

## Simultaneous photolysis of directly linked porphyrin–diazonium salt molecule

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**Abstract.** Meso-tetra-(*p*-diazoniumphenyl) porphyrin (TDSPP) can be photolyzed only under anaerobic conditions with a yield of 0.18 during simultaneous irradiation with He–Ne laser light (632.8 nm) and light of the 313 nm line of 0 mercury lamp.

The excited singlet state of TDSPP is quenched by external *p*-methoxybenzene diazoniumtetra fluoroborate (MeODS) with a rate constant of  $9.7 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ . TDSPP and MeODS interact in the ground state with an equilibrium constant of about  $16 \text{ M}^{-1}$  and form a fluorescent but photochemically inactive.

**Keywords.** Porphyrins; diazonium salts; photoinduced electron transfer; spectral sensitization.

### 1. Introduction

It is well-known that excited states of porphyrins undergo electron transfer (ET) reactions in the presence of suitable electron acceptors (Chandrashekar and Krishnan 1982; Kapinus *et al* 1982; Gasyna *et al* 1984). The singlet state can be quenched by such electron acceptors as quinones,  $k_q^s = 2.2 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$  for zinc-meso-tetra(*p*-tolyl)porphyrin and 1,4-benzoquinone (Yamada *et al* 1983) nitroaromatics,  $k_q^s = 7.32 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$  for pheophytin *a'* (Droupadi and Krishnan 1984) and 1,4-dinitrobenzene and arene diazonium salts,  $k_q^s = 1.2 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$  for zinc meso-tetraphenylporphyrin and *p*-methoxybenzene diazonium tetrafluoroborate (MeODS) (Becker *et al* 1985). Also triplet states are quenched by these compounds very effectively (Whitten *et al* 1974; Becker *et al* 1989).

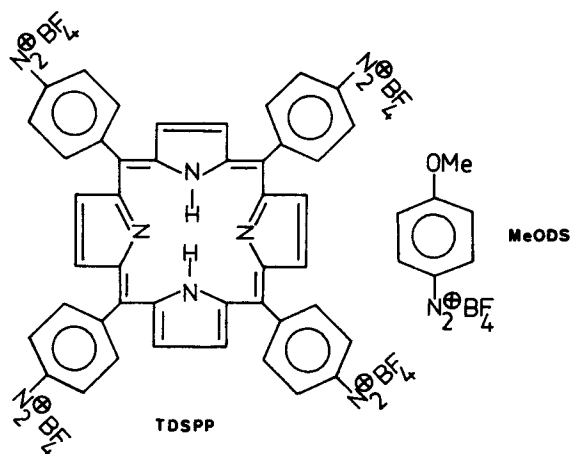
The characteristic behaviour of the fluorescence quenching of the above systems is that Stern–Volmer plots deviate upward at higher quencher concentrations [*Q*]. The proposed mechanism for the nonlinear relationship between  $I_0/I$  vs [*Q*] is static quenching due to the formation of ground state complexes of the fluorophores and the quenchers. For example  $K_{eq} = 12.4 \text{ M}^{-1}$  for 5-ethyletioporphyrin and toluquinone in benzene (Mataga *et al* 1984),  $K_{eq} = 2.7 \text{ M}^{-1}$  for chlorophyll *a* and 4-morpholino-2,5-dibutoxybenzenediazonium tetrafluoroborate (Enamanji 1987) and  $K_{eq} = 10.8 \text{ M}^{-1}$  for zinc-tetraphenylporphyrin and *sym*-trinitrobenzene in acetone (Chandrashekar and Krishnan 1981). In the systems porphyrins/diazonium salts the formation of ground state complexes decrease the quantum yield of intermolecular sensitized photodecomposition of diazonium salt and equimolar photobleaching of porphyrins.

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In viscous and rigid media a reduction of sensitization efficiency of dediazonation is observed as well. We have proposed the porphyrin-diazonium salt systems which are independent of media viscosity and which are free of ground state complexes. Our investigations were simulated by the conception of covalently linked porphyrin-electron acceptor molecules (Netzel *et al* 1982; Maiya and Krishnan 1985). In a previous study (Majka 1989; Zieba and Majka 1989) we have found that zinc meso-tetra-(*p*-diazoniumphenyl tetrafluoroborate)porphyrin (ZnTDSPP) and zinc mono-(*p*-diazoniumphenyl tetrafluoroborate)-tri-phenyl-porphyrin (ZnMDSPP) are photochemically completely inactive on the irradiation in *Q*-band region ( $\sim 546$  nm). In our opinion this phenomenon is due to the strong quinoidization of diazonium salt moieties in these molecules, see table 1. In this paper we present some of our investigation of TDSPP free base and of TDSPP/MeODS (figure 1).

