

Photodegradation Processes of Cyanine Dyes in the Film State Induced by Singlet Molecular Oxygen

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Photodegradation processes of carbocyanine dyes spin-coated on a polycarbonate plate were studied by steady-state photolysis and near-IR emission spectroscopy. The efficiency of the whole photodegradation caused by molecular oxygen directly and/or indirectly was found to strongly depend on both substituents on the 1 and 1' positions and the counterion. Singlet molecular oxygen ($^1\Delta_g$) produced at the interface between the dye thin film and a polycarbonate plate was detected by near-IR emission spectroscopy. Its yield did not depend on substituents on the 1 and 1' positions but on the counterion. The relative reactivity of carbocyanine dyes in the film state with the singlet molecular oxygen was estimated by exploiting a perinaphthenone thin film as a singlet molecular oxygen generator. The reactivity strongly depended on both substituents on the 1 and 1' positions and the counterion.

Introduction

Active oxygen species such as singlet molecular oxygen ($^1\Delta_g$), the superoxide anion ($O_2^{\bullet-}$), and the hydroxyl radical are more reactive than molecular oxygen ($^3\Sigma_g^-$). They play important roles in the immune system,¹ photodynamic therapy of cancer,^{2–4} and self-cleaning processes by using the photocatalyst.^{5,6} On the other hand, they are sometimes harmful for biological systems⁷ and functional materials.⁸

In biological systems, various active oxygen species are produced in living processes,^{9–11} by stress, agrichemicals, the exhaust of cars, and UV light from the sun.¹² Many studies have been devoted to understand formation and deactivation processes of these active oxygen species. It has been clarified that most of organisms have sophisticated defensive systems for active oxygen species^{13,14} which are making use of many types of scavengers for active oxygen species such as SOD (superoxide dismutase).¹⁵

In the degradation of functional materials caused by active oxygen species, they are mainly produced by the light irradiation. Molecules absorb light such as the sunlight to produce their excited state, and active oxygen species are produced by the reaction of excited molecules with ground-state molecular oxygen ($^3\Sigma_g^-$). These active oxygen species attack functional materials to cause photodegradation.^{16–20} Photodegradation has been the essential problem especially for photofunctional materials because they exhibit their functions by irradiation; irradiation of photofunctional materials is indispensable. Therefore, to suppress photodegradation is very important for the application and development of photofunctional materials. Organic dyes are one of the most important photofunctional materials. Most of studies on the mechanism of photodegrada-

tion processes of dye molecules have been carried out in the liquid phase. It has been known that singlet molecular oxygen ($^1\Delta_g$) is efficiently produced in the liquid phase upon irradiation of organic molecules in the presence of molecular oxygen ($^3\Sigma_g^-$).^{19–40} Singlet molecular oxygen attacks organic molecules to induce their degradation.^{20,41,42} Formation^{19–40} and deactivation processes^{19,20,43–53} of singlet molecular oxygen have also been widely studied in the liquid phase. The contribution of singlet molecular oxygen to photodegradation has been estimated for 1-(aryloxy)-2-naphthols in acetonitrile by Jansen et al.⁴⁰ In addition to this photodegradation, it has been reported that photodegradation of dye molecules by the superoxide anion ($O_2^{\bullet-}$) is also important in the liquid phase.^{8,54} The superoxide anion is produced by the electron-transfer reaction from dye molecules to singlet molecular oxygen in aqueous solution^{55,56} and from excited dye molecules to molecular oxygen.⁸

