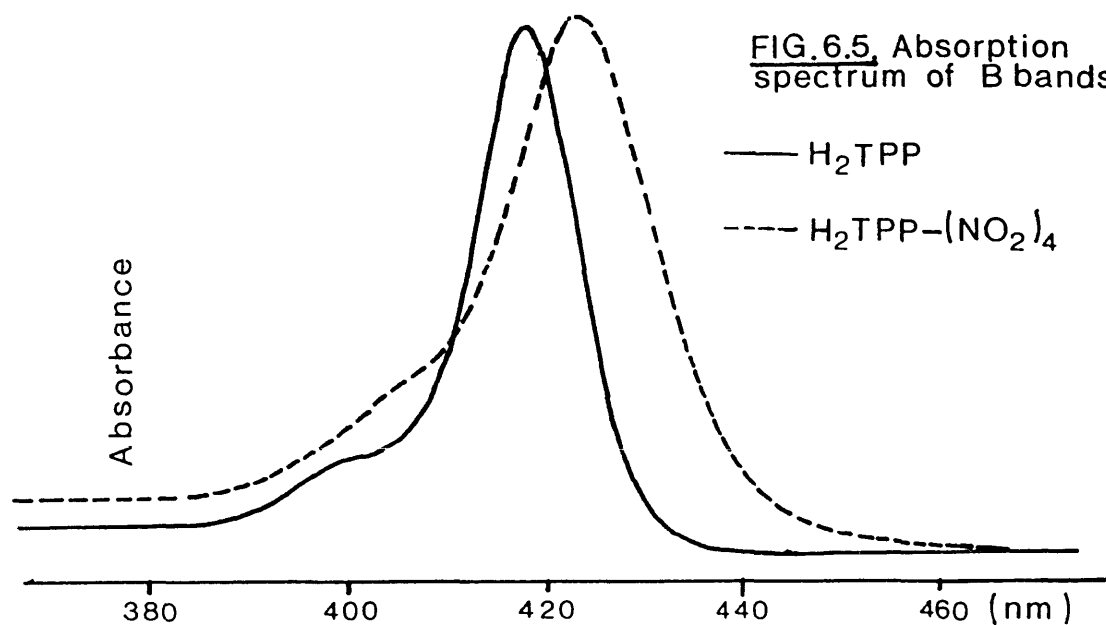
### Absorption spectra

The spectrum of the nitroporphyrin was red shifted compared to the tetra phenyl porphyrin and in addition the bands of the former were significantly broadened. The effects are illustrated by Fig. 6.5 a and b for the Zn and free base porphyrin respectively. The band for the nitro zinc porphyrin has a half width which is nearly twice that of zinc porphyrin. In the case of free base nitro porphyrin the half width is  $1\frac{1}{2}$  times greater than the free base and when acid is added to protonate the pyrrole N atoms in the latter two compounds, the half width of the two porphyrins is nearly identical. Extinction coefficients and oscillator strengths for both sets of nitro and non nitro porphyrins were calculated and are tabulated below:-

Table 6.2

| Compound                                            | Halfwidth<br>of Soret | $\epsilon$           | f<br>for Soret | f<br>total |
|-----------------------------------------------------|-----------------------|----------------------|----------------|------------|
| ZnTPP                                               | 469cm <sup>-1</sup>   | 6.43x10 <sup>5</sup> | 1.87           | 1.95       |
| ZnP-(NO <sub>2</sub> ) <sub>4</sub>                 | 828cm <sup>-1</sup>   | 1.36x10 <sup>5</sup> | 0.71           | 0.749      |
| H <sub>2</sub> TPP                                  | 716cm <sup>-1</sup>   | 3.99x10 <sup>5</sup> | 1.59           | 1.71       |
| H <sub>2</sub> P-(NO <sub>2</sub> ) <sub>4</sub>    | 1066cm <sup>-1</sup>  | 1.2x10 <sup>5</sup>  | 0.744          | 0.812      |
| (H <sub>4</sub> TPP) <sup>2+</sup>                  | identical             | 3.96x10 <sup>5</sup> |                |            |
| (H <sub>4</sub> P-(NO <sub>2</sub> ) <sub>4</sub> ] |                       | 7.73x10 <sup>4</sup> |                |            |

FIG. 6.5. Absorption spectrum of B bands.



The oscillator strength is a measure of the transition probability of the electron. If the transition is totally allowed then  $f = 1$ . The values quoted in the above table should really be divided by 2 as there are two possible transitions in porphyrins (namely  $a_{1u}$  and  $b_{1u} \rightarrow e_g$ ). Thus in all cases the oscillator strength is reduced in the nitro porphyrins. The trend however as far as band width is concerned shows that zinc porphyrin is more susceptible to changes than the free base porphyrin and protonated porphyrin when a nitro group is substituted on the phenyl ring. This fact is more greatly emphasized in the fluorescent quantum yields as shown below.

Table 6.3

| <u>Sample<br/>in benzene</u>                          | <u><math>\frac{\phi}{f}</math></u> |
|-------------------------------------------------------|------------------------------------|
| ZnTPP                                                 | 0.03                               |
| Zn(ONO) <sub>4</sub> TPP                              | 0.00003                            |
| H <sub>2</sub> TPP                                    | 0.11                               |
| H <sub>2</sub> (ONO) <sub>4</sub> TPP                 | 0.044                              |
| (H <sub>4</sub> TPP) <sup>2+</sup>                    | 0.09                               |
| [H <sub>4</sub> (ONO) <sub>4</sub> TPP] <sup>2+</sup> | 0.0076                             |
| D <sub>2</sub> TPP                                    | 0.12                               |
| D <sub>2</sub> (ONO) <sub>4</sub> TPP                 | 0.0113                             |

Thus the quenching pattern is Zn(ONO)<sub>4</sub>TPP H<sub>2</sub>(ONO)TPP [H<sub>4</sub>(ONO)<sub>4</sub>TPP]<sup>2+</sup>. The triplet appears to follow the same trend and in fact no trace of a transient was observed for Zn(ONO)<sub>4</sub>TPP on a timescale of 50ms and maximum sensitivity.

The above observations would be consistent with charge transfer from the porphyrin to the nitro group. The severity of quenching and the broadening of the Soret appear to fall in line with the  $E^0$  values of the porphyrins i.e. ZnTPP (-1.35) > H<sub>2</sub>TPP -1.05 > H<sub>4</sub>TPP<sup>2+</sup>. No products were observed at any time but this could be due to a very fast back reaction as the groups concerned are very close to each other and our time resolution is >50ns. The fluorescent measurements provide us with another interesting result if we compare the couples H<sub>2</sub>TPP - D<sub>2</sub>TPP and H<sub>2</sub>(ONO)<sub>4</sub>TPP - D<sub>2</sub>(ONO)<sub>4</sub>TPP. The deuterated species were formed by adding a drop of deuterated methanol to a solution of H<sub>2</sub>TPP and H<sub>2</sub>(ONO)<sub>4</sub>TPP. In the former case the deuterated porphyrin has a quantum yield of 0.12 which is ~10% greater than the ordinary free base. This enhancement in fluorescence is due to the slower vibration of the N-D bond on the pyrrole. Consequently the non radiative rate constant is lower and this results in a slightly longer lived excited state. However the latter couple behaves in exactly the opposite fashion. Here it is D<sub>2</sub>(ONO)<sub>4</sub>TPP which shows 30% quenching rather than H<sub>2</sub>(ONO)<sub>4</sub>TPP. There is no certain explanation for this phenomenon but one guess is that spin orbit coupling between the porphyrin and nitro group is increased or alternatively we are observing an isotope effect which catalyses electron transfer.

## 6.9 Conclusions

In organic solvents the bimolecular system is not very promising. The factor hindering satisfactory electron transfer appears to be the slow self-exchange rate of nitroaromatics. Electron transfer has, however, been shown to occur in aqueous solution [194] but protonation of the nitrobenzene radical anion ( $\text{NB}^-$ ) makes the system irreversible. In our system bimolecular association in the excited state was demonstrated with nitroanisole and ZnTPP. The linked systems do not appear to enhance electron transfer, but quenching due to the removal of electron density from the porphyrin ring is observed.

## 6.10 Quenching of Porphyrin of Excited States with Silver I Cations in Fluid Solution

As in the previous section the ensuing discussion reports the behaviour of porphyrin with quencher in two parts: the first stage dealing with the isolated species and the second with a linked system. The quencher in this system is the silver(I) cation.

The porphyrins used in this work are the zinc and free base octaethylporphyrins whose absorption spectra are shown in Figs. 6.1a and 6.1b respectively.

## 6.11 Energetic considerations

The singlet and triplet excited state energies of ZnOEP and H<sub>2</sub>OEP were measured by steady state fluorescence and low temperature phosphorescence and are as follows:-

