Singlet oxygen generation by tetrabenzoporphyrins as photosensitizer

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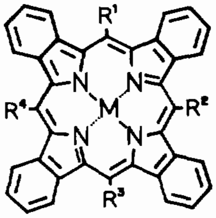
Abstract

The efficiency of the photosensitized generation of singlet oxygen ($^1O_2$) with *meso*-phenyl substituted tetrabenzoporphyrin metallo complexes as sensitizer was determined from the limiting quantum yield of the (+)-limonene photooxygenation and compared with that of hematoporphyrin (HP), which has been known to serve as an effective sensitizer, using a He–Ne laser light (633 mm). Among the diamagnetic (Mg, Zn, and Cd) complexes treated here, the Zn complexes were most efficient for the (+)-limonene photooxygenation with the limiting quantum yields of $\Phi(-A)=0.4$. This result was comparable to that of HP. The direct observation of the intensity of $^1O_2$ emission by the laser flash photolysis technique supported these results.

Introduction



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	R¹	R²	R³	R⁴	M
a	H	H	H	H	Zn
b	Ph	Ph	Ph	H	Zn
c	Ph	Ph	H	H	Zn
d	Ph	Ph	H	H	Mg
e	Ph	Ph	Ph	H	Cd

Structure of metallo–tetrabenzoporphyrin

Singlet oxygen ($^1O_2$) is receiving increasing attention as a reactive species in many chemical and biological aspects [1]. Among the many dye sensitizers, porphyrins [2] and phthalocyanines [3] have been widely studied as an effective photosensitizer for $^1O_2$ generation because of their advantageous photophysical properties such as high triplet quantum yields and long triplet lifetimes. On the other hand, tetrabenzoporphyrins (TBP), which are another type of porphyrin compound, being a structural analog of both porphyrin and phthalocyanine on the basis of the extended π-electron system by the benzo-substitution to the β,β′-pyrrole carbon atoms of porphyrin and the replacement of the aza-bridge (−N=) by the methine one (−CH=) on the phthalocyanine skeleton, have been attracting interest as a sensitizer from the standpoint of the excellent response for He–Ne laser emission (633 nm) [4]. However, there has been no useful information on $^1O_2$ generation with TBPs. This is probably due to the poor solubility of TBP in common organic solvents. As in the case of the tetraarylporphyrins, *meso*-aryl substitution is one of the successful possibilities to overcome this solubility problem and use this macrocyclic compound in practical applications [5], especially for photoimaging process based on photopolymerization, as a dye-sensitizer in combination with a radical generator [5a]. In this regard, we have recently reported and established the synthesis and structural elucidation of *meso*-phenyl substituted tetrabenzoporphyrin (PTBP) zinc complexes which have good solubility in common organic solvents [6].

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On the other hand, the unique photoimaging process, based on the ene-type reaction between $^1O_2$ and the alkyl-substituted olefin, has been proposed, where the hydroperoxide is consequently produced as the latent image and decomposed by the action of the redox catalyst to generate the free radical [7]. This prompts us to study the PTBP compounds from the standpoint of $^1O_2$ generation. In this paper, we describe the efficiency of $^1O_2$ generation with PTBP diamagnetic metallo complexes, **1b**–**1e**, in organic solutions, using two methods; one is the measurement of the limonene photooxygenation [8] and the other is the direct observation of the near infrared (NIR) emission intensity from $^1O_2$ [9]. These results are compared with that for hematoporphyrin (HP).

Experimental

Materials

Tetrabenzoporphyrin zinc complex (**1a**, ZnTBP) was prepared by the literature method [10]. Both *meso*-triphenyl- and *meso*-diphenyl-tetrabenzoporphyrin zinc complexes (**1c**: ZnP_3TBP, **1b**: ZnP_2TBP) were obtained by the previously reported reaction method and purification procedure, although they were contaminated with their benzyl adducts [6a]. The other metallo complexes, MgP_2TBP and CdP_2TBP, were prepared by the demetallation of ZnP_2TBP with trifluoroacetic acid in chloroform followed by metal ion insertion into the metal free compound, H_2P_2TBP, with magnesium perchlorate in pyridine and cadmium acetate in chloroform under reflux. In the case of the magnesium complex, the pyridine ligand on the TBP axial was removed by washing three times with 0.1 N HCl aq. solution.

H_2P_2TBP; λ_{max} (nm) in CH_2Cl_2 (log ϵ), Soret band: 421(5.09), 432(5.20); Q band: 610(4.46), 668(4.14). FD-MS, $m/z = 662$, 752, 842.

MgP_2TBP; λ_{max} (nm) in CH_2Cl_2 (log ϵ), Soret band: 414(4.66), 439(5.49); Q band: 590(4.16), 635(4.99). FD-MS, $m/z = 684$, 774, 864.