Most photofunctional materials are employed in the solid state, and therefore, for the development of photofunctional materials it is necessary to study photodegradation processes of dye molecules in the solid phase. Organic polymers are one of the most important materials for photofunctional materials, and behaviors of singlet molecular oxygen generated within polymer matrices have been studied.^{57–64} The lifetime,^{58,59,62} formation quantum yield,⁶³ mechanism of generation,⁶⁰ physical quenching,⁶¹ and chemical⁶⁴ quenching of singlet molecular oxygen were clarified in homogeneous polymer matrices by Ogilby and co-workers. The detection system of singlet molecular oxygen with spatial resolution has been developed,^{65–67} and behavior of singlet molecular oxygen in both homogeneous and heterogeneous polymer matrices has also been studied.⁶⁵ Organic dye in the film state is one of photofunctional materials and is very important for applications such as DVD-R, and therefore, photodegradation processes of the dye in the film state have been studied. It was reported that metal complexes stabilize dyes against irradiation.^{68–70} Yang et al. studied photodegradation kinetics of cyanine dyes and merocyanine dyes in thin films by direct steady-state photolysis and reported that cyanine

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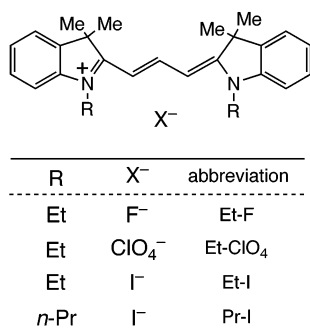


Figure 1. Molecular structure of carbocyanine dyes.

dyes in thin films have relatively good photostability compared with merocyanines in thin films.⁷⁰ However, it was not clarified what kind of active oxygen species induces the photodegradation and what kind of factor controls the efficiency of the photodegradation.

In this study, we have investigated photodegradation processes of carbocyanine dyes shown in Figure 1 spin-coated on a polycarbonate plate by focusing our attentions on the photodegradation induced by the singlet molecular oxygen. Formation processes of the singlet molecular oxygen produced by the irradiation of carbocyanine dyes in the film state have been studied by near-IR emission spectroscopy. Reactivity of carbocyanine dyes in the film state with singlet molecular oxygen has also been studied by exploiting a perinaphthenone thin film as a singlet molecular oxygen generator.^{71,72}

Experimental Section

Materials. 1,1'-Diethyl-3,3,3',3'-tetramethylindocarbocyanine fluoride (Et-F), 1,1'-diethyl-3,3,3',3'-tetramethylindocarbocyanine perchlorate (Et-ClO₄), 1,1'-diethyl-3,3,3',3'-tetramethylindocarbocyanine iodide (Et-I), and 1,1'-di-*n*-propyl-3,3,3',3'-tetramethylindocarbocyanine iodide (Pr-I) were synthesized according to the literature.⁷³ Molecular structures of these carbocyanine dyes are shown in Figure 1. Polycarbonate plates (PC: purchased from Takiron Co. Ltd.) and quartz plates were used as a substrate. The carbocyanine dyes were dissolved into 2-methoxyethanol (Wako Pure Chemical Industries, Ltd., 99%), and substrates were spin-coated by dropping these dye solutions. Their absorbances at an absorption maximum in the visible region were set to be 0.30 ± 0.02 . A thin film of perinaphthenone (Aldrich Chemical Co., 97%) was prepared by spin-coating the benzene solution of perinaphthenone on a quartz plate and was used as the sensitizer for singlet molecular oxygen production.^{40,41}

Direct Photolysis of Carbocyanine Dyes in the Film State. Direct photolysis of carbocyanine dyes in the film state was carried out under argon or oxygen. The size of the polycarbonate plate and quartz plate coated with carbocyanine dyes was 10 mm \times 25 mm \times 1 mm, and these plates were irradiated from the backside in the cuvette with a size of 10 mm \times 10 mm \times 45 mm. The PC coated with dyes was kept for 15 min under argon or oxygen gas flow to equilibrate. Further gas flow did not show any effect on the photodegradation. A 300-W Xe short arc lamp (UXL-300, Ushio) was used as a light source, and 532-nm light was selected by dispersion with a monochromator (CT-10, JASCO). To estimate the photodegradation efficiency, the second harmonic light pulse (532 nm) from an Nd³⁺:YAG laser (Quanta-Ray GCR-130, Spectra Physics) was used. Its intensity was determined to be 0.28 mJ pulse⁻¹ cm⁻² by using a joule meter (ED-200, Gentec). UV-vis absorption spectra of

carbocyanine dyes in the film state were recorded on a Hitachi U3300 spectrophotometer before and after irradiation.