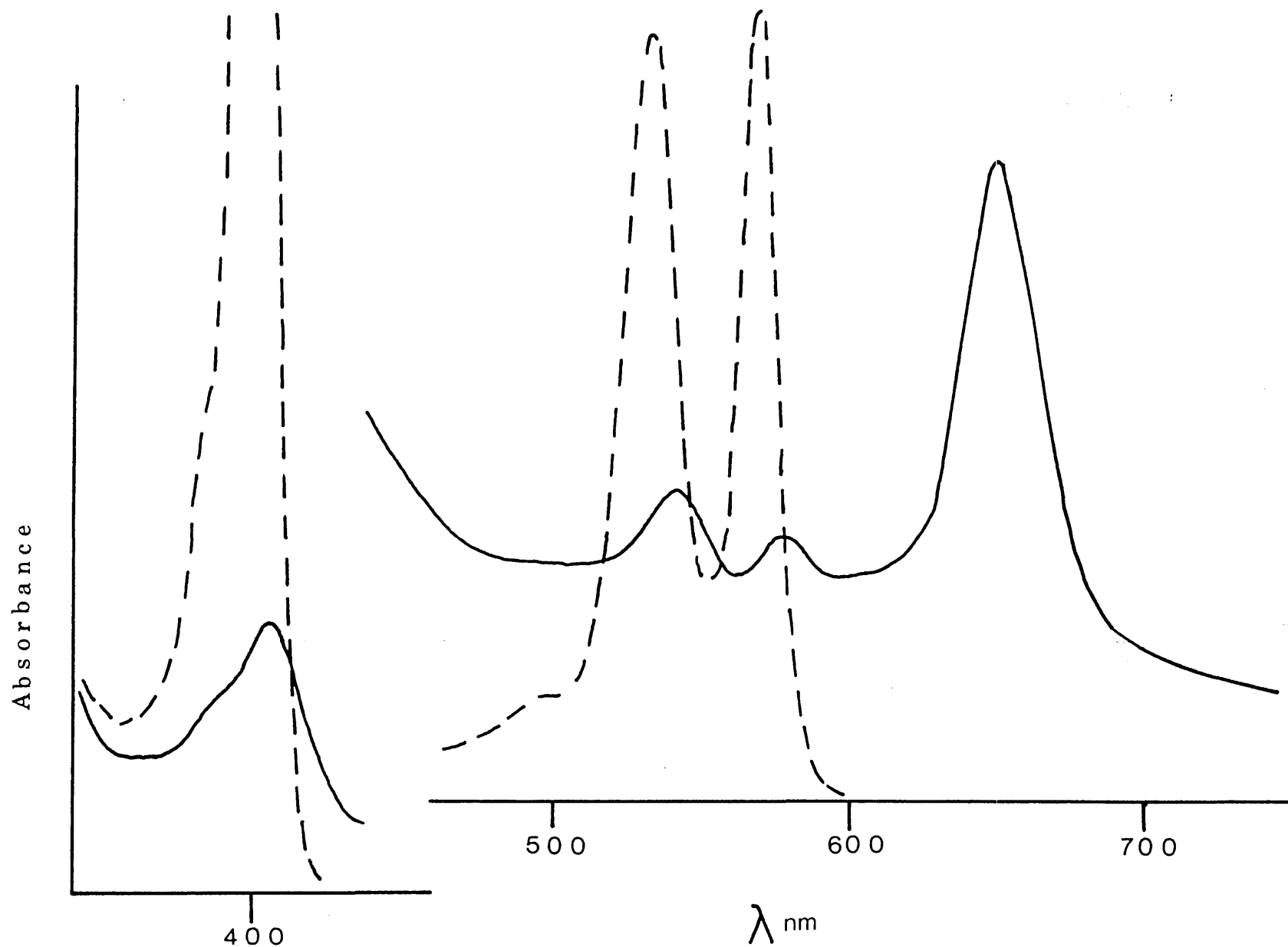
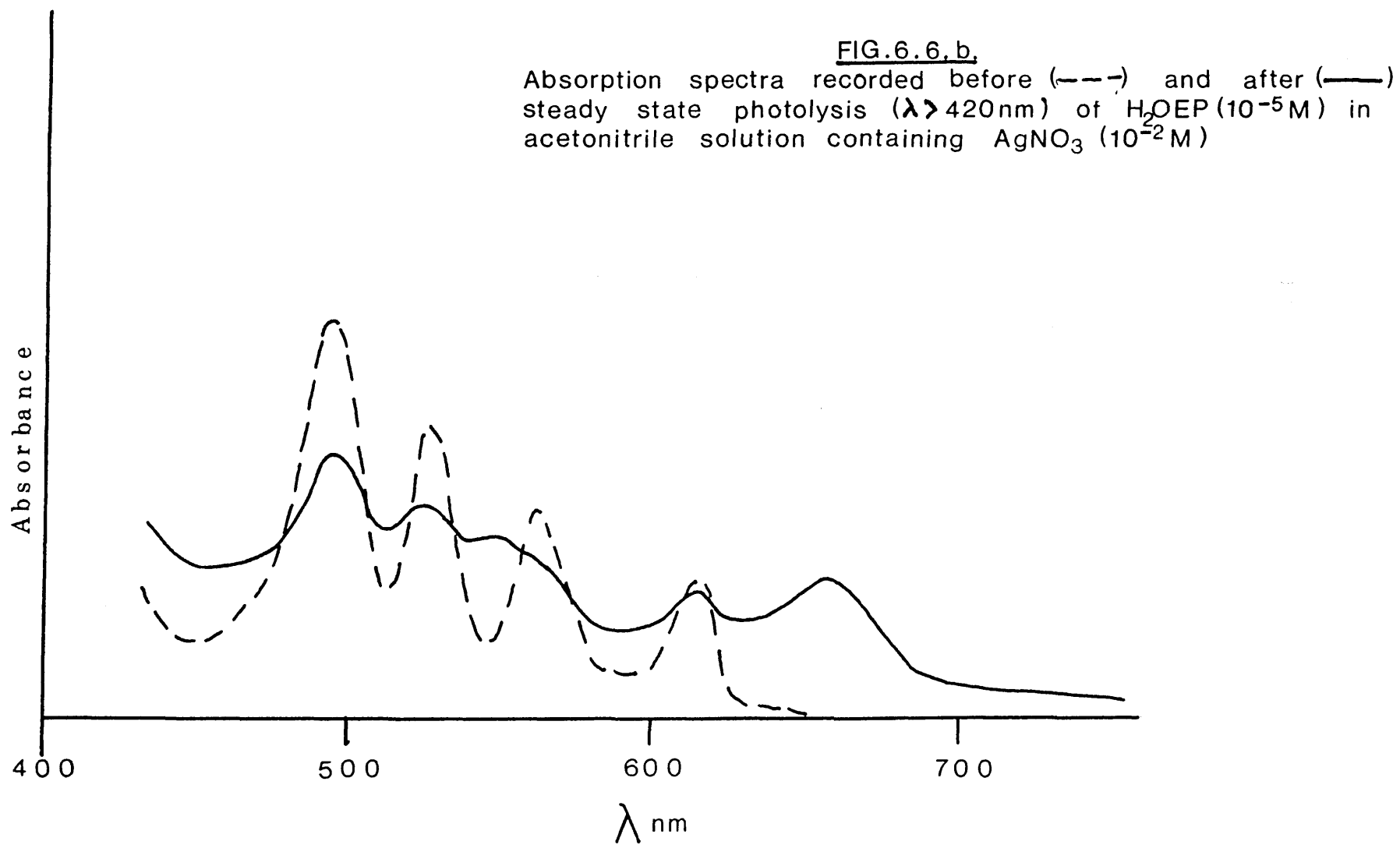
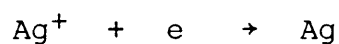


FIG.6.6 a.  
Absorption spectra recorded before (---) and after (—) steady state photolysis ( $\lambda > 420$  nm) of ZnOEP ( $10^{-5}$  M) in acetonitrile solution containing  $\text{AgNO}_3$  ( $10^{-2}$  M)



| <u>Compound</u>    | $\tau_f$<br>(nm) | $\tau_p$<br>(nm) | $E_s^*$<br>(eV) | $E_t^*$<br>(eV) |
|--------------------|------------------|------------------|-----------------|-----------------|
| H <sub>2</sub> OEP | 619              | 764              | 2.00            | 1.62            |
| ZnOEP              | 578              | 704              | 2.14            | 1.76            |

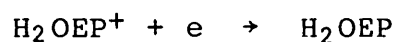
These values are not really dependent upon solvent polarity and are only affected by the addition of strongly ligating species such as pyridine. Redox potentials for both the porphyrins and silver(I) couples were determined using cyclic voltammetry. Silver nitrate was readily soluble in acetonitrile and hence most of the experiments described were carried out in this solvent.



$$E_{\frac{1}{2}} = + 0.20\text{V} \quad \text{vs SCE}$$



$$E_{\frac{1}{2}} = + 0.71\text{V} \quad \text{vs SCE}$$



$$E_{\frac{1}{2}} = + 0.11\text{V} \quad \text{vs SCE}$$

As described earlier the excited state redox potentials of the porphyrins can be estimated using the above values in conjunction with the excited state energies:

$$E_{\frac{1}{2}}^* = E_{\frac{1}{2}} - E^*$$

leading to the following values:

| Compound           | $E_{\frac{1}{2}}^s$<br>(V vs SCE) | $E_{\frac{1}{2}}^t$<br>(V vs SCE) |
|--------------------|-----------------------------------|-----------------------------------|
| H <sub>2</sub> OEP | - 0.89                            | - 0.51                            |
| ZnOEP              | - 1.43                            | - 1.05                            |

From these figures, it is expected that all the excited states will reduce silver(I) but there will be no ground state reaction. Furthermore, silver(I) has no low lying excited states, so that quenching of excited state porphyrin via energy transfer is unlikely. Also it is not paramagnetic. On this basis, the only expected quenching mechanisms will be electron transfer and heavy-atom enhanced non-radiative deactivation.

#### 6.12 Excited state quenching

The ground state absorption spectra of both ZnOEP and H<sub>2</sub>OEP remained unchanged on addition of excess AgNO<sub>3</sub>. However the fluorescence of both compounds was quenched. The Stern-Volmer (SV) quenching plots were linear over a wide range of silver(I) concentrations and gave quenching rate constants ( $k_{SV}$ ) of  $(5.9 \pm 0.3)$  and  $(15.7 \pm 0.5) \text{M}^{-1} \text{s}^{-1}$  respectively for ZnOEP and H<sub>2</sub>OEP. In separate studies carried out on the single photon counting, it was confirmed that the singlet excited state lifetimes were quenched by silver(I) ions with identical quenching constants. This shows that the excited state quenching is due to "dynamic" rather than "static" quenching.

From the Stern-Volmer equation

$$\frac{I_f^0}{I_f} - 1 = k_{SV}[Q]$$

$$k_{SV} = k_s \tau_s$$

where  $I_f^0$  and  $I_f$  refer to the fluorescence intensities in the absence and presence of quencher Q. A knowledge of the singlet excited state lifetimes allows us to calculate values of  $k_s$  which are tabulated below:

| Compound           | $k_s$<br>( $M^{-1}s^{-1}$ ) | $k_t$<br>( $M^{-1}s^{-1}$ ) |
|--------------------|-----------------------------|-----------------------------|
| H <sub>2</sub> OEP | $1.8 \times 10^9$           | $6.9 \times 10^4$           |
| ZnOEP              | $1.2 \times 10^9$           | $2.6 \times 10^5$           |

The triplet excited states of the porphyrins are long-lived in acetonitrile and were found to be 2.4ms for ZnOEP and 2.6ms for H<sub>2</sub>OEP. Again Ag(I) quenched the triplet lifetimes of both porphyrins. Bimolecular quenching rate constants ( $k_t$ ) also tabulated above were calculated from plots of  $1/\tau_T$  vs  $[Q]$ .

