Study on Oxygen Quenching Processes of the Excited State Dendrimer Molecules

Atsuya Momotake, Hiroaki Horiuchi,† Junpei Hayakawa, Takuo Mizutani,
Yoshinobu Nishimura, Hiroshi Hiratsuka,*† and Tatsuo Arai*
Graduate School of Pure and Applied Sciences, University of Tsukuba, Tsukuba 305-8571
†*Department of Chemistry, Gunma University, Kiryu 376-8515*

(Received March 1, 2005; CL-050268)

Since the excited singlet state of the core stilbene in dendrimers **G1**–**G4** has ca. 5-ns lifetime, oxygen quenched their excited singlet state producing the singlet oxygen. The efficiency of singlet oxygen production based on the quenching of the stilbene core is the highest in **G4**.

Study on reactive oxygen species has considerable importance related to the photochemical degradation of molecules as well as biological aspects.[1,2] Usually the ground state oxygen (triplet state; $^3O_2$) quenches the excited triplet state aromatic hydrocarbons producing the singlet oxygen. The efficiency is reported to be very sensitive to the properties of organic molecules in organic solvent. The quenching of the excited singlet state by oxygen can also produce the excited state oxygen (singlet state; $^1O_2^*$). In this case the molecules in the excited singlet state should undergo energy transfer to the triplet oxygen to produce singlet oxygen and triplet molecules.[3] In order to know the properties of reactive oxygen species in biologically important large molecule, it is indispensable to study the dynamic process of singlet oxygen production in large molecules mimicking the naturally occurring biological systems.

We have already reported the effect of dendrimer structure on the photochemical and photophysical properties of photoresponsive molecules, where the stilbene or azobenzene chromophore as a photoreactive core is surrounded by dendrons such as benzyl ether type dendron.[4–7] In the previous experiments we have also found that the quenching rate constant decreased with increasing the generation of the dendrimer; the quenching rate constant of the excited singlet state of stilbene core is 2.3×10^{10}, 2.0×10^{10}, 1.6×10^{10}, and 0.9×10^{10} $dm^3\,mol^{-1}\,s^{-1}$ for **G1**, **G2**, **G3**, and **G4**, respectively, decreasing in this order in tetrahydrofuran (THF).[6]

In this paper we have determined the quantum yield of singlet oxygen production on excitation of the different generation of dendrimers. We will report here the results that the highest generation stilbene dendrimer (**G4**) produced singlet oxygen most efficiently. Thus, the surrounding dendrons around the core stilbene should give a specific environment for efficient production of singlet oxygen.

The 4th harmonic of the Nd^{3+}-YAG laser at 266 nm was used as an excitation pulse laser and the chloroform was used as a solvent instead of THF. The oxygen quenching processes are summarized in Scheme 1. The singlet oxygen was monitored by its phosphorescence at 1270 nm. The spectral profile and the typical decay curve were shown in Figure 1. Phosphorescence intensity of $^1O_2^*$ observed by the 266-nm laser excitation of chloroform was negligibly small. The quantum yield of singlet oxygen production (Φ_Δ) was determined by using phenalenone ($\Phi_\Delta = 0.98 \pm 0.15$) as a standard.[8] In the decay time profiles,

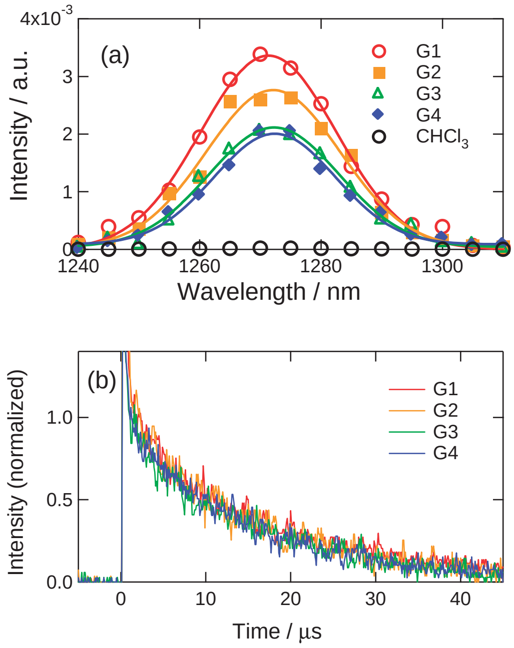


Figure 1. Phosphorescence spectra of $^1O_2^*$ produced from stilbene dendrimers **G1**–**G4** in air-saturated chloroform observed at 1.5 µs after the excitation with 266-nm light pulse. (b) Phosphorescence decay time profiles of $^1O_2^*$ at 1270 nm.

the spike signal due to the light scattering of the laser pulse was observed immediately after the laser excitation. The decay time profiles were independent of the generation of dendrimers and were the same as that of phenalenone. Thus we compared the phosphorescence intensities at 1.5 µs monitored at 1270 nm to determine Φ_Δ.

