

Photocatalytic Activity of Phthalocyaninatozinc(II) Bearing Dendritic Substituents at α Positions in Aerated Dimethyl Sulfoxide

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The title complexes acted as sensitizers for photooxidation in irradiation with visible light in aerated dimethyl sulfoxide. The reaction proceeded via a singlet-oxygen pathway. The oxidation rate decreased with increasing the number of dendrimer generation.

Metalloporphyrins encapsulated into the interior core of dendrimer (Den) have received much attention from the viewpoints of their photophysical and electrochemical properties, oxygen-binding nature, regioselective catalytic activity, and energy transferability.¹ Recently, Den-substituted derivatives of phthalocyanines and their metal complexes (Mpcs) were prepared and reported on their prominent nature such as avoiding aggregation or forming glass, as well as interesting photophysical properties.²⁻⁶

Since Mpcs intensively absorb the longer wavelengths of visible light in the solar spectrum, they are attractive sensitizers for photoreduction of water, carbon dioxide or ethylene.^{7,8} The photodecomposition of trichlorophenol in aerated solutions using tetra-*tert*-butylphthalocyanine complexes of zinc(II), magnesium(II), and aluminum(III) as a photosensitizer was also reported.⁹

Previously, we reported α -substituted dendritic phthalocyanines of zinc(II), $Znpc(\alpha-G_n)$ (α and subscript n denote substituent positions on the pc ring and a number of Den generation, respectively, as shown in Figure 1).¹⁰ The $Znpc(\alpha-G_n)$ complexes, which are more sterically crowded by Dens above the pc ring compared with those of β -substituted ones, were expected to be potential sensitizers for the regio- and shape-selective photooxidation.^{10,11} To elucidate the potentiality of photooxidation by $Znpc(\alpha-G_n)$ in aerated solution, the photooxidation of 1,3-diphenylisobenzofuran (DPBF) and 1,3,6,7-tetramethyl-4,5-dicarboxyethyl-2,8-divinyl-(*b*-13)-dihydrobilirubione (bilirubin) in the presence of the complex was examined

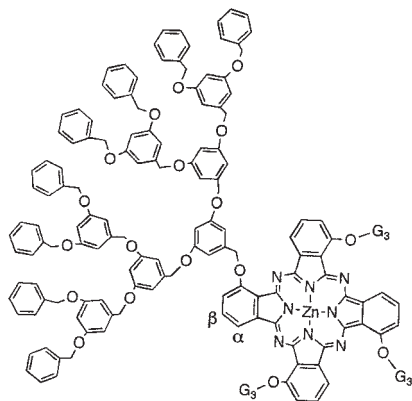
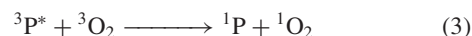
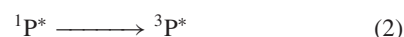


Figure 1. Schematic representation of $Znpc(\alpha-G_3)$.

with controlling the size of the cage formed by Dens over the pc ring in dimethyl sulfoxide (DMSO).

The complexes were prepared according to the method reported previously.¹⁰ The aerated DMSO solution of the complex and the substrate was irradiated by a gas laser (NEC Gas Laser GLG2032) at room temperature. In Figure 2, absorption-spectral changes are shown for the oxidative decomposition of DPBF. The reaction was followed by the absorbance changes of DPBF at 417 nm and bilirubin at 450 nm, respectively.

As the reaction was extremely depressed by the addition of a small amount of aqueous sodium azide, singlet-oxygen quencher, the reaction mechanism is expressed by following kinetic equations, where P is the photosensitizer:¹



The oxidation rate of DPBF is expressed by eq (6). The usual

$$R = k_5[{}^1O_2][DPBF] \quad (6)$$

steady-state approximation was made for estimating the concentration of singlet oxygen, and the DPBF concentration was adjusted in such a way that the rate constant for decay of singlet oxygen (k_4) was much larger than $k_5[DPBF]$. Then, eq (7) is

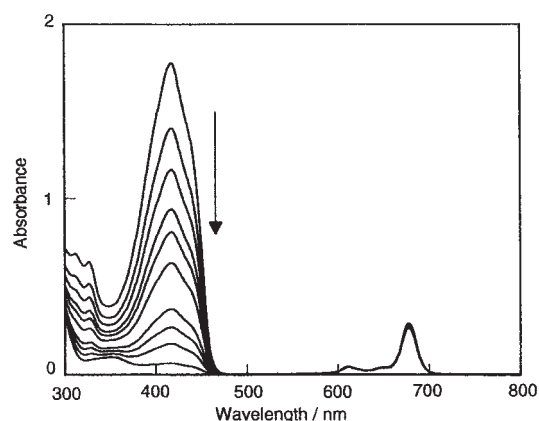


Figure 2. Absorption spectral changes of the DMSO solution of DPBF. Spectra were observed at 0, 10, 20, 30, 40, 60, 80, 100, 120 and 160 min from the starting of the irradiation with 632.8 nm light. Concentration of $Znpc(\alpha-G_3)$ and DPBF was $1.0 \times 10^{-6} \text{ mol dm}^{-3}$ and $7.5 \times 10^{-5} \text{ mol dm}^{-3}$, respectively.