The derived bimolecular rate constants are consistent with an electron transfer mechanism in so far as there is a rough dependence upon the thermodynamic driving force. Both singlet state reactions are diffusion controlled but the triplet state reactions are very slow. Even allowing for the reduced  $\Delta G^0$ , the triplet reactions seem to be

inhibited by some parameter. This infers that the singlet state reactions contain a marked contribution from the "external heavy atom effect" which is usually much more pronounced for a singlet reaction than for the corresponding triplet state process.

A series of flash photolysis experiments was performed in order to obtain information about the quenching reactions. Conventional flash photolysis gave clear evidence that the triplet state reaction resulted in net electron transfer for both ZnOEP and H<sub>2</sub>OEP. Fig. 6.7 shows the decay profile for ZnOEP with and without added silver(I) at wavelengths of  $\lambda = 470\text{nm}$  where we see mainly the triplet decaying and at  $\lambda = 650\text{nm}$  which is where we expect to see absorption of the  $\pi$  radical cation ZnOEP<sup>+</sup>. Thus the sample containing silver(I) was shown to have a very long lived species after decay of the triplet excited state at 650nm whilst the control sample had similar species present at 470nm and 650nm. Decay of the cation was complex and incomplete. As shown in Fig. 6.6a and b steady state irradiation of both ZnOEP and H<sub>2</sub>OEP in outgassed acetonitrile containing 0.01M silver(I) ions results in the formation of porphyrin  $\pi$ -radical cation as a permanent product. In the flash photolysis records, at least three separate steps in the decay of the cation can be resolved. Such steps can be explained in terms of the following tentative scheme, which is based upon aggregation of silver atoms.

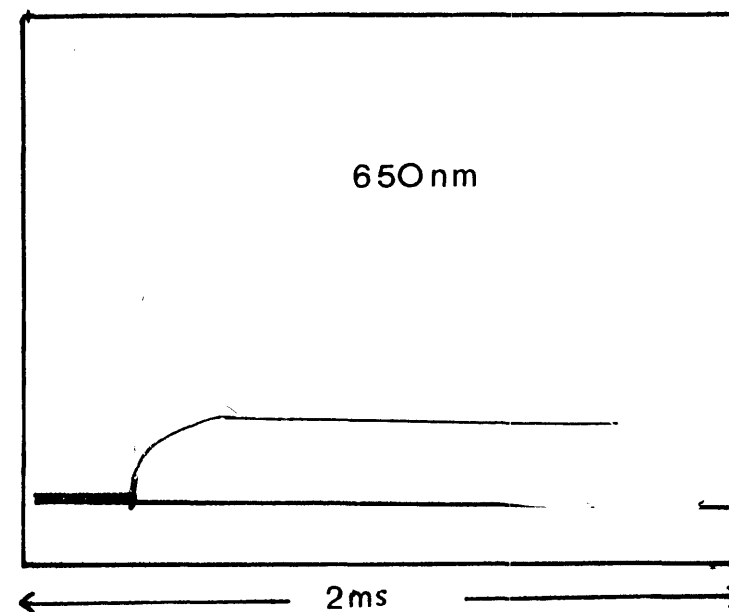
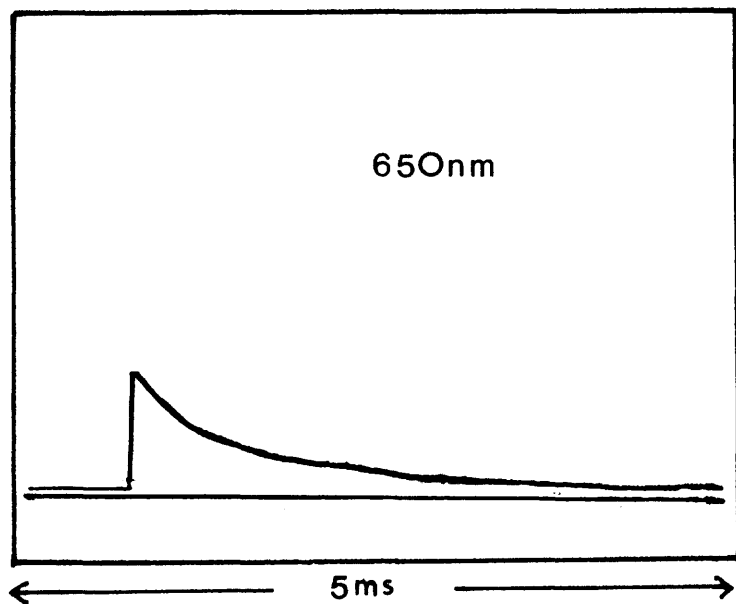
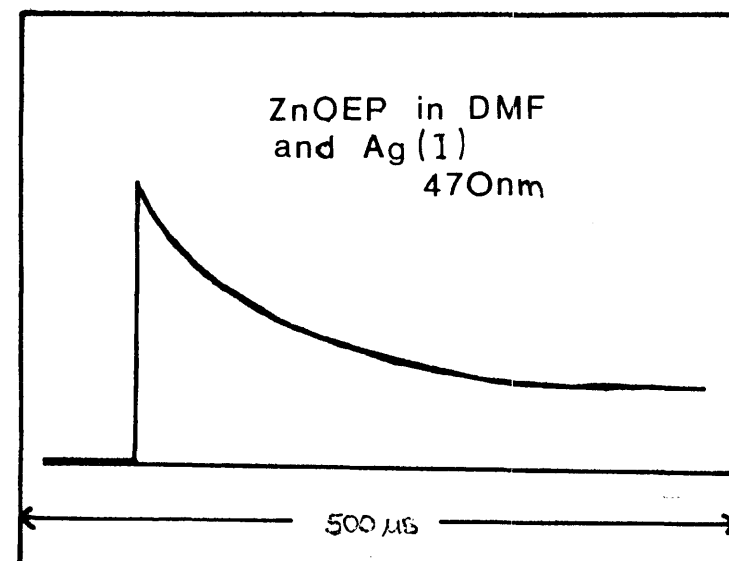
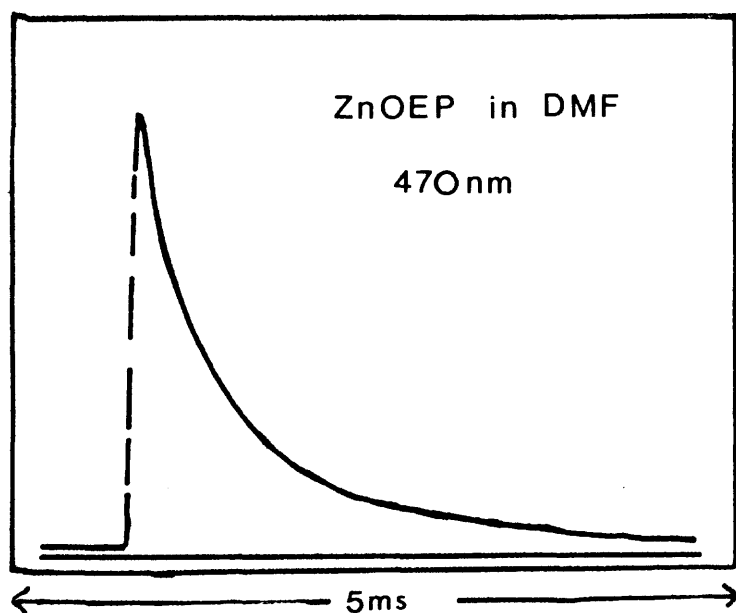
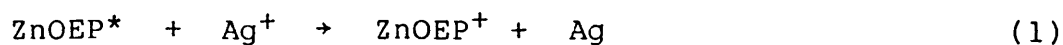
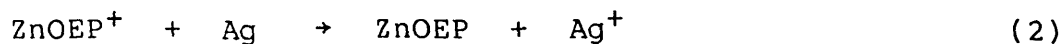


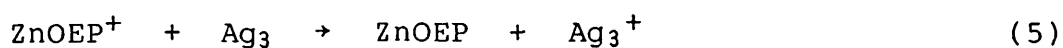
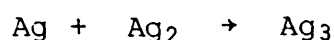
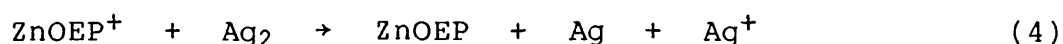
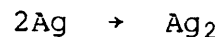
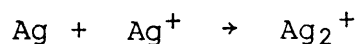
FIG.67



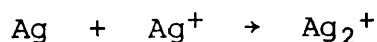
$$K_1 = 2.6 \times 10^5 \text{ M}^{-1} \text{ s}^{-1} \quad (\text{from Stern Volmer plot})$$



$$K_2 = 3.0 \times 10^7 \text{ M}^{-1} \text{ s}^{-1} \quad (\text{from pulse radiolysis})$$



In our experiments there was no direct spectroscopic evidence of aggregation of silver except that (1)  $\text{ZnOEP}^+$  is formed on steady state irradiation and there is some light scattering (2) at the end of the irradiation period, addition of  $\text{C}(\text{NO}_2)_4$  gives the colour test for silver metal. In addition Henglein [195] has shown that reduction of silver(I) salts in water results in formation of stable silver colloids and reaction between silver atoms and silver(I) is well known in water