Table 1 summarized the observed quantum yield of singlet oxygen production ($\Phi_{\Delta 1}$) on excitation of dendrimers at 266 nm. Table 1 also shows the fluorescence quantum yield values at 310 nm (Φ_{f310}) for **G1**–**G4** dendrimers. The Φ_{f310} values (Table 1) are almost identical and are not affected by peripheral dendrons since the absorption coefficient of peripheral dendrons at 310 nm is almost zero. The fluorescence quantum yield observed on 266-nm excitation (Φ_{f266}) decreased with increasing generation (Table 1), because the fluorescence is emitted from the excited state stilbene after energy transfer from the dendron to the stilbene core. The apparent $\Phi_{\Delta 1}$ value decreased with the increasing generation most likely due to the absorption at 266 nm by peripheral dendrons in higher generation. In this case, benzyl ether type dendrons in higher generation partially inhibit producing the excited singlet state of a stilbene core on excitation at 266 nm. Therefore, we should consider the really pro-

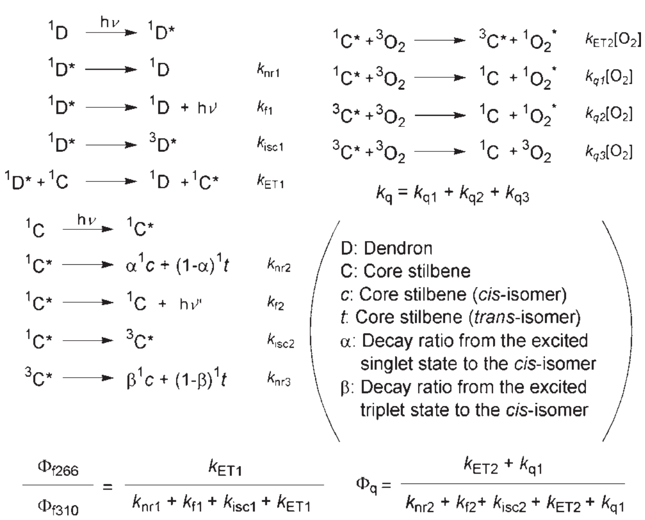
Table 1. Efficiency of singlet oxygen production ($\Phi_{\Delta 1}$ and $\Phi_{\Delta 2}$), fluorescence quantum yield (Φ_{f266} and Φ_{f310}), quenching rate constant (k_q), and efficiency of the quenching for singlet excited state of stilbene by oxygen (Φ_q)

	$\mathbf{\Phi_{\Delta 1}}$	Φ_{f266}	Φ_{f310}	Φ_{f266}/Φ_{f310}	$\mathbf{\Phi_{\Delta 2}}$	$k_q/10^{10}$ M^{-1} s^{1}	Φ_q
G1	$\mathbf{0.15_4}$	0.21_4	0.21_8	0.98_1	**0.16**	1.14	0.077
G2	$\mathbf{0.12_6}$	0.180	0.22_3	0.80_7	**0.16**	0.93	0.070
G3	$\mathbf{0.09_6}$	0.17_5	0.270	0.64_8	**0.15**	0.62	0.054
G4	**0.090**	0.110	0.25_4	0.43_3	**0.21**	0.53	0.049