**Table 1.**  $\tilde{\nu}$ -values of  $N \equiv N$  and C-N bonds vibrations for ZnTDSPP and ZnMDSPP in relation to these vibrations in MeODS.

	$\tilde{\nu}_{N \equiv N}$ ( $\text{cm}^{-1}$ )	$\tilde{\nu}_{C-N}$ ( $\text{cm}^{-1}$ )
ZnTDSPP	2090	1590
ZnMDSPP	2075	1600
MeODS	2255	1570



**Figure 1.** Meso-tetra-(diazoniumphenyl tetrafluoroborate) porphyrin (TDSPP) and *p*-methoxy-benzenediazonium tetrafluoroborate (MeODS).

## 2. Experimental

### 2.1 Materials

TDSPP<sup>†</sup> was prepared as follows: 5.6 ml (0.081 mol) of redistilled pyrrole was added to 750 ml of refluxing anhydrous acetic acid containing 12.0 g (0.081 mol) *p*-nitrobenzaldehyde and 4.0 g anhydrous zinc acetate. The solution was refluxed for 30 min. After cooling, the reaction mixture was filtered under vacuum and the damp powder was washed with 3 × 50 ml water (70°C) and 100 ml methanol. The dry product was dissolved in 500 ml methylene chloride and refluxed with 5.0 g *p*-chloranil for 1 h. The solution was concentrated to about 100 ml by rotatory evaporation, and 10 g basic alumina was added. The slurry was further dried to afford a dark powder, which was added onto the top of flash chromatography column (2.5 cm diameter) filled with alumina (50 cm in height). The column was washed with 3 l of toluene/methylene chloride/tetrahydrofuran (2:1:1). After rotatory evaporation of methylene chloride, THF and 500 ml toluene zinc meso-tetra-(*p*-nitrophenyl)porphyrin (TN02PP) crystallized from residual toluene (3.1 g TN02PP, 17.8% yield).

1.5 g TN02PP was refluxed with 150 ml conc. chloric acid and 10 g tin powder for 2 h and further diluted with 150 ml water and filtered slowly. The reaction powder (green slurry) was dried with ether by rotatory evaporation to yield a green powder, which could be poured on top of the same above mentioned chromatography column dry packed with basic alumina. The column was washed with 2 l of methylene chloride/THF (2:1). The highly coloured fractions were combined and washed with 100 ml 0.001 M ammonia solution. The yield of meso-tetra-(*p*-aminophenyl) porphyrin (TNH2PP) was 1.05 g (91.5%).

0.225 g TNH2PP (about 0.33 mmol) was dissolved in 50 ml 20% HBF and cooled to 0°C. 5 ml solution of 0.19 g (2.7 mmol) sodium nitrite was added slowly to the solution of TNH2PP and the reaction mixture was stirred for 30 min and filtered. The dark green grains of protonated TDSPP were dissolved in DMF, cooled to -10°C and precipitated with ether. The yield of TDSPP was 0.308 g (85%).

MeODS was synthesized according to Swain and Rogers (1975) and purified by precipitation from an acetone solution with isopropyl ether prior to use.

Spectroscopically pure solvents were used for all measurements.

### 2.2 Methods

The absorption spectra were recorded on a Hewlett Packard 8452A Diode Array Spectrophotometer. Fluorescence spectra were measured on a Perkin-Elmer MPF44 spectrofluorometer. The fluorescence lifetime of TDSPP was measured on a single photon counting apparatus. The light of an He-Ne laser (632.8 nm, 5.8 mW during the first 60 min) and the 546 nm lines of a high pressure Hg-lamp (50 W) were used for irradiation in the *Q*-band region of the investigated systems. The line 313 nm of the mercury lamp was used for irradiation at the absorption range of diazonium salt moieties. The probes for quantum yield determinations were bubbled with dry, oxygen-free nitrogen for 30 min.

<sup>†</sup> For preparation of TDSPP see also Semiejkin *et al* (1981).

### 3. Results

The IR spectrum of TDSPP compared with the spectrum of MeODS (figure 2) shows that in this case the diazonium salt linked with meso-position of porphyrin ring is free of quinoidization effect, see also table 1.