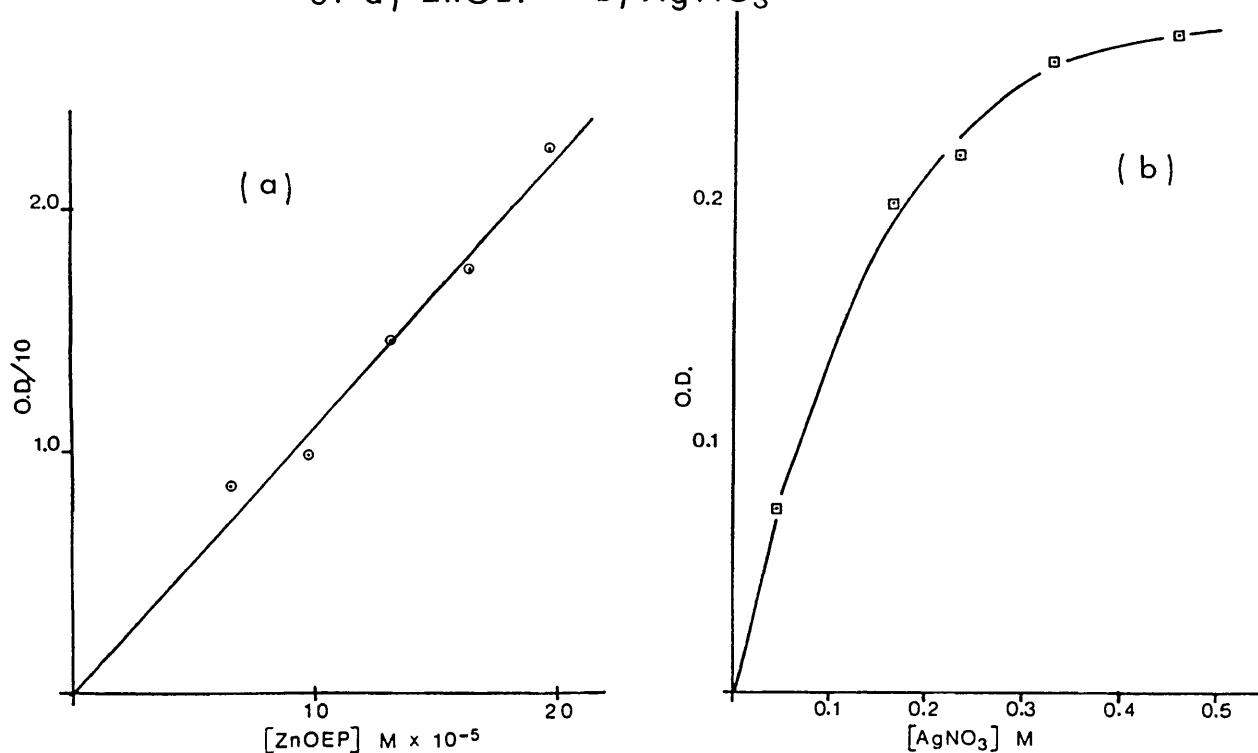
Such aggregation effects do seem to account for the observed flash photolysis results.

### 6.13 Dependence of reaction coordinates on rate

With quencher in excess the rate determining step in  $\text{ZnOEP}^+$  formation appears to be first order with respect to

porphyrin concentration as shown in Fig. 6.8a. The rate of  $\text{ZnOEP}^+$  formation is also influenced by the concentration of silver(I). Fig. 6.8b shows that there is initially a linear relationship but this levels out on further increase of silver(I). The reason for this could either

**FIG. 6.8** Formation of  $\text{ZnOEP}$  radical cation as a function of a)  $\text{ZnOEP}$  b)  $\text{AgNO}_3$



be because silver(I) is being added in excess and hence does not cause any great change in rate or that we should plot rate versus activity of silver(I) rather than concentration. The activity coefficient ( $\gamma$ ) generally decreases at higher concentrations and is also affected by changes in the ionic strength of the medium ( $\gamma \propto I$ ). The fact that the rate of reaction appears to be pseudo first order (from Fig. 6.8a) with respect to  $\text{ZnOEP}$  concentration is further evidence that the reaction involves a second order process as suggested by reaction scheme (1).

#### 6.14 Triplet state processes

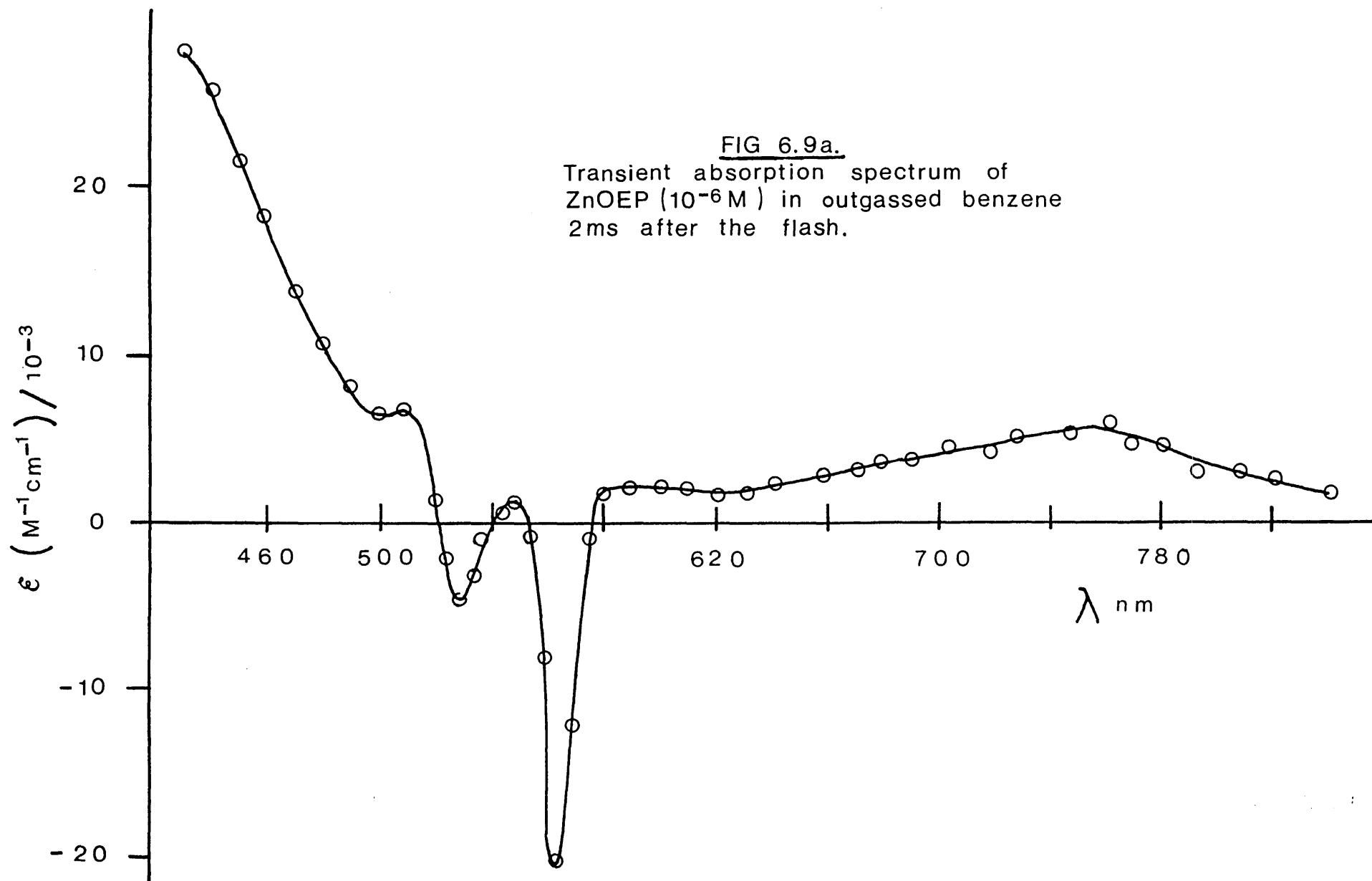
A series of ns laser flash photolysis experiments were carried out in which ZnOEP solutions containing various amounts of silver trifluorate were excited at 530nm. In each case, the fluorescence quantum yield for formation of the triplet excited state was measured. The results are given in Table 6.4.

