

Singlet molecular oxygen quantum yield measurements of some porphyrins and metalloporphyrins

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Abstract. Hematoporphyrin IX dimethyl ester (HPDME), tetraphenylporphyrin (TPP), tetra(4-methoxyphenyl)porphyrin (TMPP), tetra(3,4-dimethoxyphenyl)porphyrin (TDMPP), tetra(3,4,5-trimethoxyphenyl)porphyrin (TTMPP), tetraanthrylporphyrin (TAP) and tetraacridylporphyrin (TACP), and their Zn²⁺, SnX₂²⁺, Pd²⁺ and Pt²⁺ complexes have been prepared and characterized. The singlet molecular oxygen quantum yield (ϕ_{Δ}) values of the above porphyrins and their metal derivatives in N,N-dimethyl formamide (DMF) have been measured in the presence of 1,3-diphenylisobenzofuran (DPBF) as ¹O₂ acceptor using steady state technique after correcting for the intensity of light absorbed by the photosensitizers. The ϕ_{Δ} values for the free base porphyrins are usually around 0.60. Hematoporphyrin IX dimethyl ester and its metal derivatives follow the order: HPDME (ϕ_{Δ} = 0.60) > Zn HPDME (0.40) > PdHPDME (0.34) > Sn(OH)₂HPDME (0.28) \geq PtHPDME (0.24). Zinc(II) complexes of tetraarylporphyrins show about 65% efficiency in ϕ_{Δ} values are compared to the ϕ_{Δ} values of their corresponding free base porphyrins. These results can be explained on the basis of catalyzed intersystem crossing to the ground state. The ϕ_{Δ} values of the above free base porphyrins and their metal complexes in DMF in presence of DPBF using single-pulsed laser excitation technique follow similar trends.

Keywords. Porphyrin; metal porphyrin; photosensitizer; singlet molecular oxygen; photooxidation; quantum yield.

1. Introduction

Porphyrins and metalloporphyrins act as photosensitizers in various processes such as natural and artificial photosynthesis (Fong 1982; Norris and Meiser 1989), detection of human cancer and its treatment in presence of molecular oxygen and light-photodynamic therapy (Van de Bergh 1986; Dougherty 1987). They are also useful as photosensitizers in selective photooxidation in fine chemical industry (Cotton and Wilkinson 1988). In this article we will discuss the quantum yields of singlet molecular oxygen (O₂) production, photosensitized by some porphyrins and metalloporphyrins.

2. Experimental

Tetraarylporphyrins were prepared by refluxing pyrrole with an appropriate benzaldehyde derivative in propionic acid for half an hour (Adler *et al* 1967). They

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were purified on a silica gel column using a 1:1 mixture of benzene and petroleum ether or chloroform as an eluant. Hematoporphyrin IX was purchased from Sigma, USA, and it was esterified by diazomethane method (Fuhrhop and Smith 1975). This compound was purified on an alumina (grade III) column using 0.15% ethanol in chloroform as an eluant.

Zinc, tin, palladium and platinum hematoporphyrin dimethyl ester were prepared by refluxing an appropriate metal salt with hematoporphyrin IX dimethyl ester (HPDME) in *N,N*-dimethylformamide or glacial acetic acid in presence of sodium acetate (Buchler 1975). These complexes were purified on an alumina (grade III) column using chloroform as eluant. SnTPP(X_2) (where TPP is free base tetraphenylporphyrin and X is OH, Cl, Br, I, N_3 , NCS or OC_6H_5) were prepared by refluxing $SnCl_2 \cdot 2H_2O$ and TPP in glacial acetic acid in presence of sodium acetate and of excess of HO^- , Cl^- , Br^- , I^- , N_3^- , NCS^- or $OC_6H_5^-$ for 6 h (Gouterman *et al* 1973).