On irradiation in the *Q*-band region of TDSPP with light of an He-Ne laser or a mercury lamp (546 nm) a variation of the absorption spectrum of TDSPP in the range 300–700 nm is not observed. Also during selective irradiation in the absorption region of diazonium salt moieties (313 nm) no changes in absorption spectrum of TDSPP are observed. An observable variation in spectrum of TDSPP is obtained under nitrogen during simultaneous photolysis with 313 and 632.8 nm (figure 3). It is to be noted that the changes of absorption spectra exhibit no isobestic points. The quantum yield of this change related to He-Ne laser exposition is different for the Soret band (0.12) and the *Q*-band region ( $\sim 0.18$ ). It should be noted that these data are not very precise since the respective absorbance changes fluctuate very strongly. In the presence of oxygen (air saturated probes) no absorption changes in TDSPP spectra during simultaneous irradiation are indicated. Such behaviour is typical of ET reactions undergone by the triplet state of porphyrins, which are quenched very quickly by oxygen ( $k_q^t \sim 4 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$  Pileni *et al* 1980).

For examination of the ability of porphyrin ring in TDSPP to undergo photoinduced ET to diazonium salts we have photolysed the external diazonium salt (MeODS) on irradiation of TDSPP/MeODS system using He-Ne laser light (figure 4). Probably the reaction product is the cation radical of TDSPP and products of external diazonium salt decomposition (Becker *et al* 1985). The 0.21 value of the quantum

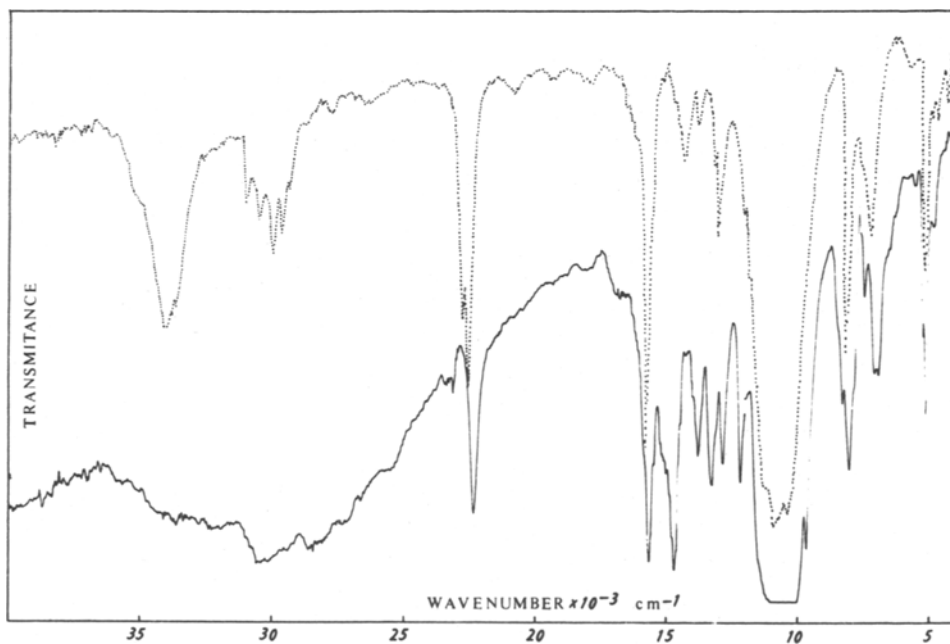


Figure 2. Infrared spectra of TDSPP (solid line) and MeODS (point line) in KBr matrix.