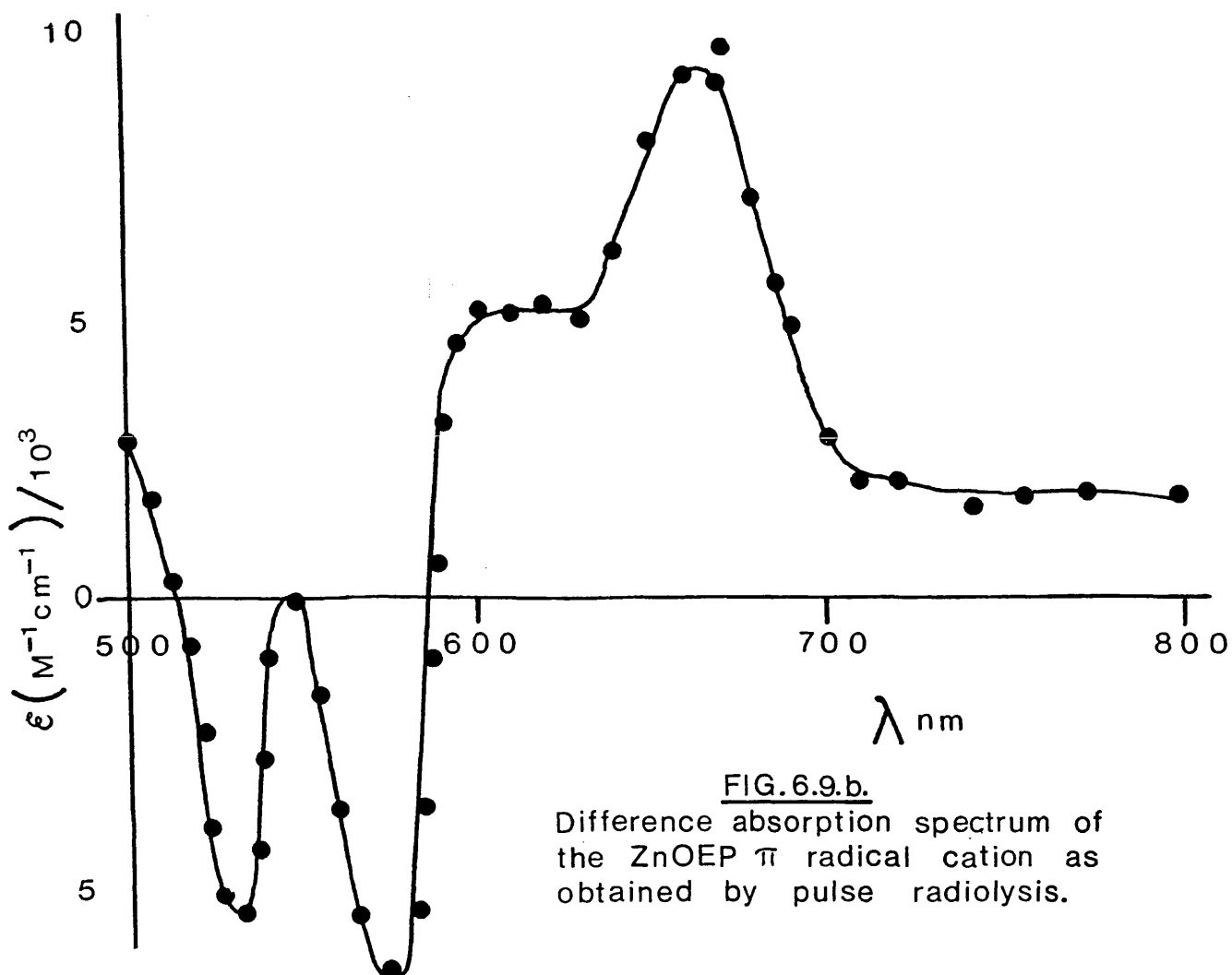
Table 6.4

Relative fluorescence and triplet state quantum yields measured for ZnOEP in acetonitrile solution as a function of the concentration of silver(I)

| (Ag <sup>+</sup> ) | $\phi$ | $\phi$ |
|--------------------|--------|--------|
| (M)                | f      | t      |
| -                  | 1.00   | 1.00   |
| 0.063              | 0.76   | 0.79   |
| 0.277              | 0.41   | 0.27   |

As table 6.4 shows, the high concentration of silver(I) quenches the excited singlet state but does not lead to enhanced triplet state formation. This suggests that the singlet excited state quenching reaction is primarily due to electron transfer and not the heavy atom effect. The external heavy atom effect is normally





associated with spin-orbital coupling perturbation of the non-radiative deactivation of excited singlet states. This results in enhanced formation of the triplet manifold and a reduced triplet lifetime. Although it cannot be ruled out entirely, the external heavy-atom effect has a more pronounced effect upon intersystem-crossing to the triplet manifold than upon the spin-allowed internal conversion to the ground state.

Fig. 6.7 showed the decay profile of the radical cation ( $\text{ZnOEP}^+$ ) recorded on the conventional flash photolysis apparatus at 680nm. Redox ion products could also be detected on the ns laser flash photolysis some 50ns after the flash. However, because of the incomplete quenching of the singlet excited state and the overlap

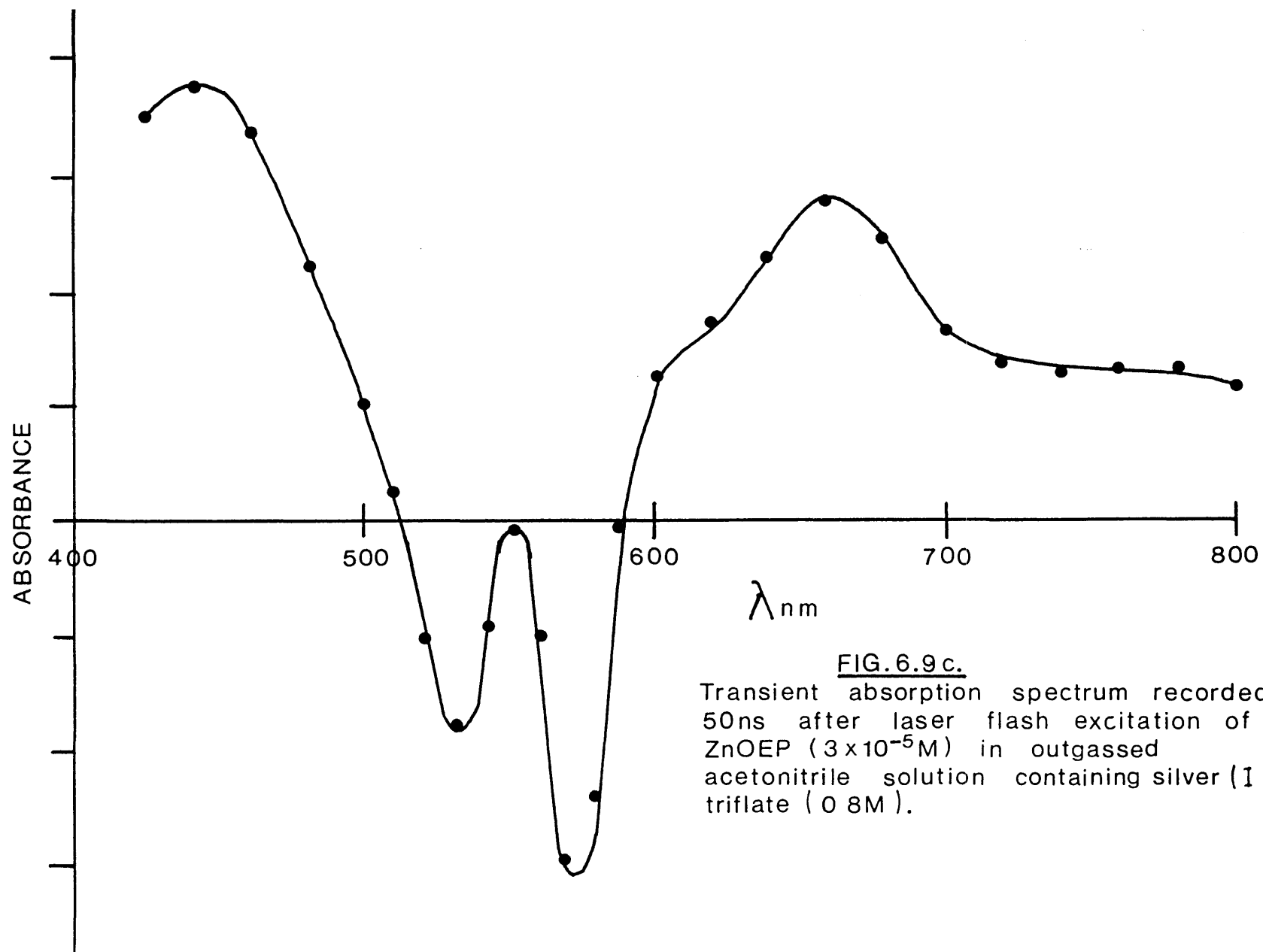


FIG.6.9c.

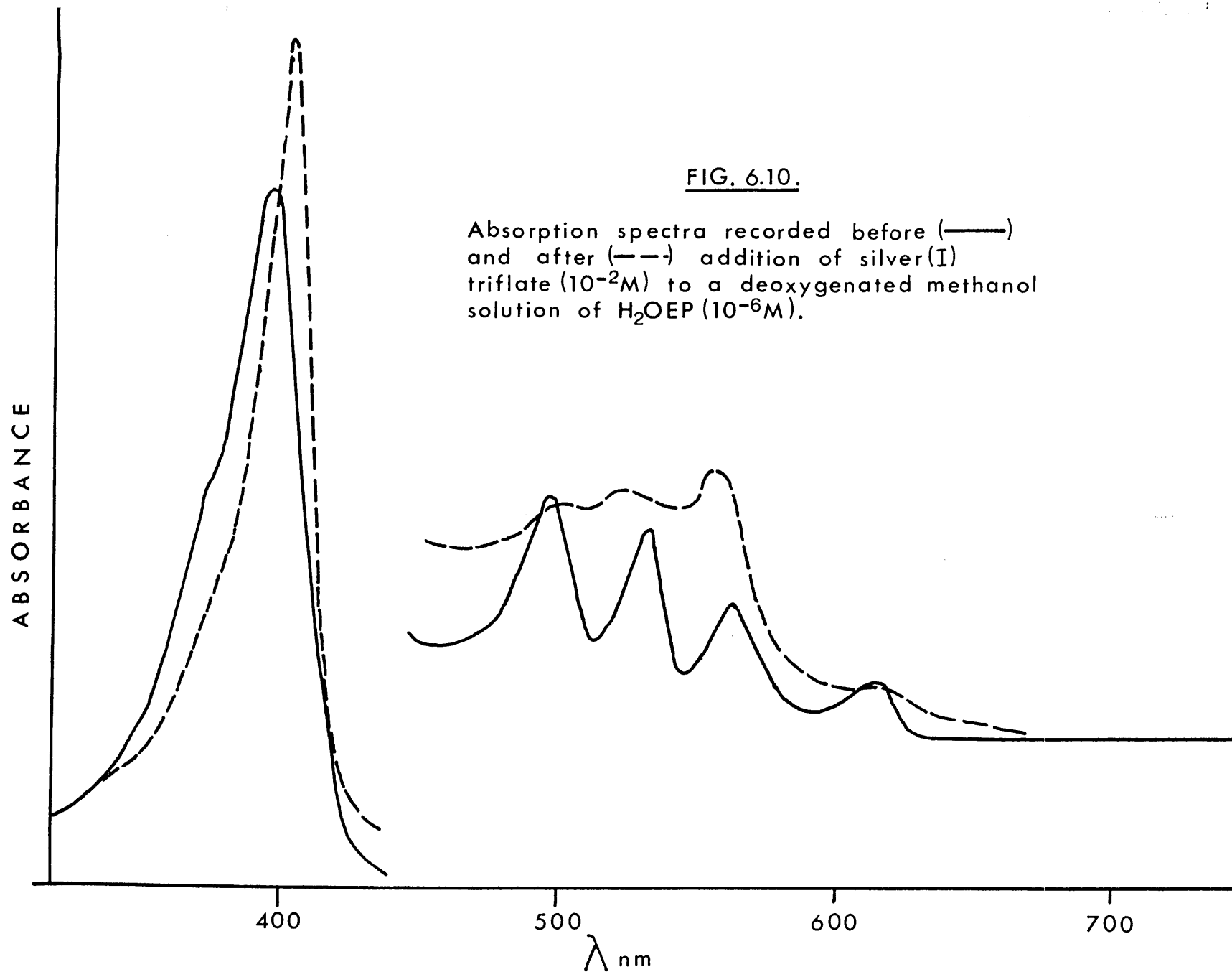
Transient absorption spectrum recorded 50ns after laser flash excitation of ZnOEP ( $3 \times 10^{-5}M$ ) in outgassed acetonitrile solution containing silver (I) triflate (0.8M).

between triplet and radical cation absorption spectra, it was not possible to estimate the quantum efficiency for formation of  $\text{ZnOEP}^+$ . Fig. 6.9a shows the triplet difference spectrum of ZnOEP in outgassed benzene as obtained 2ms after the flash in the conventional flash photolysis apparatus. Addition of silver(I) trifluorate to ZnOEP and outgassed in acetonitrile produces the spectrum shown in Fig. 6.9b which is typical of the radical cation. In fact a spectrum of  $\text{ZnOEP}^+$  produced in pulse radiolysis (in the absence of  $\text{Ag}^+$ ) gives the spectrum shown in Fig. 6.9c which is identical to Fig. 6.9b.