Near-IR Emission Measurements. For measurements of the emission of singlet molecular oxygen, the second harmonic light pulse (532 nm, 10 Hz) from an Nd³⁺:YAG laser (Quanta-Ray GCR-130, Spectra Physics) was used as the excitation light source. The carbocyanine dye spin-coated on PC was irradiated from the backside. Emission was detected with a photomultiplier tube (R5509-42, Hamamatsu) cooled at -80 °C available for the near-IR region⁷⁴ after dispersion with a monochromator. Signals from the photomultiplier tube were amplified by five times with a DC 300 MHz amplifier (SR445, Stanford Research Systems) and processed with a gated photon counter (SR400, Stanford Research Systems). Gate width of the photon counter was 10 μ s, and data acquisition time was 100 s. All measurements were carried out at room temperature under the same optical geometry to determine relative formation yields of the singlet molecular oxygen.

Reactivity of Carbocyanine Dyes in the Film State with Singlet Molecular Oxygen. The carbocyanine dye spin-coated on PC was faced to the perinaphthenone spin-coated on a quartz plate with a small intervening gap (0.5 mm) as shown in Figure 2.^{20,75} Singlet molecular oxygen was produced by the irradiation of the perinaphthenone thin film with 400-nm light from a 300-W Xe lamp with a monochromator.^{71,72} The degradation of carbocyanine dyes in the film state was studied by measuring its absorption spectrum.

Gas Chromatography-Mass Spectroscopy. Products obtained by the irradiation of Et-ClO₄ in the film state were dissolved into methanol and analyzed by gas chromatography-mass spectroscopy (GC-MS; JEOL Automass II equipped with an HP6890, column J&W DB-5). The sample was injected to the column by heating to 250 °C. The rate of temperature elevation in GC was 25 °C/min.

Results and Discussion

Photodegradation of Carbocyanine Dyes in the Film State.

Absorption spectra of Et-F and Pr-I in ethanol are shown in Figure 3a. Absorption maxima were observed at 550 and 551 nm for Et-F and Et-I, respectively, and their fwhm (full width at half-maxima) is the same for all (53 nm). Absorption spectra of Et-ClO₄ and Et-I in ethanol are the same as that of Et-F in ethanol, indicating that the electronic structure of the carbocyanine dye does not depend on the counterion. Absorption spectra of the carbocyanine dye spin-coated on PC are also shown in Figure 3b. These spectra are normalized to the absorbance at their most intense peaks. The absorption observed below 420 nm is due to PC. Absorption bands due to carbocyanine dyes are red shifted compared with those in ethanol, and their fwhm values (90–100 nm) are about two times larger than those in ethanol (53 nm), indicating that carbocyanine dyes aggregate on PC. Absorption peaks of Et-F, Et-ClO₄, Et-I, and Pr-I are at 575, 578, 578, and 585 nm, respectively.

Figure 4 shows the absorption spectral change caused by the irradiation of Et-ClO₄ spin-coated on PC with 532-nm light under argon (a) and oxygen (b). The photodegradation of Et-ClO₄ was clearly enhanced in the presence of oxygen. The absorption peak of Et-ClO₄ was observed at 578 and 574 nm before and after 40-min irradiation under oxygen, respectively. The fwhm values of Et-ClO₄ are 95 and 92 nm before and after 40-min irradiation under oxygen, respectively. This blue shift and narrowing of absorption bands indicate that the absorption spectrum of carbocyanine dye in the film state was resembling