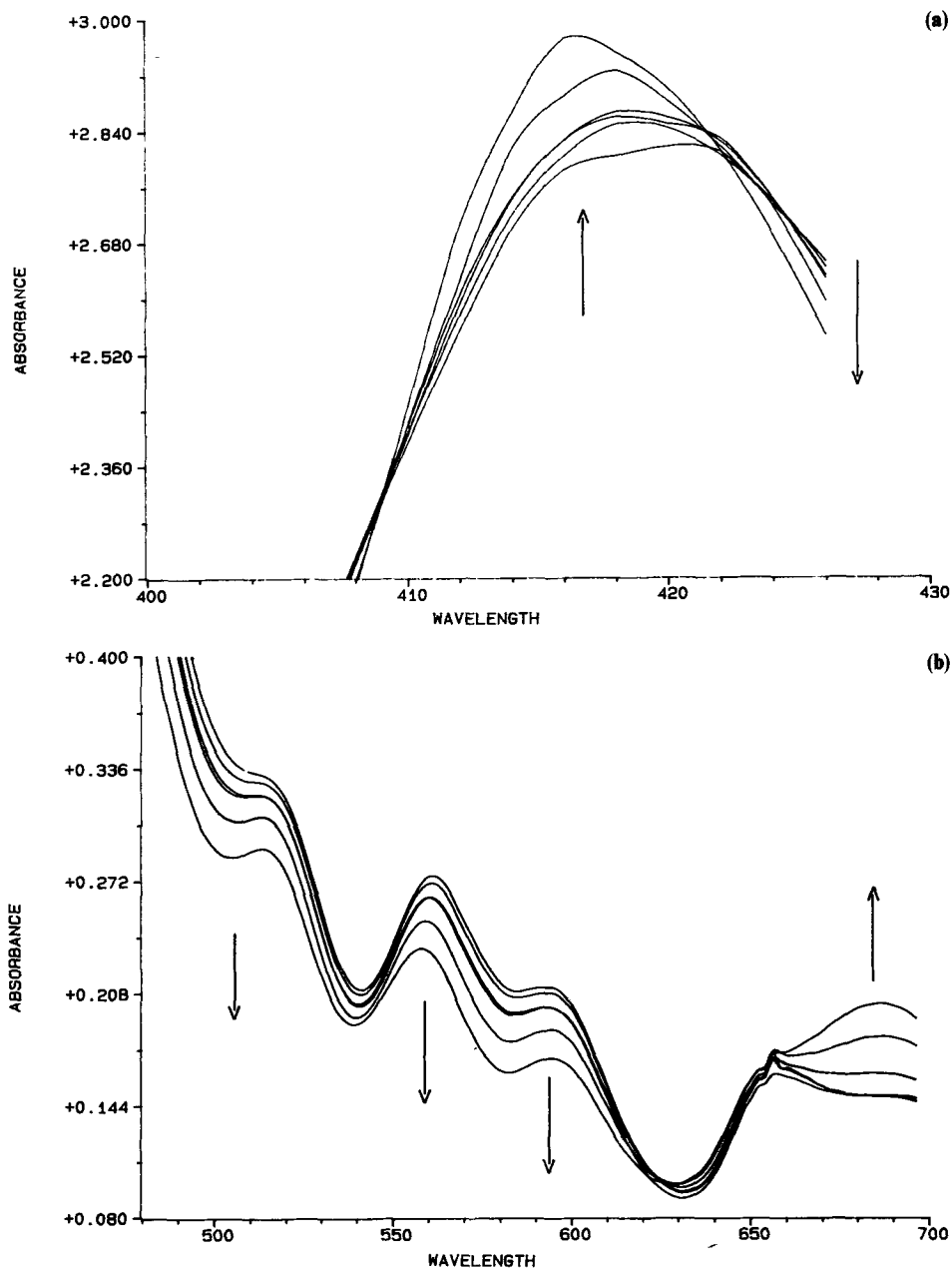
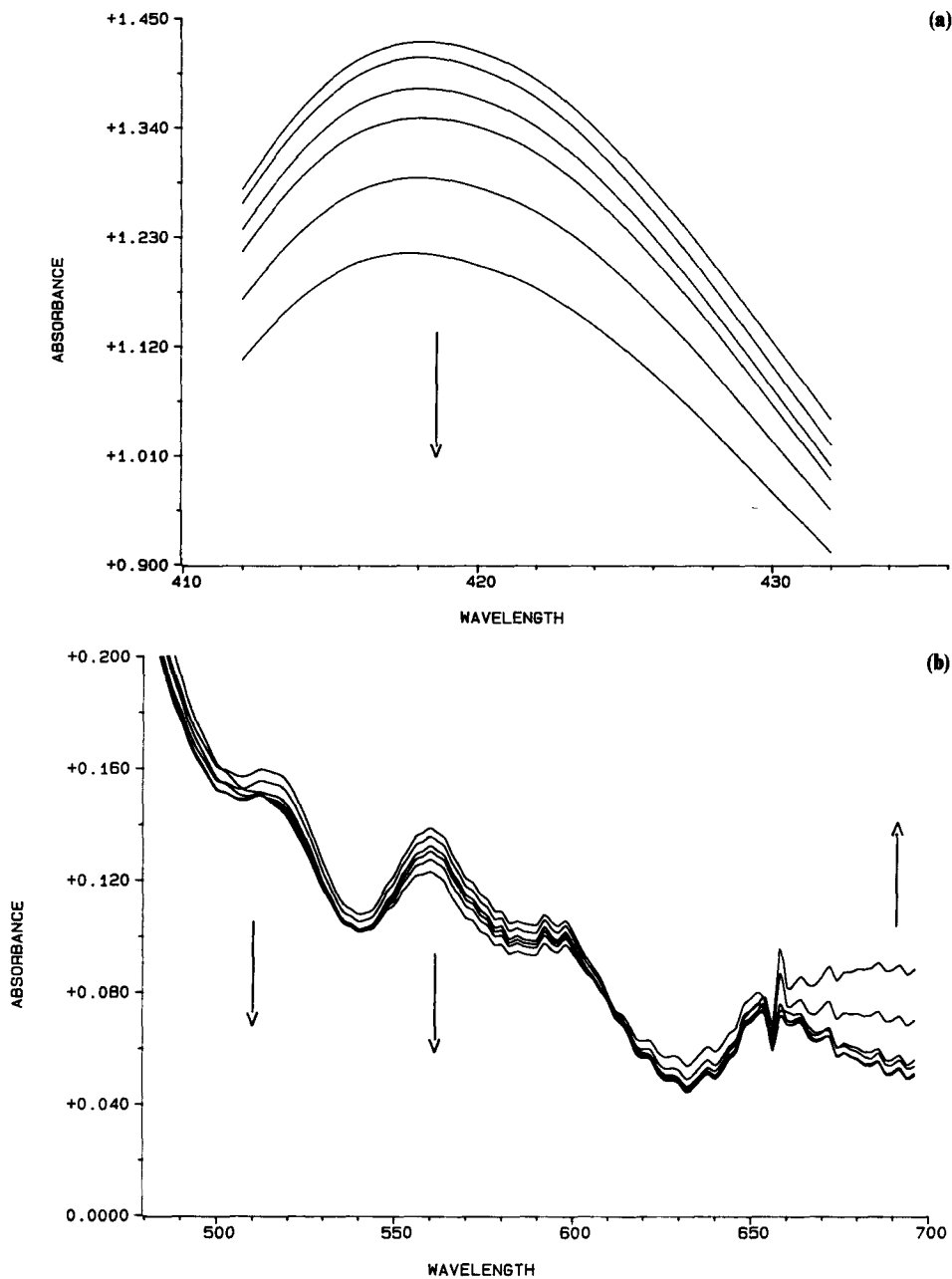