CdP_2TBP; λ_{max} (nm) in CH_2Cl_2 (log ϵ), Soret band: 413(4.71), 437(5.51); Q band: 584(4.17), 635(4.99). FD-MS, $m/z = 774$, 864, 954.

HP was purchased from Tokyo Kasei and used without purification. (+)-Limonene freshly distilled under reduced pressure, was used. The solvents used were of optical grade.

Physical measurements

Field desorption mass spectroscopy (FD-MS) was carried out with a Hitachi M-80 mass spectrometer. Ultraviolet and visible absorption spectra (UV–Vis) were obtained on a JASCO Ubest-30 spectrophotometer. Phosphorescence spectra were recorded in frozen MP glasses at 77 K on a JASCO 770FP spectrofluorometer equipped with a red-sensitive photomultiplier (Hamamatsu Photonics R928). Sample solutions were prepared after thorough purging with argon gas.

(+)-Limonene photooxygenation

(+)-Limonene photooxygenation was performed at room temperature in a quartz cell with a 10 mm optical path length using a He–Ne laser (NEC GLG-5040 with a 30 mW output power) as light source. Concentration of the TBPs was prepared to give an absorbance of *c.* 1.00 at the 633 nm light of the He–Ne laser. Limonene was used in the concentration range from 2×10^{-3} to 2×10^{-2} M. Solutions including the appropriate concentration of the TBPs and limonene were purged with O_2 gas under irradiation. Limiting quantum yields of limonene photooxygenation were determined by measuring the decrease in limonene with GC. The laser irradiation was stopped within the time when the decrease in limonene reached 5–10% versus the initial concentration. Double reciprocal plots of the concentration of limonene versus the quantum yield of limonene consumption gave a straight line where the limiting quantum yields could be calculated from the intercepts of the line by the least-squares method.

Results and discussion

Table 1 summarizes the absorption properties of these diamagnetic complexes of PTBPs such as zinc (**1b, c**), magnesium (**1d**) and cadmium (**1e**) in dichloromethane, in addition to those of ZnTBP in pyridine and HP in a mixture of pyridine and dioxane. These absorption data show that these metallo complexes effectively absorb red light at their characteristic Q-bands with a high extinction coefficient ($\epsilon > 50\,000$). It is especially noteworthy that the Q-bands are favorably located around the emission wavelength of the He–Ne laser (633 nm), suggesting that these complexes are convenient for the use in laser irradiation applications [5a]. Since the phosphorescence could be observed for all cases in argon gas purged MP glasses at 77 K, the triplet energy levels of these compounds are calculated from the peaks of the spectra. Table 1 also lists their emission maxima at 77 K and triplet energy levels. Consequently this allows us to expect them to serve as a photosensitizer for the generation of $^1O_2$ because their excitation energies in the triplet state are high enough to excite the ground state triplet oxygen.

To determine the efficiencies of generation of $^1O_2$ by PTBPs, two methods were used. One is the indirect

TABLE 1. Optical properties of metallo–tetrabenzoporphyrins and hematoporphyrin (HP)

Compound	Absorption data λ (nm)[c]						Emission data[d]	
	Soret band		Q band				λ (nm)	E_T (kcal mol^{-1})
ZnTBP[a] (**1a**)	408 (4.77)	432 (5.70)	582 (4.23)	628 (5.21)				36.0
ZnP_2TBP (**1b**)	408 (4.49)	432 (5.49)	584 (4.10)	633 (4.86)			811	35.2
ZnP_3TBP (**1c**)	420 (4.47)	445 (5.36)	594 (3.92)	640 (4.72)			808	35.3
MgP_2TBP (**1d**)	414 (4.66)	439 (5.49)	590 (4.16)	635 (4.99)			800	35.7
CdP_2TBP (**1e**)	413 (4.71)	437 (5.51)	584 (4.17)	635 (4.99)			808	35.3
HP[b]		402 (4.95)	502 (4.01)	535 (3.83)	573 (3.69)	624 (3.41)		

[a] Prepared by the high temperature reaction of 2-acetylbenzoic acid in the presence of ammonia and zinc acetate, reported by Vogler and Kunkely [10]. [b] Purchased from Tokyo Kasei Kogyo Co., Ltd. [c] **1a** in pyridine, **1b**–**1e** in dichloromethane, and HP in pyridine/dioxane (1/1 vol. ratio). The data in parenthesis denote log ε. For ZnTBP, see ref. 11. [d] In deoxygenated MP glasses at 77 K. For ZnTBP, see ref. 12.

determination by (+)-limonene photooxygenation [8] and the other is the direct observation of the near infrared (NIR) emission (1270 nm) intensity of $^1O_2$ ($^1\Delta_g$) to its ground triplet state, $^3O_2$ ($^3\Sigma_g^-$) [13] by laser flash photolysis.