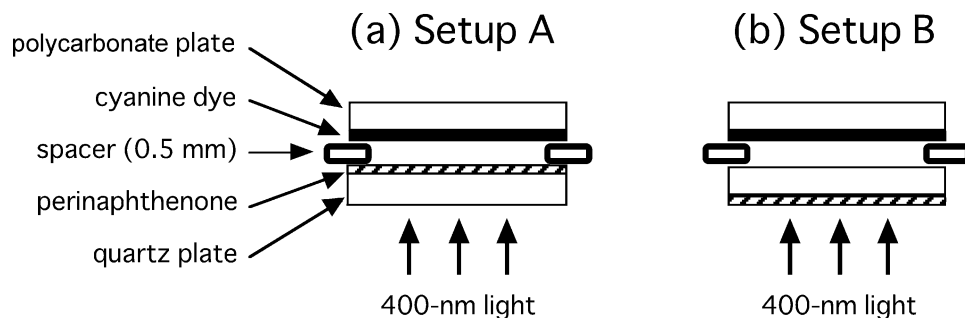


Figure 2. Experimental setup for the measurements of reactivity of the carbocyanine dye in the film state with singlet molecular oxygen (a) and the control experiment (b).

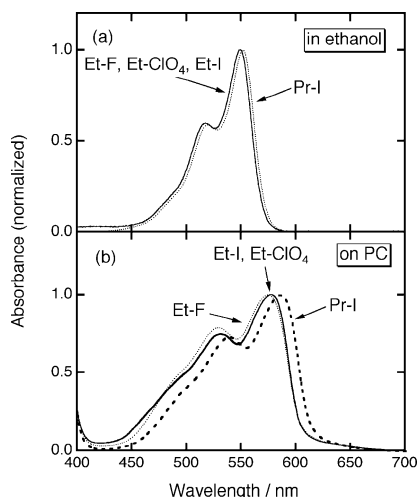


Figure 3. Absorption spectra of the carbocyanine dye in ethanol (a) and spin-coated on a polycarbonate plate (b).

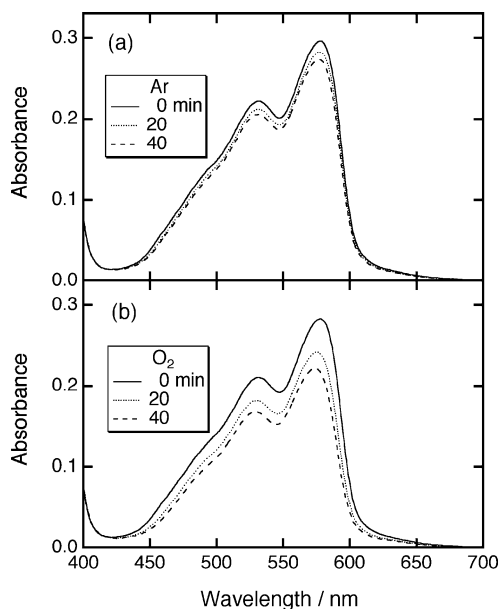


Figure 4. Absorption spectral change of Et-ClO₄ spin-coated on a polycarbonate plate observed upon the irradiation with the 532-nm light under argon (a) and oxygen (b).

that in solution more and more upon irradiation and part of the carbocyanine dyes in aggregates photodegraded to decrease their aggregate size.

To clarify the photodegradation mechanism, product analysis was carried out. Photoproducts of Et-ClO₄ in the film state were dissolved into methanol. GC-MS study was carried out by injecting the sample into the column at 250 °C. At this