#### 6.15 Conclusions for bimolecular system

It has been shown that silver(I) ions quench both singlet and triplet excited states of ZnOEP and  $\text{H}_2\text{OEP}$  in fluid solution. Both quenching reactions give rise to net electron transfer products but the yields are far from quantitative. There is no experimental evidence to show that silver(I) ions enhance intersystem crossing in ZnOEP via the external heavy atom effect. Possibly, this process makes some contribution towards the observed rate constant.

Similar reactions occur in methanol solution. For ZnOEP, quenching rate constants are slightly lower in methanol ( $k_S = 1.0 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ ;  $k_t = 1.5 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$ ) than found in acetonitrile. This could be due to viscosity and polarity effects and the nature of the  $\text{Ag(I)}$  species in the different solvents. With  $\text{H}_2\text{OEP}$  in methanol, there



seems to be a ground state reaction at high concentrations of silver. This prevents meaningful analysis of the quenching rate constants. An absorption spectrum showing this effect is given in Fig. 6.10.

#### 6.16 Linked Systems

As the results with the bimolecular system described above were so promising, progression to a linked system was the natural course to follow. One way of linking an inorganic species such as silver to a porphyrin is via a crown ether complex as shown below in Fig.6.11.

The corresponding free base compounds (1)  $-H_2$  and (2)  $H_4$  were also studied. All the synthesis was done by Prof. Lehn's group in France. The crown ethers are held in place either by a bridging biphenyl (1) or a second porphyrin molecule (2) so that the overall molecule has a well defined structure. The absorption spectra of the first type of compound were similar to the respective ZnOEP and H<sub>2</sub>OEP species. However type (2) compounds showed a split in the Soret band in acetonitrile solution indicating that the porphyrin rings are perturbing each other.

The  $N_2O_4$  crown ether moieties by virtue of their hydrophilicity are both efficient and selective complexing agents for the silver(I) ion. This can be shown by Fig. 6.12a where the emission of the porphyrin crown ether molecules is greatly quenched on addition of small concentrations ( $\sim 10^{-6}M$ ) of silver(I) ions. Equivalent

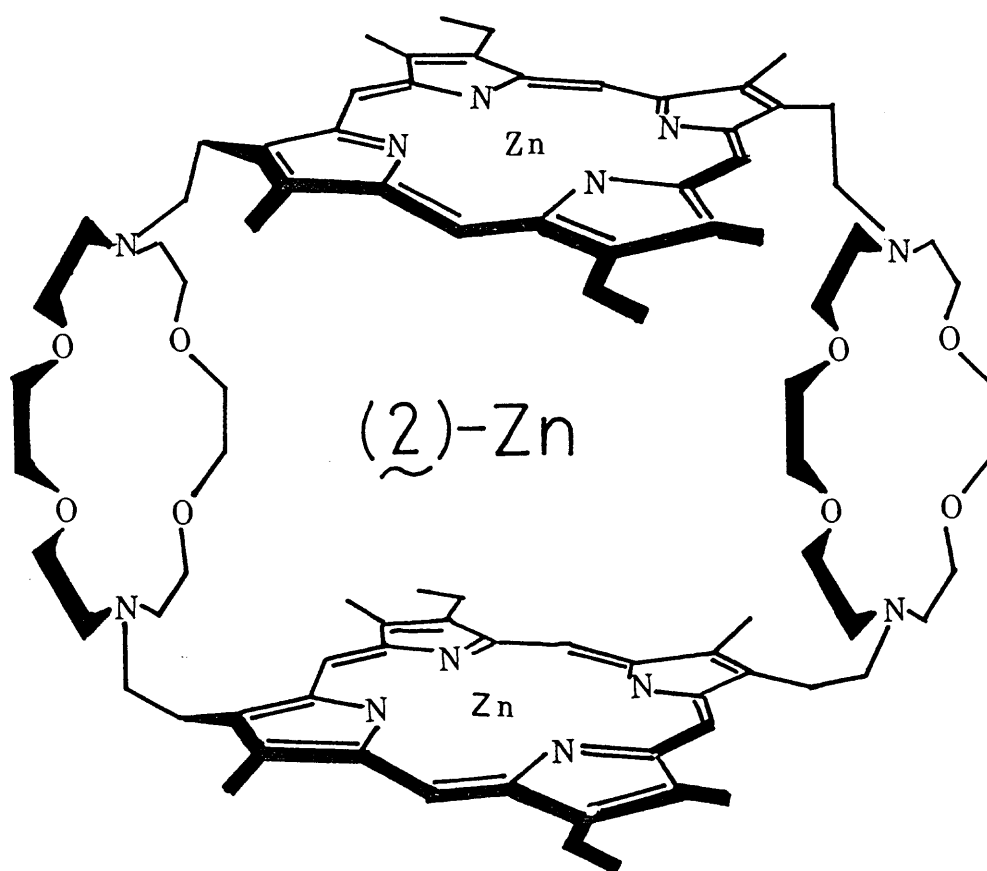
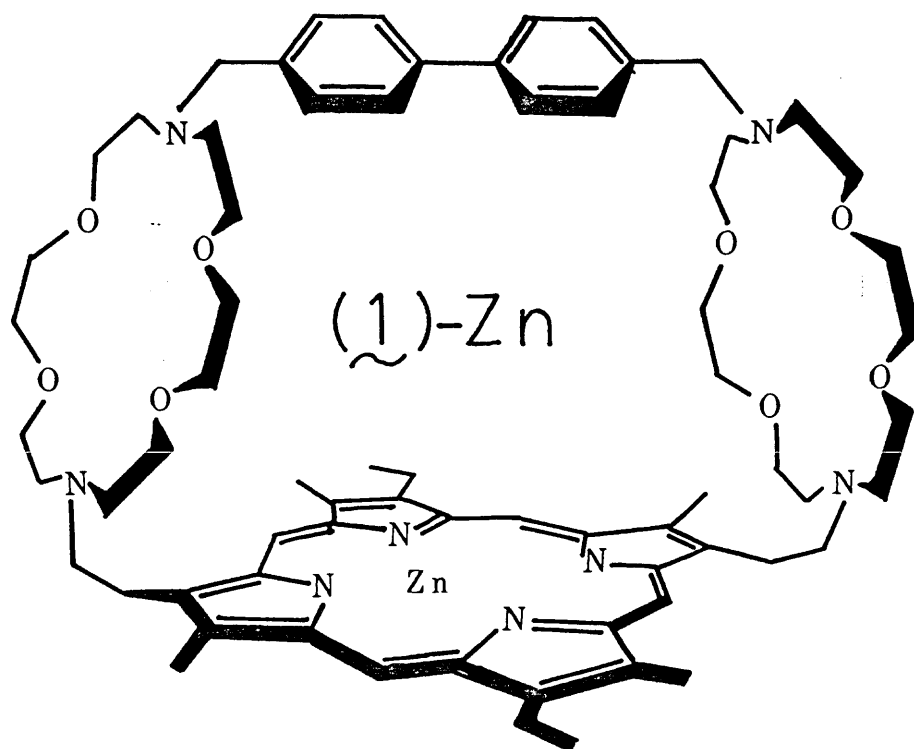


FIG.6.11.