The absorption and emission spectra of the above compounds were measured on a Shimadzu UV-265 recording spectrophotometer and Spex spectrofluorimeter, respectively. The triplet state lifetime and decay kinetics were performed by exciting the sample at 532 nm using 15–30 ns pulsed laser of Nd:YAG laser and using probe light from 200 W xenon arc lamp. The experimental details of this technique are given elsewhere (Periasamy 1984; Srivatsavoy 1990). The quantum yield measurements for photooxidation of 1,3-diphenylisobenzofuran (DPBF) using free base porphyrins and their metal derivatives were carried out using steady state and single-pulsed laser techniques (Bellus 1978; Foote 1979; Periasamy 1984; Srivatsavoy and Periasamy 1991). In the steady state method, DMF solutions of photosensitizer (1 or 2×10^{-6} M) and DPBF (0.5 or 1×10^{-4} M), in 10 mm path-length quartz cuvettes in presence of molecular oxygen, were irradiated between 500 and 550 nm by a 150 W xenon lamp using a monochromator with 10 or 15 nm band-pass (Applied Photophysics) at different irradiation times. The depletion of DPBF was monitored at 410 or 415 nm using difference absorption spectroscopy. Absorption intensity was measured by a chemical actinometer of Reinecke's salt (Wegner and Adamson 1966). In the single-pulsed laser method, DMF solutions of photosensitizer ($2 \mu M$) and DPBF (2 to 5×10^{-4} M), in 2 mm path-length quartz cuvettes, were irradiated at 532 nm by a pulsed laser of 15–30 ns from a Nd:YAG laser (Moleatron MY 35), in the presence of continuously bubbled molecular oxygen. The depletion of DPBF was monitored at 420 or 425 nm by a probe light from a 200 W xenon arc lamp as described elsewhere (Periasamy 1984; Srivatsavoy 1990). The transmitted probe light after passing through a monochromator, was detected by a photomultiplier tube (IP 28). The output was captured by a transient digitizer (Biomation 8100). The results were displayed on an oscilloscope and then plotted on an *X-Y* recorder. The total depletion of DPBF was monitored as its absorbance change at infinite time ($> 350 \mu s$) after exciting the sample by a single pulsed laser beam.

3. Results and discussion

3.1 Syntheses, characterization and structures of porphyrins and metalloporphyrins

Zinc, tin, palladium and platinum complexes of hematoporphyrin IX dimethyl ester and free base hematoporphyrin IX dimethyl ester were prepared and characterized by electronic absorption and emission spectroscopy (Gouterman 1978). In addition,

infrared spectroscopy was used to characterize ester groups. Six tetraarylporphyrins such as tetraphenylporphyrin (TPP), tetra(4-methoxyphenyl)porphyrin (TMPP), tetra(3,4-dimethoxyphenyl)porphyrin (TDMPP), tetra(3,4,5-trimethoxyphenyl)porphyrin (TTMPP), tetraanthrylporphyrin (TAP) and tetraacridylporphyrin (TACP) and their zinc complexes were prepared and characterized by electronic absorption and emission spectroscopy. In addition, SnTPP(X₂) (where X = OH, Cl, Br, I, N₃, NCS or OC₆H₅) was prepared and characterized (Gouterman 1978). The structures of HPDME and its metal complexes are given in figure 1 and the electronic spectrum of HPDME in DMF is shown in figure 2. The structures of tetraarylporphyrins and their zinc and tin complexes are given in figure 3.

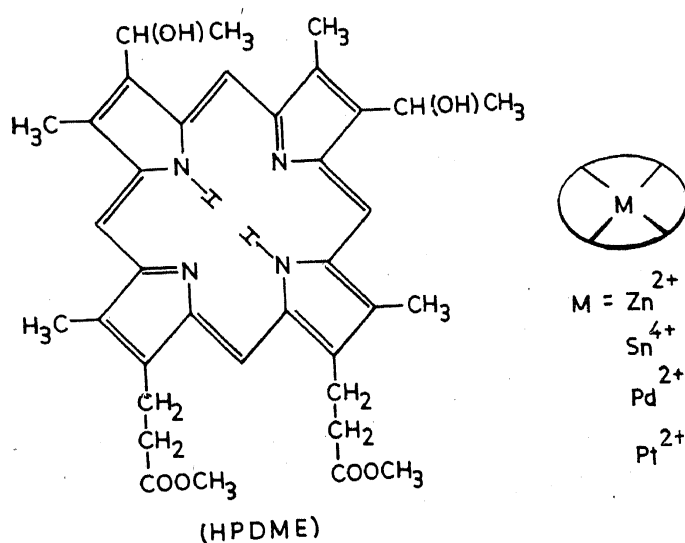


Figure 1. Structure of HPDME and its metal complexes.