obtained, where R_3 is the formation rate of singlet oxygen in eq

$$\ln\{[\text{DPBF}]_0/[\text{DPBF}]_t\} = (k_5R_3/k_4)t \quad (7)$$

(3).¹³ Eq (7) is deformed to eq (8), where D_0 and D_t represent the absorbance of DPBF at 417 nm and that at t minutes after starting

$$\ln D_0 - \ln D_t = k_{obsd}t, \quad k_{obsd} = k_5R_3/k_4 \quad (8)$$

irradiation, respectively. As shown in Figure 3, first-order plots gave a linear line with a slope of k_{obsd} , which demonstrates that the assumptions made above are reasonable. A similar linear line was also obtained in the case of bilirubin.

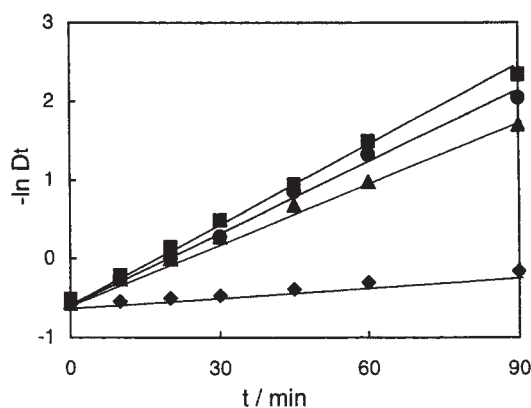


Figure 3. Effects of the scavengers on the photooxidation of DPBF in DMSO. ■: without scavenger, ◆: sodium azide, ●: BHT, ▲: TBAP.

The k_{obsd} value decreased with the addition of a small amount of aqueous sodium azide, to the DMSO solution, while such a decrease was not observed by the addition of a small amount of 3,5-di-*tert*-butyl-4-hydroxytoluene (BHT), the superoxide quencher, suggesting that the reaction proceeds via the pathway with singlet oxygens (Figure 3). It is known that the pathway with superoxides is accelerated by the addition of salt,^{14,15} but the k_{obsd} value was not affected by the addition of a small amount of tetrabutylammonium perchlorate (TBAP). These results show the predominant contribution of singlet oxygens to the reaction, which also supports the reaction mechanism presented.

The k_{obsd} values for the photooxidation of DPBF and bilirubin decreased with increasing the generation number of Den (Table 1). As k_4 is constant in the present experimental, the k_{obsd} value would depend on R_3 and k_5 . Because the generation number of Den scarcely affects the pc-photoexcitation and the oxygen-incorporation into the cage formed by Dens (the oxygen

molecule is too small to be obstructed by the Den-substituents even though their generation becomes larger), the k_{obsd} value is mainly related to k_5 . Hence, the decrease in the k_{obsd} value with increasing the generation number can be interpreted by the difficult penetration of the substrate into the cage to encounter with singlet oxygens generated near the pc ring.¹⁶ Further study on the shape-selectivity of the photooxidation is under progress in our laboratory.

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References and Notes

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- 16 Znpc(α -G₁) showed clear oxidation couples of the pc ring between 0.4 to 1.3 V (vs Ag/AgCl) in the cyclic voltammogram using TBAP (0.1 mol dm⁻³) as an electrolyte in dichloromethane. However, the oxidation waves of Znpc(α -G₂) were vague and those disappeared in the case of Znpc(α -G₃). This results from the fact that the increase of sterical crowdedness around the pc ring restricts the access of the pc ring to the electrode surface, as shown in the case of dendritic porphyrin complexes of zinc(II); K. W. Pollak, J. W. Leon, J. M. J. Frechet, M. Maskus, and H. D. Abruna, *Chem. Mater.*, **10**, 30 (1998).

Table 1. The pseudo first-order rate constants for DPBF and bilirubin

Complexes	$k_{obsd}/10^{-2} \text{ min}^{-1}$	
	DPBF	Bilirubin
Znpc(α -G ₁)	3.20	1.62
Znpc(α -G ₂)	2.23	1.39
Znpc(α -G ₃)	1.89	1.19