

## Short Communication

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### Fluorescence quenching effect of substituted tetraphenylporphyrins

ANTHONY HARRIMAN and R. JOHN HOSIE

*Davy Faraday Research Laboratory, The Royal Institution, 21 Albemarle Street, London W1X 4BS (Gt. Britain)*

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#### 1. Introduction

Intensive study over the past decade or so has led to a general acceptance that the primary photochemical process in green plant and bacterial photosynthesis involves a one-electron transfer between a "special" chlorophyll molecule and an electron acceptor. The redox reaction takes place at a reaction centre and for the simpler bacterial systems there has been some success in the isolation and characterization of this reaction centre complex. Such preparations have been shown [1] to contain four chlorophyll molecules, two pheophytin molecules and a ubiquinone-iron complex. The primary photochemical reaction is believed [2] to involve electron transfer from a chlorophyll dimer to a pheophytin molecule and is followed by the transfer of an electron from reduced pheophytin to the ubiquinone complex.

Armed with this knowledge, it should soon become possible to construct *in vitro* models for the bacterial reaction centres but the natural plant has mastered the ability to hold reactants at optimum sites by the careful use of membranes. However, it may be possible to surmount this problem by the synthesis of porphyrin donor-acceptor complexes. For example, in recent work [3 - 5] the preparation of compounds where a quinone acceptor moiety is held at close proximity to the porphyrin chromophore by covalent linkages has been described and it has been reported [4, 5] that for such systems fluorescence quenching is extremely efficient. In this work we describe the synthesis of several porphyrins in which various donor or acceptor groups are attached to the ring. The compounds show fluorescence in fluid solution and the fluorescence quantum yield and lifetimes are used as a measure of the intramolecular electron transfer in the excited singlet state.

#### 2. Experimental details

A series of substituted *meso* tetraphenylporphines (Fig. 1) was prepared by condensation of pyrrole with the substituted benzaldehyde. The syntheses were achieved either by refluxing the reactants in glacial acetic acid (I - V) or by heating them in a sealed bomb at 190 °C (VI - VIII). IX was

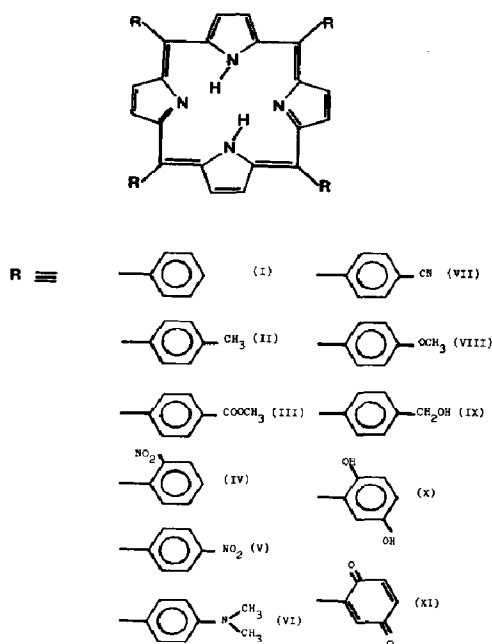


Fig. 1. A series of substituted *meso* tetraphenylporphines.

prepared by the  $\text{LiAlH}_4$  reduction of III, and X and XI were prepared by a procedure similar to that given by Dalton and Milgrom [5]. The compounds were purified either by repeated chromatography on alumina using a  $\text{CHCl}_3\text{-C}_6\text{H}_6$  eluent or by recrystallization from cold pyridine. All the compounds (except XI which was not isolated but was used *in situ* after oxidation of X with chlorine) gave satisfactory elemental analyses.

### 3. Results and discussion

The compounds I - XI represent a series of porphyrins in which the substituent has been varied from a good electron donor (VI) to a good electron acceptor (XI). The nature of the substituent has some effect on the absorption and fluorescence spectral profiles since the relative intensities of the vibronic bands depend on the substituent. In fact, in the most extreme case the absorption spectrum of VI is more characteristic of a rhodo type of porphyrin than of an etio type as shown by I and II. However, the most pronounced effects are on the fluorescence quantum yield  $\phi_F$  and the singlet state lifetime  $\tau_s$ , as is shown in Table 1;  $\phi_F$  values were measured in outgassed benzene solutions using the optically dilute method, as described in ref. 6, and the  $\tau_s$  values were measured by single-photon counting. For some of the substituents (II, III, VIII and IX) there is virtually no fluorescence quenching but for the porphyrins with good electron-accepting groups (IV, V and XI) there is a substantial reduction in both  $\phi_F$  and  $\tau_s$ . Similar quenching effects have been reported for porphyrins containing an intramolecular quinone unit. Thus, Dalton and Milgrom [5] report that XI has  $\phi_F < 10^{-3}$ , whilst a related porphyrin containing a single quinone moiety shows [4] a 90% reduction in