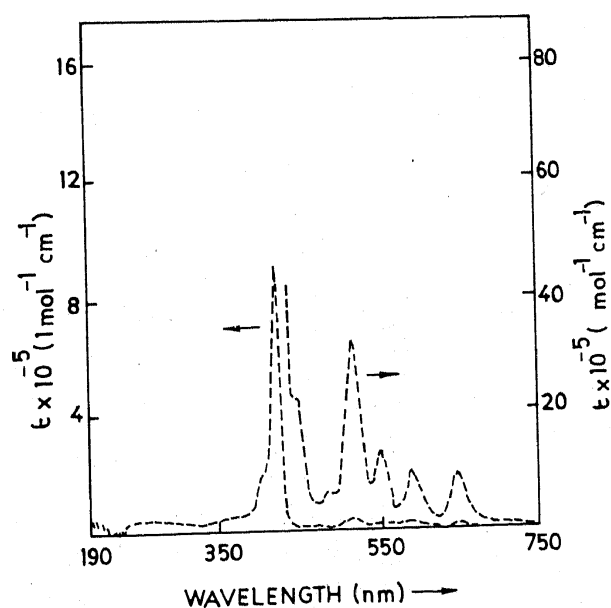


Figure 2. Electronic absorption spectrum of HPDME in DMF.

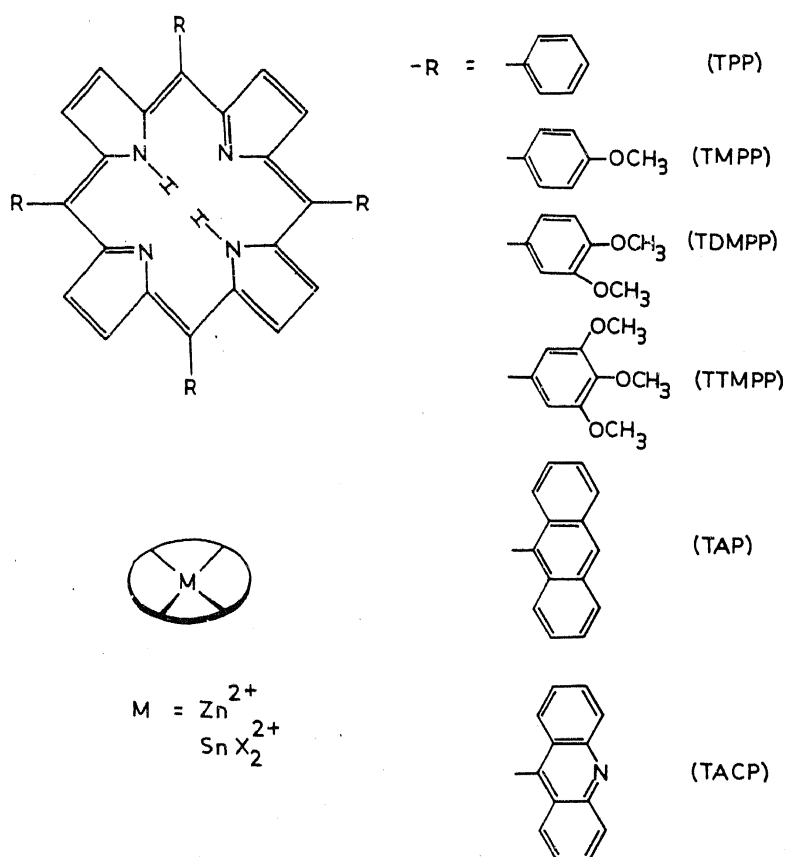


Figure 3. Structures of tetraarylporphyrins and their zinc and tin complexes.