temperature, the parent molecule is considered to be not vaporized and only photoproducts can be studied. Even for the unirradiated Et-ClO₄, many kinds of products were observed in the chromatogram, indicating that a small portion of parent molecules decomposed by heating and therefore detailed analysis was very difficult. Under argon, prominent signals were observed at retention times of 4.0 min ($m/z = 103$) and 7.4 min ($m/z = 189$). These signals are ascribable to photoproducts under argon but not oxidized product. Under oxygen, prominent signals were observed at retention times of 7.1 min ($m/z = 187$) and 14.2 min ($m/z = 405$) besides the above signals at 4.0 min ($m/z = 103$) and 7.4 min ($m/z = 189$). The former two signals are ascribable to oxidized products. In the case of 3,3-diethyl-2,2'-thiatricarbocyanine iodide in acetonitrile, *N*-ethylbenzothiazolone, 3-ethyl-2-(7-oxohepta-1,3,5-trienyl)-benzothiazol-3-ium and 2-(6-carboxyhexa-1,3,5-trienyl)-3-ethylbenzothiazol-3-ium were reported to be the main oxidized products.⁵⁴ If one takes these oxidized products into consideration, 1-ethyl-3,3-dimethyl-1,3-dihydroindol-2-one ($m/z = 189$), 1-ethyl-3,3-dimethyl-2-(3-oxopropenyl)-3*H*-indolium ($m/z = 114$), and 2-(2-carboxyvinyl)-1-ethyl-3,3-dimethyl-3*H*-indolium ($m/z = 122$) were expected to be oxidized products but were not detected.

The efficiency of the photodegradation caused by the molecular oxygen ($\Phi_{\text{PD-O}_2}$) is expressed as follows:

$$\Phi_{\text{PD-O}_2} = (N_{\text{cyanine}}^{\text{O}_2} - N_{\text{cyanine}}^{\text{Ar}}) / N_{\text{photon}} \quad (1)$$

Here $N_{\text{cyanine}}^{\text{O}_2}$ and $N_{\text{cyanine}}^{\text{Ar}}$ are the number of carbocyanine dye molecules degraded by the irradiation under oxygen and argon, respectively, and N_{photon} is the number of absorbed photons. At present the absorption cross-section of the carbocyanine dye spin-coated on PC is not known. Therefore we could not estimate the absolute number of carbocyanine dye molecules degraded by the irradiation. As shown in Figure 3b, the absorption spectral shapes of these dyes are similar to each other and their absorbances at an absorption maximum in the visible region were almost the same (0.30 ± 0.02). Therefore, their integrated absorption intensities in the visible region are similar to each other. Also in ethanol, absorption spectra and molar absorption coefficients of these dyes are similar to each other. Thus, we can assume that the absorption cross sections of these dyes are equal to each other. From values of the absorbance change/unit irradiation time, the relative efficiency of the photodegradation caused by the molecular oxygen ($\Phi_{\text{PD-O}_2}^{\text{rel}}$) can be expressed as follows:

$$\Phi_{\text{PD-O}_2}^{\text{rel}} = \Delta A_{\text{O}_2} - \Delta A_{\text{Ar}} \quad (2)$$

Here ΔA_{O_2} and ΔA_{Ar} are the absorbance change/unit irradiation time under argon and oxygen, respectively. Figure 5 shows the absorbance change ($\Delta \text{absorbance}$) of Et-ClO₄ at the peak wave-

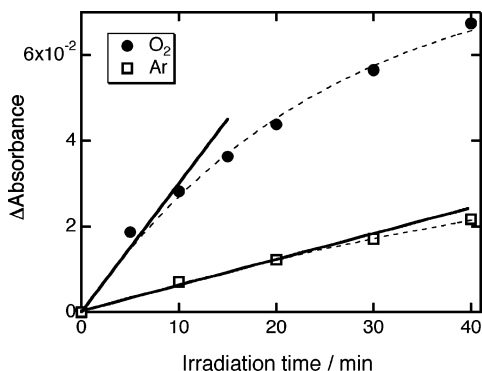


Figure 5. Absorbance changes of Et-ClO₄ spin-coated on a polycarbonate plate observed upon the irradiation with the 532-nm light under argon (open squares) and oxygen (full circles) as a function of the irradiation time. The dotted lines and full lines are the fitted curve (see text) and its tangent, respectively.