The former method leads to the results of the limiting quantum yields for the consumption of limonene by the photosensitized oxygenation with the PTBPs, measuring the decrease in (+)-limonene with GC. In this experiment, a He–Ne laser (633 nm) was used as the light source, because the Q-bands of these PTBP metallo complexes are favorably suited to this light and our purpose is keenly focused on the laser imaging process [14]. The 10^{-5} M solutions of PTBPs were prepared to transmit the He–Ne laser light with *c.* 10% and the range 2–20 mmol of limonene was used with *p*-methoxytoluene as an internal standard. The laser irradiation was stopped within the time when the decrease in the limonene reached 5–10% of the initial concentration, where this reaction is treated as first-order kinetic. If the double reciprocal plots of the concentration and the quantum yield, $1/\Phi(-\text{A or AO}_2)$ versus $1/[\text{A}]$, for the photooxygenation of (+)-limonene gives a straight line on the basis of Scheme 1 and eqn. (3), where S, A and AO_2 are PTBP (photosensitizer), (+)-limonene and photooxygenation product of (+)-limonene, respectively and $^1S_0$, $^1S^*$ and $^3S^*$ are the singlet ground state, first excited singlet state and first excited triplet state of S, respectively, the limiting quantum yield for PTBP sensitized photooxygenation of (+)-limonene will be given by the intercept at the *y* axis.

$$\Phi(-\text{A or AO}_2)=\frac{k_3}{k_1+k_2+k_3}\times\frac{k_5[\text{O}_2]}{k_4+k_5[\text{O}_2]}\times\frac{k_7[\text{A}]}{k_6+(k_7+k_8)[\text{A}]} \tag{1}$$

$$=\Phi(^1\text{O}_2)\times\frac{k_7[\text{A}]}{k_6+(k_7+k_8)[\text{A}]} \tag{2}$$

$$k_7 \gg k_8$$

$$\frac{1}{\Phi}(-\text{A or AO}_2)=\frac{k_6}{\Phi(^1\text{O}_2)k_7}\times\frac{1}{[\text{A}]}+\frac{1}{\Phi(^1\text{O}_2)} \tag{3}$$

Since the plots gave straight lines in all cases, the limiting quantum yields for these porphyrins could be calculated from the intercepts of each line by the least-squares method. Figure 1 illustrates the results of the photooxygenation using either ZnP_2TBP (**1b**) in dioxane or HP in dioxane/pyridine (1/1). HP is known to effectively generate $^1O_2$ [15]. Pyridine was used in order to eliminate the factor of the aggregation of HP. Although the slope for HP is slightly steeper in comparison with the one for **1b**, the intercepts for these two sets are focused on the same value of 2.5, that is, $\Phi=0.4$. This indicates that the limiting quantum yields of (+)-limonene photooxygenation, i.e. the efficiency of $^1O_2$ generation, by these two different types of porphyrins are

$^1S_0 + h\nu \xrightarrow{I_{abs}} {}^1S^*$	Absorbance
$^1S^* \xrightarrow{k_1} {}^1S_0 + h\nu'$	Fluorescence
$^1S^* \xrightarrow{k_2} {}^1S_0$	Internal conversion
$^1S^* \xrightarrow{k_3} {}^3S^*$	Intersystem crossing to triplet state
$^3S^* \xrightarrow{k_4} {}^1S_0$	Intersystem crossing to singlet ground state
$^3S^* + {}^3O_2 \xrightarrow{k_5} {}^1S_0 + {}^1O_2$	Formation of singlet oxygen
$^1O_2 \xrightarrow{k_6} {}^3O_2$	Deactivation of singlet oxygen
$^1O_2 + A \xrightarrow{k_7} AO_2$	Product formation (consumption of A)
$^1O_2 + A \xrightarrow{k_8} {}^3O_2 + A$	Physical quenching of singlet oxygen by A

Scheme 1.

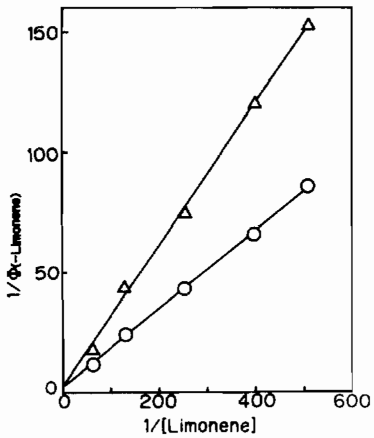

Fig. 1. Double reciprocal plots of the concentration of (+)-limonene, 1/[Limonene], and the quantum yield for the decrease of the limonene by photooxygenation, 1/Φ(−A), using either ZnP_2TBP (○) in dioxane or HP (△) in pyridine/dioxane (1/1). He–Ne laser was used as a light source. The irradiation was stopped within the time when the decrease in the limonene reached 5–10% against the initial concentration. The limiting quantum yield for the limonene photooxygenation was calculated from the intercepts at the *y* axis by the least-squares method.