3.2 Photochemical generation of singlet molecular oxygen by irradiation in presence of photosensitizer and molecular oxygen

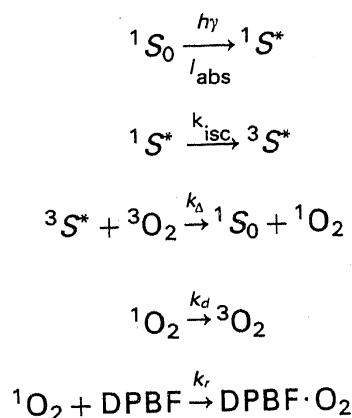
The lowest energy electronic configuration of $^1\text{O}_2$ contains two electrons in π^* orbitals. This gives rise to three states $^3\Sigma_g^-$ (ground state, 0 kJ/mol energy), $^1\Delta_g$ (first excited state, 92 kJ/mol), and $^1\Sigma_g^+$ (second excited state, 155 kJ/mol). The $^1\Delta_g$ state (singlet molecular oxygen, $^1\text{O}_2$) has a much longer lifetime than the $^1\Sigma_g^+$ state. The most important methods of generation of singlet molecular oxygen are: (1) the chemical method, and (2) the photochemical method on irradiation of photosensitizer in presence of molecular oxygen. We discuss here $^1\text{O}_2$ generation photosensitized by some porphyrins and metalloporphyrins.

3.3 Photooxidation of 1,3-diphenylisobenzofuran (DPBF) photosensitized by porphyrins and metalloporphyrins by steady state excitation and $^1\text{O}_2$ quantum yield measurements

A mixture of free base porphyrin/metalloporphyrin ($1-2 \times 10^{-6}$ M) and BPBF ($5-10 \times 10^{-5}$ M) in molecular oxygen saturated DMF solution was irradiated with light of 550 nm (band-pass: 10 nm) for different periods of time. The depletion of DPBF was monitored using a spectrophotometer at 410/415 nm. The depletion of DPBF [$-\ln(A_t/A_0)$] was plotted against different irradiation times in the presence of HPDME as photosensitizer. The slope of this first-order plot seems to represent the rate of $^1\text{O}_2$ production. Similar plots were obtained for other free base porphyrins and metalloporphyrins.

The mechanism of the above photooxidation of DPBF photosensitized by por-

phyrin/metalloporphyrin based on singlet molecular oxygen as an intermediate is given in scheme 1.



Scheme 1.

where I_{abs} is the intensity of light absorption, k_{isc} , k_{Δ} , k_d and k_r the rate constants for intersystem crossing, energy transfer, quenching of 1O_2 by DMF molecules and photooxidation of DPBF to $\text{DPBF}\cdot\text{O}_2$ by 1O_2 , and S_0 , ${}^1S^*$ and ${}^3S^*$ are ground singlet, first excited singlet and first excited triplet states of the photosensitizer.

Using steady state approximation and $k_d \gg (k_r + k_q) \times [\text{DPBF}]$, the following equation can be written

$$-\frac{d[\text{DPBF}]}{Dt} = \frac{I_{\text{abs}} \phi_{\Delta} k_r [\text{DPBF}]}{k_d + k_r [\text{DPBF}]} \quad (1)$$

On integration of (1), after assuming $k_d \gg k_r [\text{DPBF}]$ at low concentrations of DPBF,

$$-\ln \frac{[\text{DPBF}]_t}{[\text{DPBF}]_0} = \frac{I_{\text{abs}} \phi_{\Delta} k_r t}{k_d} \quad (2)$$

If $-\ln[\text{DPBF}]_t/[\text{DPBF}]_0$ is plotted versus t , a straight line is obtained as shown in figure 4 (as a representative example) with slope $I_{\text{abs}} \phi_{\Delta} k_r/k_d$. ϕ_{Δ} can be obtained from this slope if the values of I_{abs} , k_d and k_r are known. The value of I_{abs} was obtained by chemical actinometer of Reinecke's salt (Wegner and Adamson 1966). The value of k_d in DMF was used as reported in the literature (Bellus 1978). However, the value of k_r can be calculated from the following relationship.