TABLE 1: Summary of the Relative Efficiencies of Carbocyanine Dyes Spin-Coated on a Polycarbonate Plate

	Et-F	Et-ClO ₄	Et-I	Pr-I
Efficiency of the Photodegradation				
ΔA_{Ar} (10^4 abs/min)	2.6 ± 1.0	6.2 ± 1.0	3.7 ± 1.0	0.7 ± 1.0
ΔA_{O_2} (10^4 abs/min)	12.3 ± 1.0	30.0 ± 1.0	16.3 ± 1.0	4.3 ± 1.0
$\Delta A_{O_2} - \Delta A_{Ar}$ (10^4 abs/min)	9.7 ± 2.0	23.8 ± 2.0	12.6 ± 2.0	3.7 ± 2.0
$\Phi_{PD-O_2}^{rel}$	0.41 ± 0.1	1.00	0.53 ± 0.1	0.15 ± 0.1
Formation Yield of Singlet Molecular Oxygen				
ϕ_{Δ}^{rel}	0.8 ± 0.2	1.0	1.6 ± 0.2	1.6 ± 0.2
Reactivity with Singlet Molecular Oxygen				
$\phi_{\Delta-cyanine}^{rel}$	0.6 ± 0.1	1.0	0.4 ± 0.1	0.1 ± 0.1
Efficiency of the Photodegradation Induced by Singlet Molecular Oxygen				
$\Phi_{PD-\Delta}^{rel a}$	0.5 ± 0.2	1.0	0.6 ± 0.2	0.2 ± 0.2
^a $\Phi_{PD-\Delta}^{rel} = \phi_{\Delta}^{rel} \times \phi_{\Delta-cyanine}^{rel}$.				

length (578 nm) caused by the irradiation under argon (open squares) and oxygen (full circles) as a function of the irradiation time. The plot of results for oxygen does not show a line but a curve. For the reason of this deviation from the line, oxygen consumption may be pointed out. To confirm this idea, oxygen gas was reflowed in the cuvette after the 10 min of irradiation, but the photodegradation rate was not recovered. This indicates that the deviation is not ascribed to oxygen consumption. In this experiment, amounts of molecular oxygen in the cuvette and carbocyanine dye molecules on PC were estimated to be 2×10^{-4} mol and ca. 10^{-8} mol, respectively. This also supports that the deviation is not ascribed to oxygen consumption. It is concluded that as mentioned before, decrease in the size of the aggregate of carbocyanine dyes upon irradiation induces the deviation from the line in Figure 5; i.e., the decrease in the aggregate size is responsible for the change in photochemical processes of carbocyanine dyes in the film state. The plots were fitted by a single-exponential function, and we determined ΔA_{Ar} and ΔA_{O_2} from the tangent of the fitted curve. By assuming that the molar absorption coefficient (absorption cross-section) of Et-ClO₄ on PC is the same as that in ethanol (1.2×10^5 M⁻¹ cm⁻¹ (4.4×10^{-16} cm² molecule⁻¹)), the magnitude of Φ_{PD-O_2} of Et-ClO₄ is estimated to be $\sim 10^{-5}$. Values of ΔA_{Ar} and ΔA_{O_2} for all carbocyanine dyes are summarized in Table 1. From values of ΔA_{Ar} and ΔA_{O_2} , the value of $\Phi_{PD-O_2}^{rel}$ was estimated and normalized to that of Et-ClO₄ as Et-ClO₄ (1.00) > Et-I (0.53 \pm 0.1) > Et-F (0.41 \pm 0.1) > Pr-I (0.15 \pm 0.1) (Table 1), indicating that the value of $\Phi_{PD-O_2}^{rel}$ strongly depends on both substituents on the 1 and 1' positions and the counterion of