Figure 3. Simultaneous irradiation of TDSPP.  $[\text{TDSPP}] = 5.0 \times 10^{-5} \text{ M}$ , acetonitrile,  $T = 293 \text{ K}$ . (a) Soret band region and (b) Q-band region.

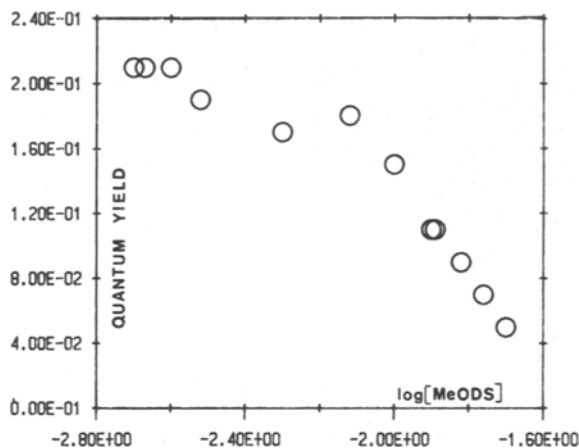
yield of this process is related to the changes of TDSPP absorbance\*. Under aerobic conditions the same value of quantum yield was determined. A similar effect has been found in Becker *et al* (1989). The quantum yield of intermolecular sensitized photolysis

\* Actually, the quantum yield of oxidative bleaching of TDSPP was measured. In Becker *et al* (1985), the existence of a 1:1 relationship between dediazotization and bleaching of porphyrin was proved.

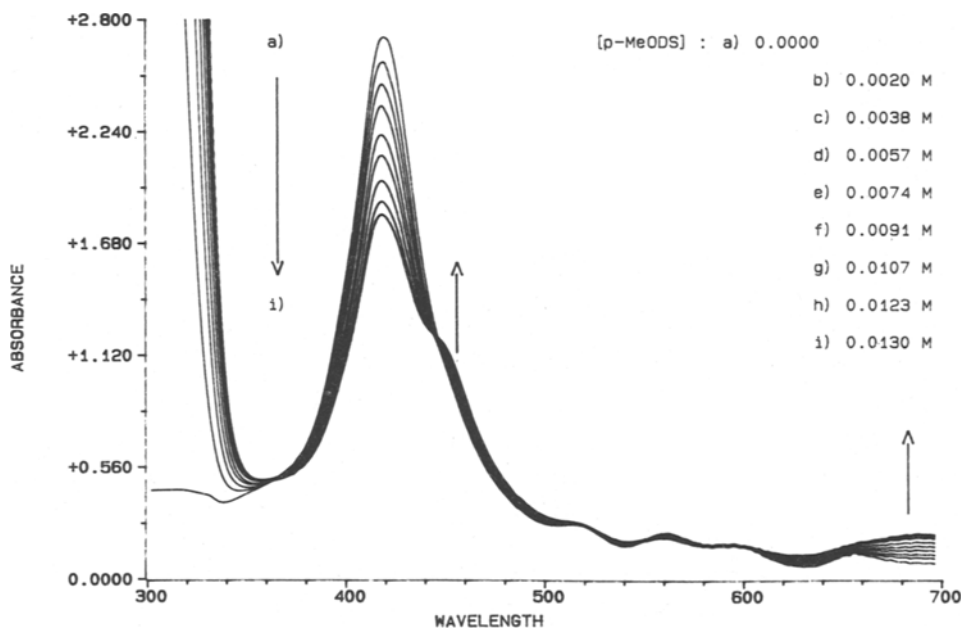


**Figure 4.** Inter-molecular sensitized photolysis of MeODS  $[\text{TDSPP}] = 2.5 \times 10^{-5} \text{ M}$ ,  $[\text{MeODS}] = 2.0 \times 10^{-3} \text{ M}$ , acetonitrile. (a) Soret band region and (b) Q-band region.