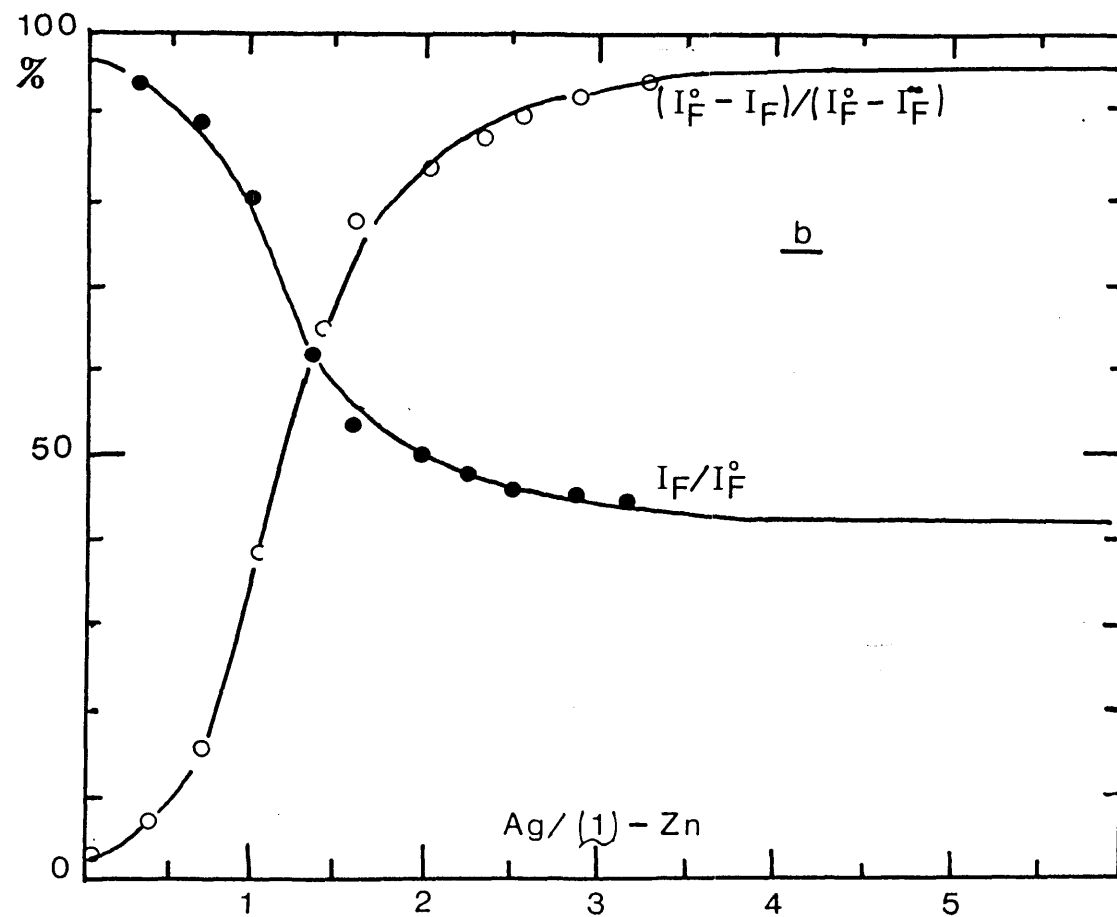
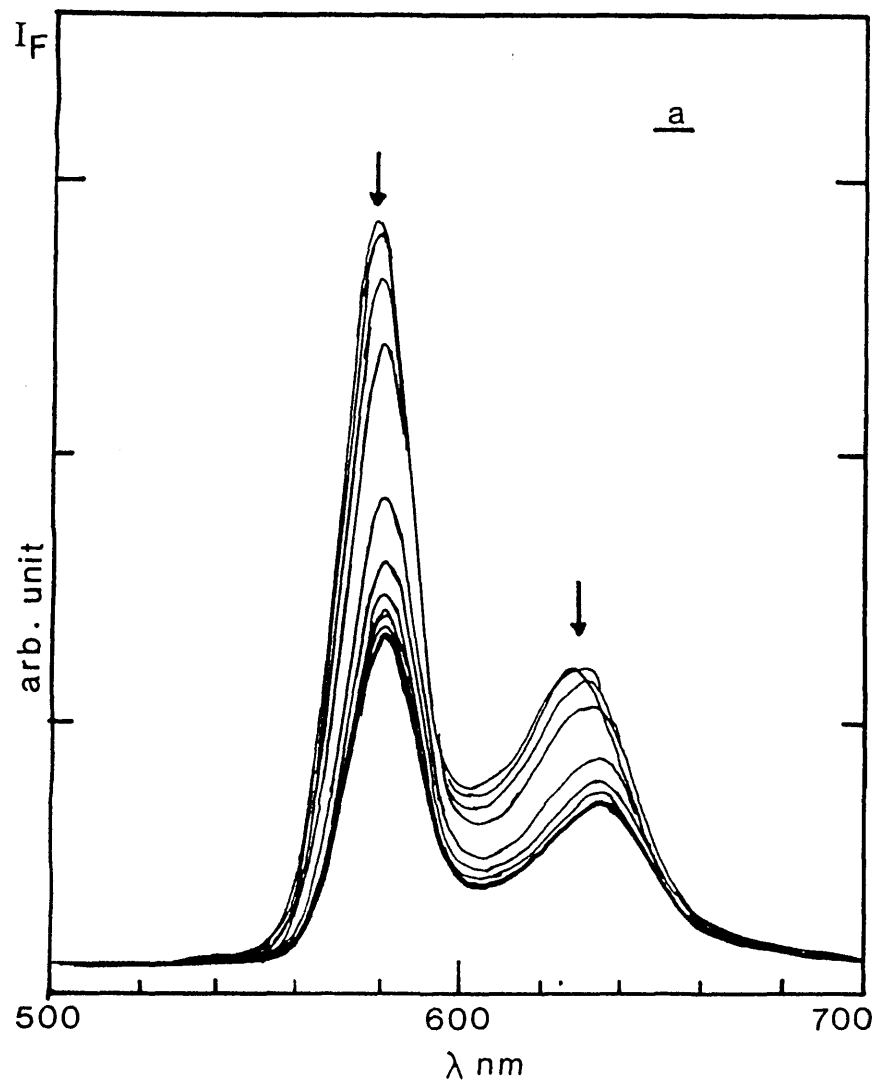


FIG.6.12.

- a) Steady state fluorescent quenching of (1)-Zn ( $166 \times 10^{-5} \text{M}$ ) in  $\text{CH}_3\text{Cl}:\text{MeCN}$  (9:1).  
 b) Percentage porphyrin quenching vs silver equivalents.

concentrations of silver(I) added to uncomplexed ZnOEP and H<sub>2</sub>OEP hardly effect the fluorescence spectra.

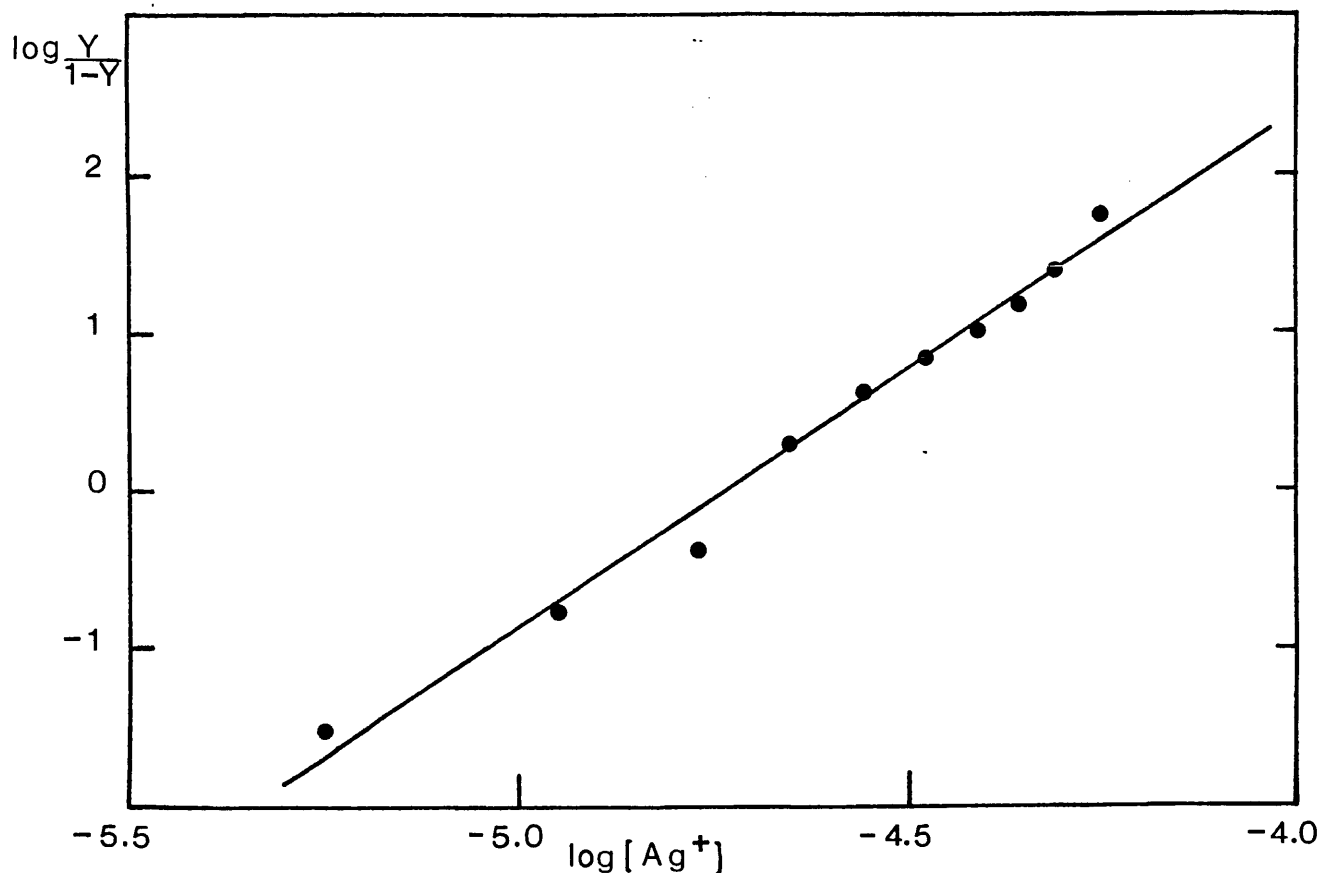
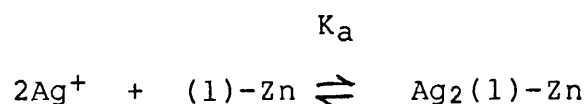


FIG. 6.12c.

Treatment of data by the Hill equation.

From the fluorescence data in Fig. 6.12a, values for percentage porphyrin quenched or percentage unquenched porphyrin can be obtained as a function silver(I) concentration. The data are plotted in Fig. 6.12b. The plot resembles a titration curve and shows that an equivalent concentration of ~2.2 moles silver(I) ions per mole of (1) -Zn results in both complete complexation of silver(I) and also complete quenching of fluorescence. This result is in close agreement with the expected value

of 2 moles of silver(I) ion per mole of (1)-Zn in accordance with the stoichiometry of the reaction:



Complexation of  $\text{Ag}^+$  with the crown ether moieties results in quenching of porphyrin fluorescence. On the basis of the bimolecular results described previously the quenching mechanism is electron transfer. Thus the percentage quenching observed (Y) is directly proportional to the percentage of  $\text{Ag}_2(1)\text{-Zn}$  is inversely proportional to (1)-Zn

$$\text{i.e.} \quad Y \propto \frac{[\text{Ag}_2(1)\text{-Zn}]}{[(1)\text{-Zn}]} \propto \frac{Y}{1-Y}$$

In addition according to the above equilibrium the ratio  $[\text{Ag}_2(1)\text{-Zn}]/[(1)\text{-Zn}]$  is dependent upon the value of the equilibrium constant  $K_A$  and the concentration of silver(I) ions

$$\text{i.e.} \quad \frac{Y}{1-Y} \propto K_A [\text{Ag}^+]^n$$

where  $n$  = moles of  $\text{Ag}^+$  participating in the reaction.