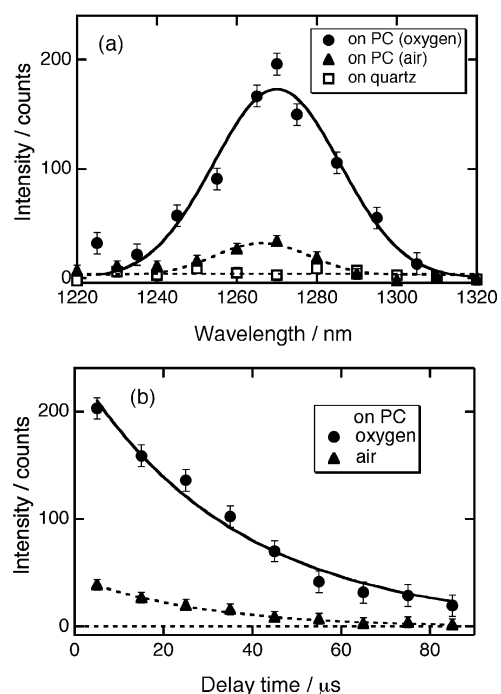


Figure 6. Emission spectra of singlet molecular oxygen produced from Pr-I spin-coated on a polycarbonate plate under oxygen (full circles) and air (full triangles) and that on a quartz plate under oxygen (open squares) observed immediately after the excitation with the 532-nm light pulse (a). Emission decay time profile of singlet molecular oxygen produced from Pr-I on a polycarbonate plate at 1270 nm under oxygen (full circles) and air (full triangles) (b).

carbocyanine dyes. Photodegradation is considered to be mainly induced by active oxygen species such as the singlet molecular oxygen. Therefore, $\Phi_{PD-O_2}^{rel}$ depends on the formation yield of active oxygen species and the reactivity of active oxygen species with carbocyanine dyes.

Relative Formation Yield of Singlet Molecular Oxygen.

To estimate the formation yield of singlet molecular oxygen ($^1\Delta_g$), we tried to measure the emission of the singlet molecular oxygen produced by irradiation of carbocyanine dye thin films. Figure 6a shows emission spectra observed upon the irradiation of Pr-I spin-coated on PC just after the excitation with 532-nm light pulse under oxygen (full circles) and air (full triangles). In this experiment, the noise level was estimated by using a polycarbonate plate (for example 34 ± 2 counts at 1270 nm). The noise level was not changed by changing the delay time, and thus, this noise was simply subtracted from emission data. The emission band was observed around 1270 nm, indicating that this emission can be attributed to the singlet molecular oxygen produced by the irradiation of Pr-I spin-coated on PC. It is noted that the emission intensity at 1270 nm under air was about five times weaker than that under oxygen.

Molecular oxygen is considered to exist in the dye thin film and in PC, because the dye thin film was prepared in air and it is known that the molecular oxygen is permeable to polycarbonate film.⁷⁶ Thus, singlet molecular oxygen can be produced at the interface between the dye thin film and gas (oxygen or air), at the interface between the dye thin film and PC, and in the dye thin film. Singlet molecular oxygen produced at the interface between the dye thin film and the gas can diffuse into the gas. Also singlet molecular oxygen produced at the interface between the dye thin film and PC can diffuse into PC. Therefore, singlet molecular oxygen is considered to exist in gas, in PC, and in the dye thin film. To examine where singlet molecular oxygen detected exists, the decay time profile of the singlet

TABLE 2: Efficiency of Photodegradation of Et-ClO₄ Spin-Coated on a Quartz Plate and Polycarbonate Plate

	quartz plate	polycarbonate
ΔA_{Ar} (10 ⁴ abs/min)	7.5 ± 1.0	5.8 ± 1.0
ΔA_{O_2} (10 ⁴ abs/min)	24.9 ± 1.0	30.0 ± 1.0

molecular oxygen was measured. Figure 6b shows decay time profiles of the emission of singlet molecular oxygen observed at 1270 nm under oxygen (full circles) and air (full triangles). These were analyzed by the single-exponential function with lifetimes of 33 ± 5 and 31 ± 5 μ s, respectively. The lifetime of singlet molecular oxygen in air was reported to range from 0.08 to 8 s^{77,78} and is much longer than the observed value. Therefore, singlet molecular oxygen detected in this experiment is not assigned to that in gas. To clarify whether singlet molecular oxygen detected exists in PC or not, by use of Pr-I on a quartz plate, we tried to measure the emission spectrum of singlet molecular oxygen. The absorption spectrum of Pr-I spin-coated on a quartz plate was the same as that on PC. The emission spectrum observed upon irradiation of Pr-I on a quartz plate under oxygen is shown in Figure 6a by open squares. No emission was observed, indicating that singlet molecular oxygen detected upon irradiation of Pr-I on PC is assigned to that in PC.