of MeODS depends on diazonium salt concentration (figure 5). This behaviour reflects the fact that at low concentrations of diazonium salts only a triplet electron transfer is possible, whereas at higher concentrations, above 0.001 M, the reaction of excited singlet state of porphyrin is dominant. This reaction proceeds with lower efficiency because of the back-electron transfer (Becker *et al* 1985). Our investigations have



**Figure 5.** Dependence of quantum yields of photo-bleaching of TDSPP on the concentration of MeODS. Irradiation at 632.8 nm, [TDSPP] =  $2.5 \times 10^{-5}$  M, acetonitrile.



**Figure 6.** The UV/VIS absorption spectra of [TDSPP] =  $2.5 \times 10^{-5}$  M (a) and on increasing addition of MeODS in acetonitrile.

shown an additional source of this dependence. Addition of MeODS causes a decrease in intensity of the Soret band. An increase in the Q-band region above 600 nm and isosbestic points at 363, 452, 547, 590 nm are observed (figure 6). The relative increase of the absorbance at 700 nm with the increasing concentration of MeODS was analyzed using the Benesi–Hildebrand equation (1), Benesi and Hildebrand (1949) (figure 7):

$$[\text{TDSPP}]_0 \times d/\Delta E^{700} = (K_{\text{eq}} \epsilon_{\text{comp}}^{700})^{-1} [\text{MeODS}]^{-1} + 1/\epsilon_{\text{comp}}^{700} \quad (1)$$

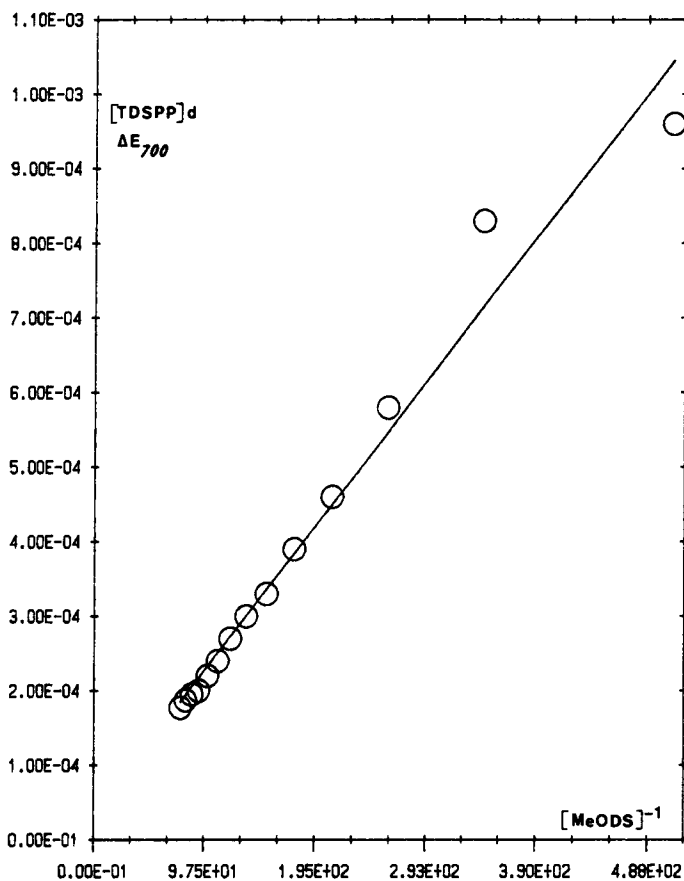


Figure 7. Benesi-Hildebrand plot of TDSPP interaction with MeODS in acetonitrile.