From (1) we can obtain on integration the relationship given below.

$$\begin{aligned}
 \frac{[{}^1O_2]}{[\text{DPBF}_{\text{ox}}]} &= -k_d \ln \left[1 - \frac{[\text{DPBF}_{\text{ox}}]_t}{[\text{DPBF}]_0} \right] + k_r [\text{DPBF}_{\text{ox}}] = I_{\text{abs}} \phi_{\Delta} k_r t, \\
 \frac{1}{[\text{DPBF}_{\text{ox}}]} &= \frac{1}{\alpha} \left\{ \frac{k_d}{k_r [\text{DPBF}]} + 1 \right\}, \quad \text{if } \frac{[\text{DPBF}_{\text{ox}}]_t}{[\text{DPBF}]_0} \ll 1
 \end{aligned} \quad (3)$$

where $[\text{DPBF}_{\text{ox}}]$ is the concentration of oxidized DPBF after a given irradiation time and $\alpha = I_{\text{abs}} \phi_{\Delta} t$. If we plot $[\text{DPBF}_{\text{ox}}]^{-1}$ against $[\text{DPBF}]^{-1}$, we get a straight line with a slope of $k_d/k_r [{}^1O_2]$, and an intercept of $[{}^1O_2]^{-1}$. From the ratio of slope and intercept, k_r is calculated as $1.1 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ taking k_d is equal to $1.0 \times 10^5 \text{ s}^{-1}$ from the literature (Bellus 1978). Thus using the k_r value of $1.1 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$, ϕ_{Δ}

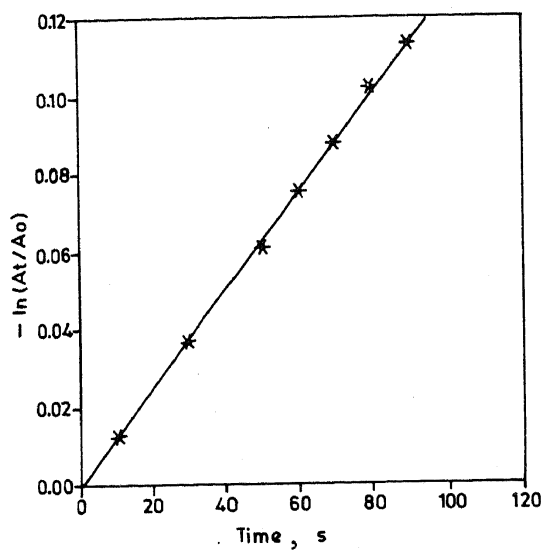


Figure 4. First order $-\ln(A_t/A_0)$ plot of depletion of DPBF ($50 \mu\text{M}$) in DMF as a function of irradiation time in seconds in presence of TTMPP ($2 \mu\text{M}$) and molecular oxygen.

values of free base porphyrins and metalloporphyrins can be calculated. These values vary from 0.11 to 0.67. The order of ϕ_Δ for free base porphyrins relative to HPDME is $\text{TAP} \approx \text{TACP} > \text{THPP} > \text{HPDME} > \text{TPP} \approx \text{TDMPP} > \text{TMPP} > \text{TDMPP} \approx \text{TDHPP}$ [where THPP is tetra(4-hydroxyphenyl)porphyrin and TDHPP is tetra(3,4-dihydroxyphenyl) porphyrin]. The order of ϕ_Δ values for metallohematoporphyrin IX dimethyl ester is $\text{HPDME} > \text{ZnHPDME} > \text{PdHPDME} > \text{SnHPDME} \cdot (\text{Cl}_2) > \text{PtHPDME}$. The order of ϕ_Δ values for zinc tetraarylporphyrins is $\text{ZnTTMPP} \approx \text{ZnTACP} > \text{ZnTPP} \approx \text{ZnTDMPP}$, and that of ϕ_Δ values for $\text{SnTPP}(\text{X}_2)$ is $\text{SnTPP}(\text{Cl}_2) > \text{SnTPP}(\text{OH})_2 > \text{SnTPP}(\text{NCS})_2 \approx \text{SnTPP}(\text{N}_3)_2$. The ϕ_Δ values of HPDME at various concentrations ($1 \mu\text{M}$ to $120 \mu\text{M}$) are nearly constant.