duced singlet excited state of a stilbene core on excitation at 266 nm, so that the efficiency of the singlet oxygen production from the stilbene core on excitation at 266 nm can be compared among dendrimer generations. In other words, the apparent $\Phi_{\Delta 1}$ values are based on the production of the singlet oxygen from the excited whole dendrimers on irradiation at 266 nm, but we should know the $\Phi_{\Delta 2}$ values, based on the production of the singlet oxygen from the excited stilbene core on irradiation at 266 nm. The fluorescence quantum yield values both at 310 nm (Φ_{f310}) and at 266 nm (Φ_{f266}) are reflecting the production of an excited singlet state stilbene core on excitation at each wavelength, and therefore, can be used to correct $\Phi_{\Delta 1}$ values to give the $\Phi_{\Delta 2}$ values. One can use the Φ_f values (Φ_{f266} and Φ_{f310}) determined on excitation at 266 nm and 310 nm for the correction. Actually, the fluorescence quantum yield values at 266 nm (Φ_{f266}) are strongly affected by peripheral dendrons. In the higher generation dendrimer more photons of 266 nm are absorbed by the benzyl ether chromophore than by the core stilbene, followed by the production of the excited singlet state of dendron chromophore, which may undergo energy transfer to the core stilbene to give the excited singlet state of a stilbene core. Therefore, Φ_{f266} values are compromise between the fluorescence via energy transfer from the dendrons to the core stilbene and that via direct excitation of the core (Scheme 1). Because the value of Φ_{f266}/Φ_{f310} essentially stands for the inhibition effect of peripheral dendrons on the excitation of a stilbene core on irradiation at 266 nm, the apparent $\Phi_{\Delta 1}$ value should be corrected with Φ_{f266}/Φ_{f310} to give $\Phi_{\Delta 2}$:

$$\Phi_{\Delta 2} = \Phi_{\Delta 1}/(\Phi_{f266}/\Phi_{f310}) \quad (1)$$

As shown in Table 1, the $\Phi_{\Delta 2}$ value thus obtained is the highest in **G4** among **G1–G4** indicating the effect of surrounding dendron groups on the efficiency of $^1O_2{}^*$ production.



Scheme 1.

The quenching rate constant is also necessary to determine the corrected value of the production of singlet oxygen based on the quenching of the produced singlet excited state of stilbene by oxygen on excitation at 266 nm. The quenching rate constant of the singlet excited state of stilbene core (k_q) is observed to be 1.14×10^{10}, 0.93×10^{10}, 0.62×10^{10}, and 0.53×10^{10} dm^3 mol^{-1} s^{-1} for **G1**, **G2**, **G3**, and **G4**, respectively, decreasing in this order in chloroform ($CHCl_3$). From these results, we can calculate the efficiency of the quenching of the singlet excited state of stilbene (Φ_q) by oxygen to be 7.7, 7.0, 5.4, and 4.9%, respectively for **G1**, **G2**, **G3**, and **G4** in $CHCl_3$. It should be noted that stilbene dendrimers may undergo intersystem crossing to the triplet state either unimolecularly or accelerated by the oxygen quenching of the singlet excited state. Therefore, the difference in value among **G1–G4** should be discussed not only by the quenching of the singlet excited state but also the triplet excited state. These works are in progress.

However, the results described in this paper clearly indicate that the $\Phi_{\Delta 2}$ value is dependent on the generation of the dendrimer and the higher generation dendrimers seem to produce singlet oxygen more efficiently. This is the first clear evidence of the effect of dendrimer on the oxygen quenching process and the singlet oxygen production yield in the quenching of excited state molecules by molecular oxygen.

This work was supported by a Grant-in-Aid for Scientific Research on Priority Areas (417), a Grant-in-Aid for Scientific Research (Nos. 15350004, 16350005, and 16750110) and the 21st Century COE Program from the Ministry of Education, Culture, Sports, Science and Technology (MEXT) of the Japanese Government, by University of Tsukuba Research Projects, Asahi Glass Foundation and JSR Corporation.

References

1 A. A. Frimer, "Singlet Oxygen Vols. I-IV," CRC Press, Boca Raton, FL (1985).
2 P. Wentworth, L. H. Jones, A. D. Wentworth, X. Y. Zhu, N. A. Larsen, I. A. Wilson, X. Xu, W. A. Goddard, K. D. Janda, A. Eschenmoser, and R. A. Lerner, *Science*, **293**, 1806 (2001).
3 J. Saltiel and B. W. Atwater, *Adv. Photochem.*, **14**, 1 (1988).
4 A. Momotake and T. Arai, *J. Photochem. Photobiol., C*, **5**, 1 (2004).
5 M. Uda, T. Mizutani, J. Hayakawa, A. Momotoke, M. Ikegami, R. Nagahata, and T. Arai, *Photochem. Photobiol.*, **76**, 596 (2002).
6 A. Momotake, J. Hayakawa, R. Nagahata, and T. Arai, *Bull. Chem. Soc. Jpn.*, **77**, 1195 (2004).
7 A. Momotake and T. Arai, *Tetrahedron Lett.*, **45**, 4131 (2004).
8 R. Schmidt, C. Tanielian, R. Dunsbach, and C. Wolff, *J. Photochem. Photobiol., A*, **79**, 11 (1994).

Published on the web (Advance View) April 9, 2005; DOI 10.1246/cl.2005.684