The equilibrium constant  $K_{\text{eq}} = 16.6 \text{ M}^{-1}$  and the absorption coefficient  $\epsilon_{\text{comp}}^{700} = 30300 \text{ M}^{-1} \text{ cm}^{-1}$  were determined. The ground state product shows no photochemical activity. The influence of the ground state interactions can be observed by TDSPP fluorescence quenching by MeODS (figure 8). The linear plot of data presented in figure 8, plotted according to (2) (see the inset in figure 8) is satisfied and two values of  $K_{\text{eq}}^{\text{fl}}$  and  $K_{\text{sv}}$  (Stern-Volmer constant) were obtained (table 2),

$$(I_0/I)/[\text{MeODS}] = k_q^s \tau_0^s + K_{\text{eq}}^{\text{fl}} + k_{\text{eq}}^s \tau_0^s K_{\text{eq}}^{\text{fl}} [Q]. \quad (2)$$

Analysis of fluorescence excitation spectra of systems TDSPP and TDSPP/MeODS (figure 9) show that the static part of fluorescence quenching is connected with the ground state interaction between TDSPP and MeODS ( $K_{\text{eq}} = 16.6 \text{ M}^{-1}$ ; compare the spectrum "r" figure 6 and the excitation spectrum of TDSPP/MeODS, figure 9). In our opinion the correlation between  $K = 16.6 \text{ M}^{-1}$  (for Benesi-Hildebrand equation) and  $K_{\text{eq}}^{\text{fl}} = 15.5 \text{ M}^{-1}$  [one of the solutions of (2)] is good. Therefore we use for estimation of the quenching rate constant of TDSPP by MeODS the value of  $K_{\text{sv}} = 77.9 \text{ M}^{-1}$ . Contrary to the data of Netzel *et al* (1982) for covalently linked quinone-porphyrins we were able to observe the fluorescence decay in the nanosecond



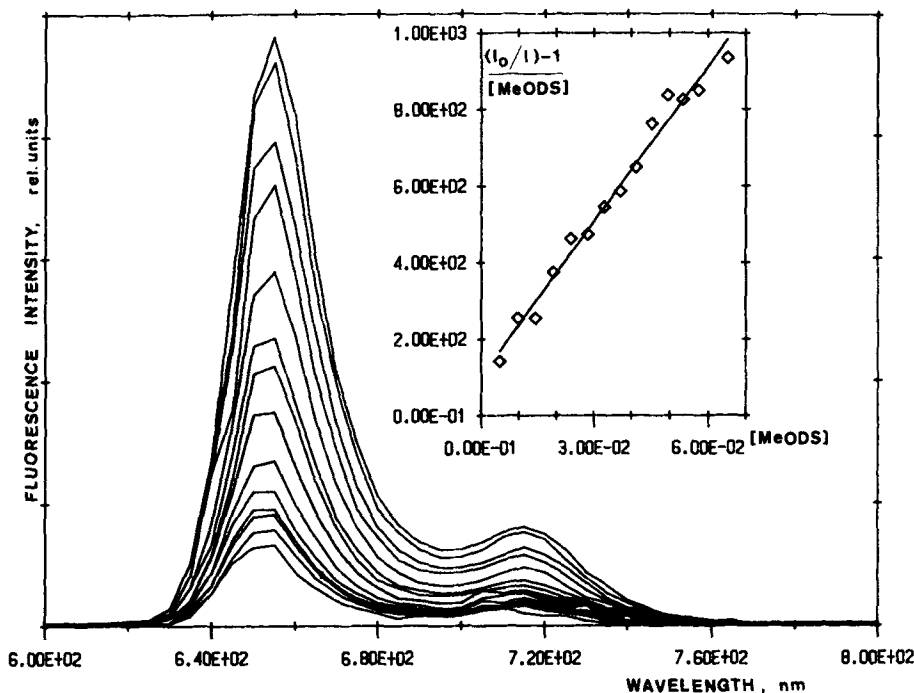


Figure 8. The quenching of TDSPP fluorescence by MeODS in acetoneitrile. In inset the plot according to (2).

Table 2. Values of solutions of (2).

	(1)	(2)
$K_{sv} [M^{-1}]$	77.9	2.96
$K_{eq}^I [M^{-1}]$	15.5	408.25

range (figure 10). The fluorescence decays monoexponentially according to the first-order process. The fluorescence lifetime is 8.0 ns.

With this value the  $k_q^s$  constant of  $^1\text{TDSPP}^*$  quenching by MeODS equals  $9.7 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ .

#### 4. Conclusions

- (1) The meso-tetra-(*p*-diazoniumphenyl tetrafluoroborate) porphyrin can be photo-lysed only under anaerobic conditions on simultaneous irradiation in regions of absorption of the porphyrin ring and diazonium salt moieties.
- (2) Excited TDSPP transfers electrons to an external diazonium salt (MeODS).
- (3) TDSPP interacts with MeODS in the ground state with an equilibrium constant  $\sim 16 \text{ M}^{-1}$ .
- (4) The excited singlet state of TDSPP is quenched by MeODS with a rate constant of  $9.7 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ .