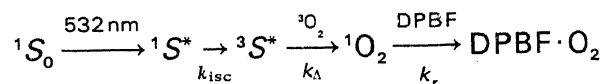
The quenching of the photooxidation of DPBF photosensitized by TTMPP in the presence of different concentrations of *bis*(dibutyl-dithiacarbamato)nickel(II) as a physical quencher was also studied and the quenching rate constant, k_Q , obtained. The value of k_Q obtained is $2.0 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$. The reported value of k_Q in toluene is $4.3 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$.

The triplet state lifetime and decay kinetics were performed at 532 nm using 15–30 ns pulsed Nd:YAG laser. The deaerated solution of the photosensitizer in benzene ($\sim 1 \times 10^{-5} \text{ M}$) on irradiation shows decreasing single-exponential decay back to the ground state. The decay rate constant obtained is $8.2 \times 10^3 \text{ s}^{-1}$. The triplet state of TTMPP is efficiently quenched by dissolved molecular oxygen and this quenching rate constant, k_q , of TTMPP is $1.3 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ which is around the diffusion rate constant (Bellus 1978). This suggests that the triplet state of the photosensitizer is completely quenched by molecular oxygen.

3.4 Photooxidation of 1,3-diphenylisobenzofuran photosensitized by porphyrins and metalloporphyrins by single-pulsed laser excitation and $^1\text{O}_2$ quantum yield measurements

A mixture of porphyrin/metalloporphyrin ($1\text{--}2 \mu\text{M}$) and DPBF ($0.5\text{--}1 \times 10^{-4} \text{ M}$) in molecular oxygen saturated DMF solution was excited at 532 nm by a single-pulsed

laser. A representative example of decay of DPBF in presence of HPDME as a photosensitizer, versus function of time after laser excitation is given in figure 5. The depletion of DPBF monitored at 420/425 nm as a decrease in absorbance ($-\Delta A$) of DPBF is due to its oxidation with 1O_2 . The mechanism of 1O_2 generation and its subsequent reaction can be represented in scheme 2.



Scheme 2.

In this reaction, 1O_2 behaves as an intermediate and the depletion of DPBF can be expressed as

$$-\Delta[\text{DPBF}] = \frac{k_r k_\Delta [\text{O}_2] [^3S]_{t=0} [\text{DPBF}]_0}{k_r [\text{DPBF}]_0 - k_\Delta [\text{O}_2]} \times \left\{ \frac{1}{k_\Delta [\text{O}_2]} (1 - \exp\{-k_\Delta [\text{O}_2] t\}) - \frac{1}{k_r [\text{DPBF}]_0} \times (1 - \exp\{-k_r [\text{DPBF}]_0 t\}) \right\} \quad (4)$$

where k_r is the rate constant of chemical reaction of 1O_2 with DPBF, k_Δ is the rate constant of decay of the triplet state of the photosensitizer in the presence of molecular oxygen, $[^3S]_{t=0}$ is the concentration of triplet state of the photosensitizer at zero time after laser excitation, and t is the time.