approximately the same in spite of both the probable differences in the photophysical properties and the addition of pyridine. Figure 2 shows the log plots of the NIR emission intensity versus time in the oxygen saturated dioxane/pyridine (9/1) solutions of these compounds having the same transmittance of *c.* 10% at 633 nm, using laser flash photolysis with the XeCl excimer laser (Lamda Physics EMG101) excited dye laser (Lamda Physics FL300, Rhodamine B was used as dye) with a 6 ns pulse width (7 mJ/pulse at 633 nm). These two emissions decay with the same lifetime (22–23 μs) and the same intensity (5.5–5.7×10^{-3}), as extrapolated to the initial laser pulse, to indicate that they have similar abilities for $^1O_2$ generation. The results of the (+)-limonene photooxygenation and the comparison of the NIR emission intensity by the other metallo PTBPs including the previously mentioned results are summarized in Table 2. The NIR emission efficiency is denoted as the intensity ratio against that for ZnP_2TBP. It is shown that all these diamagnetic complexes (**1a**, **1c**–**1e**) also certainly generate $^1O_2$ with a reasonable yield on the basis of both the limonene photooxygenation and $^1O_2$ emission with

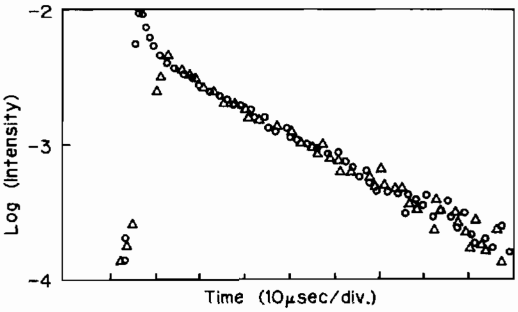

Fig. 2. Decay profiles of the near infrared (NIR) emissions (log intensity vs. time plot) from $^1O_2$ in the oxygen saturated pyridine/dioxane (19) solutions of either ZnP_2TBP (○) or HP (△), after a 6 ns laser pulse irradiation from an excimer laser (XeCl) excited dye laser (Rhodamine B was used for 633 nm emission). The concentrations of the dyes were prepared to give an absorbance of *c.* 1.0 at 633 nm.

TABLE 2. Efficiency for $^1O_2$ generation by metallo–tetrabenzoporphyrins and hematoporphyrin (HP)

Compound	Φ(-Limonene)[a]	$I(^1O_2)/I(^1O_2)_{1b}$[b]	
ZnTBP (**1a**)	0.40		1.06
ZnP_2TBP (**1b**)	0.40	1.00	1.00
ZnP_3TBP (**1c**)	0.40	1.07	
MgP_2TBP (**1d**)	0.33	0.68	
CdP_2TBP (**1e**)	0.27	0.81	
HP	0.40		1.00

[a] Limiting quantum yield for (+)-limonene photooxygenation in dioxane. For ZnTBP, pyridine/dioxane (1/9 vol. ratio) was used. For HP, pyridine/dioxane (1/1) was used.
[b] Relative intensity of NIR emission from $^1O_2$, compared with that for **1b** as standard. Data in left column were obtained in dioxane solutions and those in right one in pyridine/dioxane solutions.

a lifetime of *c.* 20 μs which agrees with the previously reported one in dioxane [9]. The results obtained by the former method almost agree with those obtained by the latter method.

Among the PTBP complexes treated here, the zinc complexes (**1a**–**1c**) more effectively generate $^1O_2$ in comparison with the other PTBPs. Interestingly, the number of *meso*-phenyl substituents does not affect the efficiency of $^1O_2$ generation, as shown in the case of the zinc complexes. This makes us presume that the *meso*-phenyl substitution is a promising method for the improvement of the solubility in common organic solvents probably without a drastic change in the photophysical properties of the parent compound, ZnTBP. Furthermore, it is evidently advantageous that the required concentration of the PTBPs, *c.* 10^{-5} M, to generate $^1O_2$ in the same quantity is about 1/100, compared to that of HP, 10^{-3} M, because they have high extinction coefficients. These results reveal that the metallo PTBPs are employable for the study of photopolymerization base on the ene-type reaction [7, 14].

Conclusions

In conclusion, the PTBP metallo complexes treated in this paper advantageously serve as an effective $^1O_2$ generator in the red light region based on the high quantum yields of the limonene photooxygenation, their absorption properties, and good solubility in common organic solvents. The direct observation of $^1O_2$ emission intensity supports the previous results obtained by the limonene photooxygenation.

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