The above equation is known as the Hill Equation and can be rewritten in the form:

$$\log \frac{Y}{1-Y} = n \log[Ag^+] + \log K_A$$

where  $n$  = moles of  $Ag^+$  participating in the reaction.

Knowledge of  $Y$  used in Fig. 6.12b together with the corresponding values of  $[Ag^+]$  can thus be used to obtain another value for  $n$  and also a value for the equilibrium constant. The data are plotted in Fig. 6.12c and yield a value for  $n = \sim 3$ . This suggests that some silver(I) ions are probably sandwiched in between the crown ether and porphyrin macrocycles as shown in Fig. 6.12c.  $K_A$  is in excess of  $10^6$  i.e. complexation is very efficient. In contrast  $n$  for e.g.  $K^+$  (potassium ions) is 28.

#### 6.17 Lifetime Data

Both singlet and triplet lifetimes were recorded for the porphyrin-crown ether molecules in presence and absence of silver(I) ions. ZnOEP and H<sub>2</sub>OEP were used as controls. In the absence of silver(I) ions the type (1) molecules show values for  $\phi_F$  and singlet lifetimes that are comparable to their controls, though their triplet lifetimes are slightly quenched. Type (2) compounds are similar to type (1) in their triplet state characteristics but their  $\phi_F$  and singlet lifetimes are smaller than type (1). This is probably due to perturbations taking place in the singlet state due to the proximity of the porphyrin rings. Evidence for this was observed in the absorption spectra.

The above results are summarised in Table 6.5. Complexation of silver in the crown ether moieties results in quenching of all the lifetimes, especially of the triplet state. Quenching rate constants can be calculated from these data and are shown in Table 6.6. As with the bimolecular system when the solvent was changed to methanol, the quenching was more efficient as shown also in Table 6.6.

Unlike the bimolecular system no longer-lived transient species persisted after decay of the triplet state. Hence, any redox products must have lifetimes less than  $\mu\text{s}$ . Also steady state photolysis of the cryptanols complexed with  $\text{Ag}^+$  show that the porphyrin cation is not formed as a permanent product. Flash photolysis in methanol however does show the presence of a slowly decaying species ( $\tau_{\frac{1}{2}} = 1\text{-}10\mu\text{s}$ ) after decay of the triplet. The (2)- $\text{H}_4$  and (1)- $\text{H}_2$  compounds like their bimolecular counterparts showed strange characteristics when dissolved in methanol and therefore results are unreliable.

A general idea of the sequence of events leading to the quenching observed in methanol is shown in Fig. 6.13. Electron transfer occurs from the singlet state and leads to formation of the porphyrin cation and silver(0) in the cryptanol. At this stage the  $\text{Ag}(0)$  may drop out of its crown-ether due to increase in radius. Such an event may explain the slow return ( $\sim 2 \times 10^4 \text{sec}^{-1}$ ) to initial reactant.

Table 6.5

LINKED SYSTEM

Photophysical properties (MeCN)

| compound            | Fluo.Quan.Yield                   |                                 | Sing. lt./ns        |                     | Trip. lt./ $\mu$ s  |                     |
|---------------------|-----------------------------------|---------------------------------|---------------------|---------------------|---------------------|---------------------|
|                     | absence of Ag <sup>+</sup><br>(-) | pres. of Ag <sup>+</sup><br>(+) | Ag <sup>+</sup> (-) | Ag <sup>+</sup> (+) | Ag <sup>+</sup> (-) | Ag <sup>+</sup> (+) |
| ZnOEP               | 0.040                             | 0.040                           | 5.07                | 5.04                | 2400                | 2400                |
| H <sub>2</sub> OEP  | 0.130                             | 0.130                           | 12.1                | 12.1                | 2600                | 2600                |
| (1)-H <sub>2</sub>  | 0.146                             | 0.019                           | 13.1                | 1.7                 | 1500                | 15.5                |
| (1)-Zn              | 0.042                             | 0.0094                          | 5.29                | 1.08                | 410                 | 1.5                 |
| (2)-H <sub>4</sub>  | 0.032                             | 0.0165                          | 1.77                | 1.35                | 2890                | 24                  |
| (2)-Zn <sub>2</sub> | 0.014                             | 0.0147                          | 3.05                | 1.42                | 390                 | 9.2                 |

Table 6.6

Quenching rate constants ( $k_Q$ ) in  
the presence of  $\text{Ag}^+$  ions (8 mol. equiv.)

| compound           | $k_Q(\text{Sing.}) \times 10^8$ |      | $k_Q(\text{Trip.}) \times 10^4$ |      |
|--------------------|---------------------------------|------|---------------------------------|------|
|                    | MeCN                            | MeOH | MeCN                            | MeOH |
| (1)- $\text{H}_2$  | 5.12                            | 14.0 | 6.7                             | 1430 |
| (1)-Zn             | 7.37                            | 23.0 | 66.7                            | 910  |
| (2)- $\text{H}_4$  | 1.76                            | 147  | 4.2                             | 490  |
| (2)- $\text{Zn}_2$ | 3.76                            | 21   | 11.1                            | 500  |

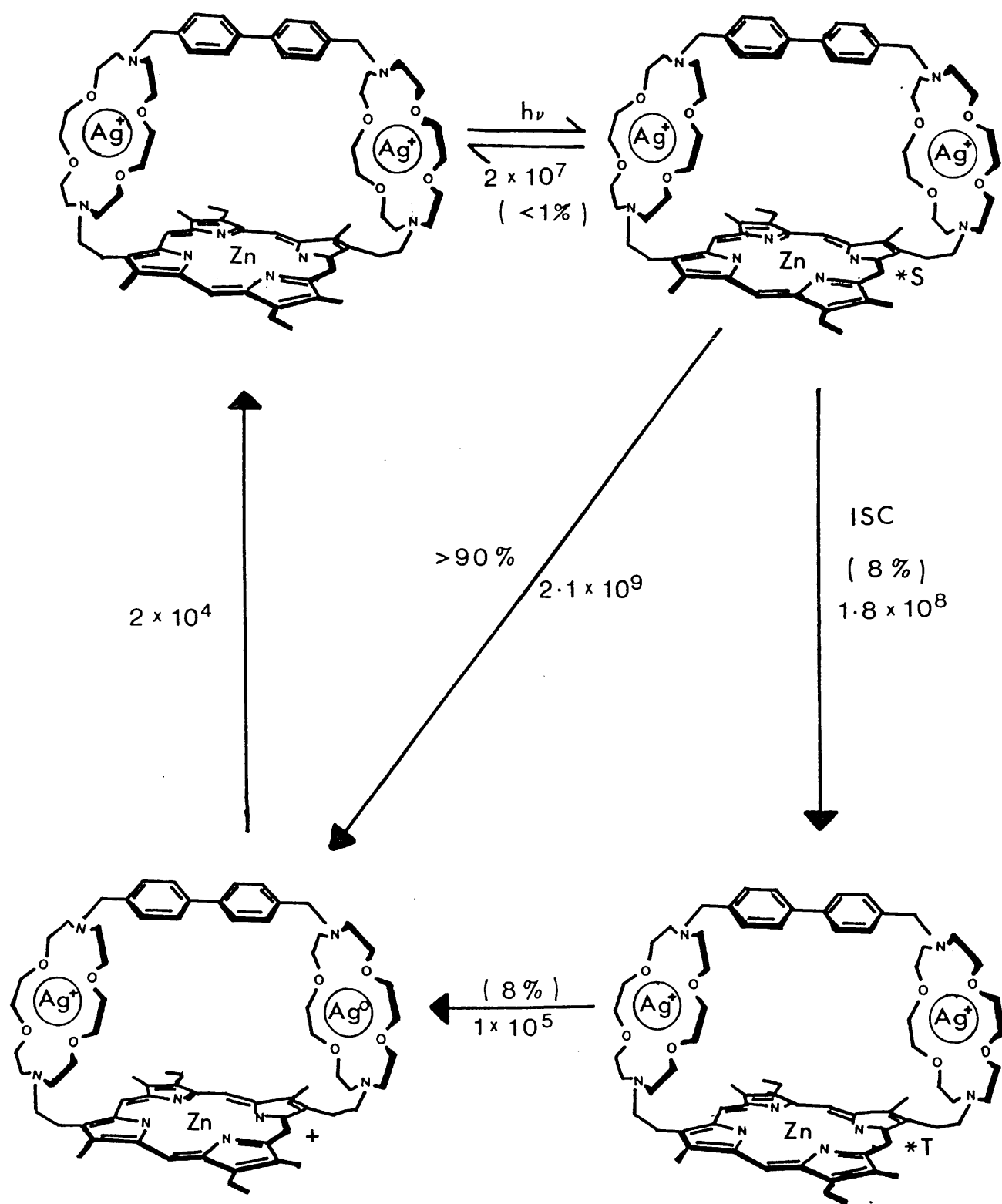


FIG.6.13.

## Conclusions

Silver(I) ions are very good quenchers for excited state porphyrins resulting in electron transfer. Permanent ion products are formed in the bimolecular system where silver(I) undergoes a phase change to form silver metal. This phase change could explain the efficient charge separation of the caged ion pair formed during electron transfer. The crown-ether system on the other hand has a much more efficient quenching rate constant but permanent ion products are not observed. The system is attractive as very small amounts of quencher are needed. However the back reaction is still too fast for consideration as a photogalvanic device. Thus improving the system would involve slowing down the back reaction and at the same time trying to retain the efficiency of the forward reaction.

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