From (4), $-\Delta[\text{DPBF}] \propto [^3S]_{t=0}$ or $[^3S]_{t=0} = k_{isc}$. Thus the photosensitizer with higher quantum triplet state yield (ϕ_T) is expected to deplete more of DPBF for a

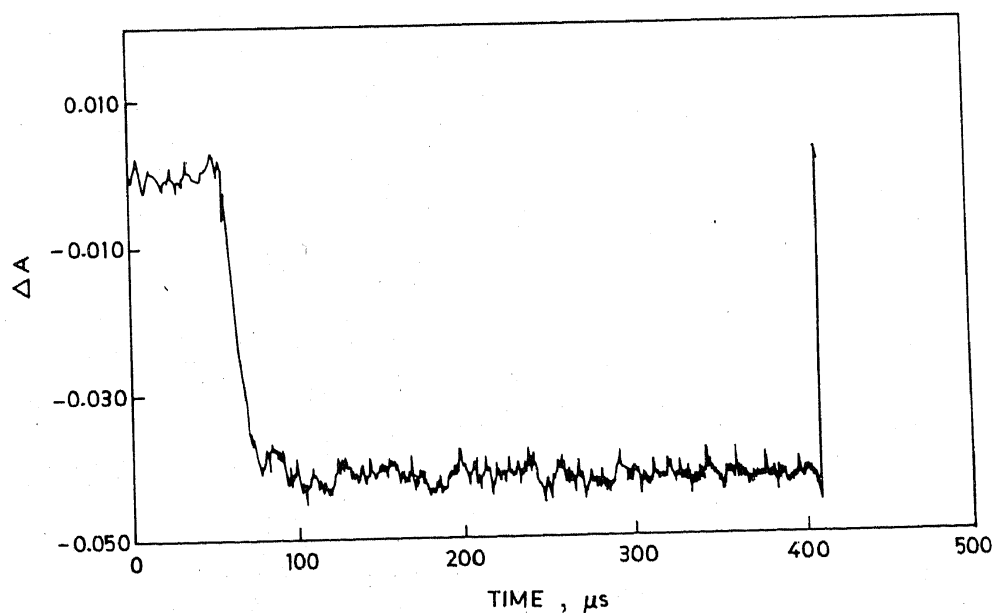


Figure 5. Decrease in absorbance of DPBF (500 μM) in DMF versus time in μs after 532 nm single pulsed laser excitation in presence of HPDME (2 μM) and molecular oxygen.

given single-pulsed laser energy (~ 1 mJ). If all the triplet molecules are quenched by O_2 to produce 1O_2 , $-\Delta[DPBF]_\infty$ will be proportional to ϕ_Δ and $\phi_\Delta \propto (-\Delta A)_\infty$ [where $(-\Delta A)_\infty$ is change in absorbance of DPBF on reacting with 1O_2 at infinite time]. If the depletion of DPBF by an unknown photosensitizer is compared with a photosensitizer of known ϕ_Δ^{ref} (HPDME: $\phi_\Delta^{\text{ref}} = 0.60$, Reddi *et al* 1983, the same value was also obtained by the steady state technique), the following relationship can be obtained as

$$\phi_\Delta^x / \phi_\Delta^{\text{ref}} \propto (-\Delta A)_\infty^x / (-\Delta A)_\infty^{\text{ref}}, \quad (5)$$

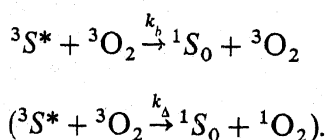
(where ϕ_Δ^x and ϕ_Δ^{ref} are quantum yields of unknown and reference photosensitizers respectively, and $(-\Delta A)_\infty^x$ and $(-\Delta A)_\infty^{\text{ref}}$ are the decreases in absorbance of DPBF at infinite time ($> 350 \mu\text{s}$) in the presence of unknown and reference photosensitizers respectively). In (4) the reference HPDME photosensitizer and the unknown porphyrin or metalloporphyrin photosensitizer have the same values of k_r , k_Δ , t , $[O_2]$ and $[DPBF]_0$, therefore,

$$\frac{\phi_\Delta^x}{\phi_\Delta^{\text{ref}}} = \frac{I_{532}^{\text{ref}}}{I_{532}^x} \times \frac{OD_{532}^{\text{ref}}}{OD_{532}^x} \times \frac{(-\Delta A)_\infty^x}{(-\Delta A)_\infty^{\text{ref}}}, \quad (6)$$

(where I_{532} and OD_{532} refer to intensity of 532 nm pulsed laser (~ 1 mJ) and optical density of the photosensitizer at 532 nm (~ 0.1) respectively for the reference and unknown photosensitizers. Knowing the values of the other parameters in (6), ϕ_Δ^x can be calculated.