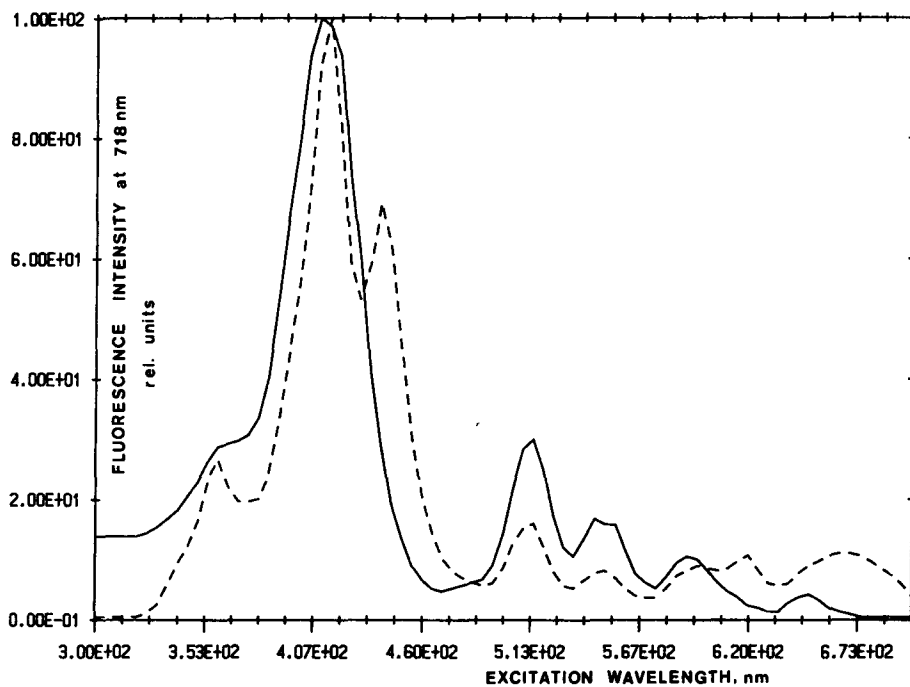


Figure 9. Fluorescence excitation spectra of TDSPP (solid line) and TDSPP/MeODS (dashed line) in acetonitrile,  $[TDSPP] = 10^{-5} M$ ,  $[MeODS] = 0.063 M$ , measured at 718 nm.

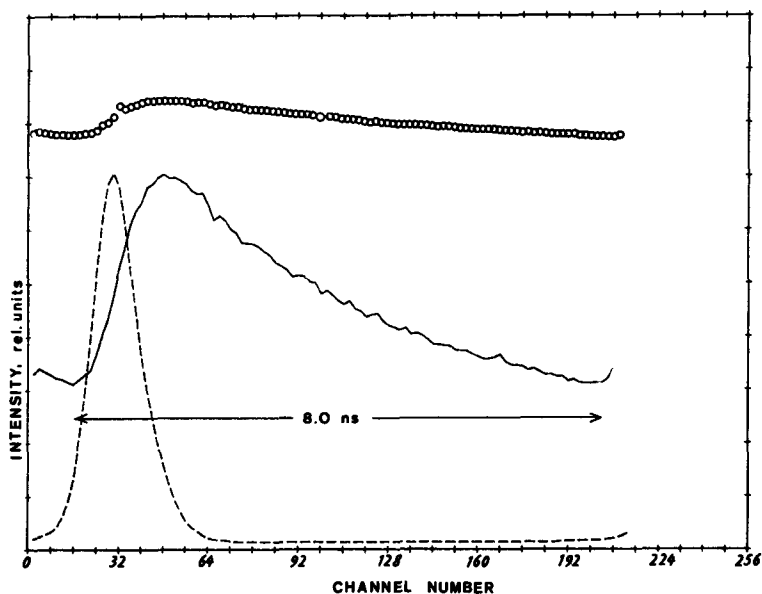


Figure 10. Fluorescence decay of TDSPP in acetonitrile (solid line). Ar-laser excitation impulse (dashed line) and the plot  $\ln(I_0/I_1)$  vs  $t$  (circles).

(5) The static quenching of TDSPP fluorescence by MeODS,  $K_{eq}^{fl} = 15.5 M^{-1}$  is equal to the equilibrium constant of ground state interactions (determined according to the Benesi-Hildebrand equation).

### Acknowledgement

The Hewlett Packard 8452 A Diode Array Spectrophotometer is a generous gift from Hewlett Packard to our Institute. JZ is thankful to Dr Klaus Urban from Technische Hochschule, Merseburg (GDR), for his help in determination of the lifetime of <sup>1</sup>TDSPP\*.

The materials for synthesis of all compounds used in our work were provided by the Photochemical Works BZF, Foton, Bydgoszcz, Poland.

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