TABLE 1

Fluorescence properties of substituted tetraphenylporphyrins in outgassed benzene solutions

Compound	$\lambda_{\max}$ (nm)	$\phi_F$ ( $\pm 15\%$ )	$\tau_s$ ( $\pm 0.2$ ) (ns)
I	419	0.13	15.7
II	421	0.15	14.0
III	422	0.13	13.9
IV	421.5	0.02	6.4
V	422	0.045	8.3
VI	440	0.025	8.4
VII	421	0.064	12.2
VIII	421	0.15	12.3
IX	421.5	0.11	13.4
X	422	0.030	7.5
XI	422	0.007	2.5

$\phi_F$ . There are no reports describing fluorescence from porphyrins with electron-donating groups (VI and X) but our results show that these compounds also exhibit fluorescence quenching. Presumably, the fluorescence quenching mechanism in all cases involves intramolecular electron transfer and further work is in progress to evaluate this hypothesis. Typical absorption and fluorescence spectra are shown in Fig. 2.

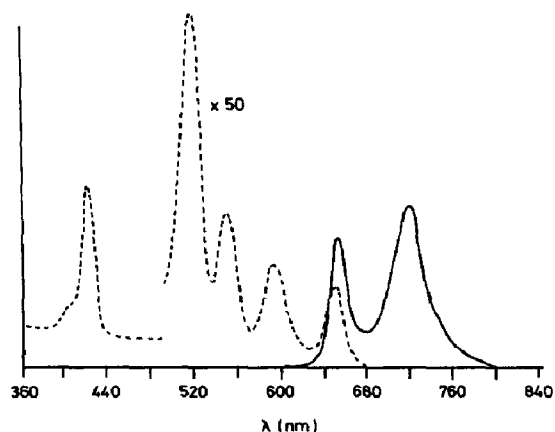


Fig. 2. Typical absorption (---) and fluorescence (—) spectra of substituted tetraphenylporphyrins in benzene solution.

The fluorescence of I is quenched by the presence of electron donor and acceptor molecules in the solution. For these systems the bimolecular quenching rate constant  $k_Q$  can be determined from the Stern-Volmer relationship

$$I_F^0/I_F = 1 + k_Q\tau_s[Q]$$

where  $I_F^0$  and  $I_F$  are the fluorescence yields in the absence and presence respectively of a quencher Q. Quenching rate constants for some of the relevant quenchers are collected in Table 2 and in some cases approach the diffusion-controlled limit. As expected, there is a general correlation between  $k_Q$  and the redox potential of the quencher, which is consistent with a charge transfer quenching mechanism.

TABLE 2

Bimolecular rate constants for the quenching of the fluorescence of tetraphenylporphine in ethanol solution

Quencher	$k_Q$ ( $\pm 15\%$ ) ( $M^{-1} s^{-1}$ )
1,4-Benzoquinone	$9.6 \times 10^9$
1,3-Dinitrobenzene	$3.3 \times 10^9$
1,4-Benzohydroquinone	$2.7 \times 10^8$
<i>N,N</i> -Dimethylaniline	$1.6 \times 10^8$
1,4-Dimethoxybenzene	$6 \times 10^7$
Cyanobenzene	$7 \times 10^6$
Benzyl alcohol	$<10^6$
Methyl benzoate	$<10^6$

Comparison of these  $k_Q$  values with the quenching effects of the substituted porphyrins shows the high quenching efficiency obtained by fixing the quencher at an intramolecular site. Thus, for XI the effective concentration of benzo-1,4-quinone is about 0.11 M based on the reduction in  $\phi_F$ . This observation accounts for the high efficiency of the primary photoredox reaction of photosynthetic organisms, where the reactants are held in close proximity by proteins. Work is now in progress to extend these studies by the synthesis of porphyrins in which the distance between the porphyrin ring and the substituent is varied. In this manner it may be possible to obtain optimum quenching and to observe the redox intermediates by flash spectroscopy.

#### 4. Summarizing remarks

*meso*-Tetraphenylporphine exhibits intense fluorescence in fluid solution which is quenched on addition of electron donor or acceptor molecules. Quenching by benzo-1,4-quinone or *N,N*-dimethylaniline is very efficient, with the bimolecular quenching rate constant approaching the diffusion-controlled limit, and the quenching mechanism is believed to involve charge transfer. If the electron-donating or electron-accepting moiety is attached directly to the porphyrin ring, then intramolecular fluorescence quenching is observed. Here, quenching is extremely efficient and for 5,10,15,20-tetra-

(2,5-dioxophenyl)porphine the effective concentration of benzo-1,4-quinone is 0.11 M. The relevance of the high quenching efficiency obtained with intramolecular complexes to bacterial photosynthesis is inferred.

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