The values of ϕ_Δ^x for free base porphyrins and metalloporphyrins can be calculated and they vary from 0.14 to 0.97. The values of ϕ_Δ for free base porphyrins relative to HPDME follow the order: TAP > TACP > TPP > HPDME > TTMPP > TMPP > TDMPP. The ϕ_Δ values of HPDME and its metal complexes follow the order: HPDME > ZnHPDME > PdHPDME \approx SnHPDME(Cl_2) > PtPDME. Zinc tetraarylporphyrin ϕ_Δ values follow the order: ZnTPP > ZnTAP > ZnTACP > ZnTTMPP, and the ϕ_Δ values of SnTPP(X_2) follow the order: SnTPP(OH) $_2$ > SnTPP(Cl_2) > SnTPP(N_3) $_2$ > SnTPP(NCS) $_2$. These orders, obtained from the single-pulsed laser excitation technique, are similar to those obtained from the steady state technique with few exceptions. These exceptions are not unexpected because the bases of both the methods are different.

Comparison of the above results obtained from the steady state and the single-pulsed laser techniques, suggests that the trend in ϕ_Δ values for free base porphyrins and metalloporphyrins are nearly the same, and the ϕ_Δ values for metalloporphyrins are usually lower than those of the corresponding free base porphyrins with the exception of SnTPP(OH) $_2$. These observations can be explained by adding one additional step (Schermann *et al* 1990) in the mechanism of photooxidation of 1,3-diphenylisobenzofuran photosensitized by porphyrins and metalloporphyrins (see scheme 1). This additional step, with the energy transfer step given in parentheses, is as below.



If S_{Δ} is the efficiency of $^1\text{O}_2$ formation accompanying the quenching of the first triplet state of photosensitizer by O_2 , and ϕ_T denotes the photosensitizer's quantum yield of the first excited singlet state to first excited triplet state intersystem crossing in the presence of O_2 , ϕ_{Δ} can be expressed as

$$\phi_{\Delta} = S_{\Delta} \cdot \phi_T, \quad \left(\text{where } S_{\Delta} = \frac{k_{\Delta}}{k_{\Delta} + k_b} \right). \quad (7)$$

On using (7) to explain the order as given above, the values of S_{Δ} should be smaller for metalloporphyrins than for the corresponding free base porphyrins. The reported value of ϕ_T for TPP in benzene is 0.88 (Merkel and Kearns 1972). There is a ten percent increase in ϕ_T value for ZnTPP than for TPP. If we assume the same values in DMF for TPP and ZnTPP, it is possible to calculate, from (7), the S_{Δ} value of 0.68 for TPP taking $\phi_{\Delta} = 0.56$ from the steady state technique, and similarly, the S_{Δ} value for ZnTPP, taking $\phi_{\Delta} = 0.53$. Thus, there is 23% decrease in S_{Δ} value for ZnTPP than in the S_{Δ} value of TPP. Verlhac *et al* (1984) have observed a lower ϕ_{Δ} value for tetra(N-methylpyridyl)porphyrinatopalladium(II) than for the corresponding free base porphyrin. However, they have observed a higher value for tetra(N-methylpyridyl)porphyrinatozinc(II) than for the corresponding free base.

4. Conclusions

Increase in the atomic weight of the metal in metalloporphyrins usually lowers the $^1\text{O}_2$ quantum yield due to the heavy atom effect. The $^1\text{O}_2$ quantum yield of SnTPP(X_2) depends on the nature of the axial ligands. The $^1\text{O}_2$ quantum yield photosensitized by methoxy derivatives in tetraphenylporphyrin depends on the number of methoxy groups present in the phenyl groups of TPP. However, the bulky substituents in the meso positions of the porphyrins such as TAP and TACP do not change the $^1\text{O}_2$ quantum yield.

Acknowledgement

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