To examine the reactivity of singlet molecular oxygen detected in PC with the dye thin film, the efficiency of the photodegradation of Et-ClO₄ spin-coated on a quartz plate was studied under argon and oxygen. Values of ΔA_{Ar} and ΔA_{O_2} are summarized in Table 2 in comparison with those for Et-ClO₄ spin-coated on PC. Values of ΔA_{Ar} and ΔA_{O_2} for Et-ClO₄ on a quartz plate are similar to those on PC, indicating that singlet molecular oxygen detected in PC is not responsible for the photodegradation of the dye in the film state so that photodegradation is mainly caused by active oxygen species produced in the dye thin film. Quenching of singlet molecular oxygen by 1-(aryloxy)-2-naphthols adsorbed on cotton linter has been studied by Jansen et al.⁴⁰ Quenching rate constants of singlet molecular oxygen by 1-(aryloxy)-2-naphthols were reported to be $> 10^7$ M⁻¹ s⁻¹ in methanol, and these dyes adsorbed on cotton linters quench singlet molecular oxygen.⁴⁰ It was reported that cyanine dyes efficiently quench singlet molecular oxygen with quenching rate constants of 0.76×10^8 – 200×10^8 M⁻¹ s⁻¹ in acetonitrile.⁵¹ To determine the quenching rate constant of the singlet molecular oxygen, we measured the emission lifetime of the singlet molecular oxygen sensitized by perinaphthenone in acetonitrile with various concentrations of carbocyanine dyes (0 – 5×10^{-4} M). Quenching rate constants (k_q) were estimated to be 4.1×10^7 , $< 0.2 \times 10^7$, 0.4×10^7 , and 1.8×10^8 M⁻¹ s⁻¹ for Et-F, Et-ClO₄, Et-I, and Pr-I in acetonitrile, respectively. Although quenching rate constants are small, the density of dye molecules on PC is much higher than that in solution. Therefore, the singlet molecular oxygen in the dye thin film can be efficiently quenched by dye molecules, so that we could not detect the singlet molecular oxygen in the dye thin film.

Ogilby and co-workers studied the behavior of singlet molecular oxygen in a polymer matrix in detail^{58–64} and reported that, in a solid organic polymer, the quenching of triplet sensitizer is inefficient because of the low oxygen diffusion coefficient, so that the lifetime of the triplet sensitizer (phenazine) was longer than intrinsic lifetime of the singlet molecular oxygen. Therefore, the time-dependent behavior of the phosphorescence signal of singlet molecular oxygen principally reflects that of its precursor (triplet sensitizer). In the case of carbocyanine dye spin-coated on PC, singlet molecular oxygen detected in PC can be produced by diffusion-controlled quench-

ing of the triplet carbocyanine dye at the interface between the dye thin film and PC. The oxygen diffusion coefficient at the interface is considered to be low as in the case in solid organic polymer. Therefore, the observed lifetime of the singlet molecular oxygen (33 ± 5 μ s) may reflect that of the triplet carbocyanine dye. To determine the lifetime of the triplet carbocyanine dye, we have tried to measure the transient absorption spectrum of the carbocyanine dye spin-coated on PC. However, no transient signal was observed attributable to the triplet state. Any other transient species was also not observed in the transient absorption spectrum. The following two reasons are pointed out for these results: (1) low absorbance of the dye on PC; (2) low laser intensity to avoid laser ablation of the dye. The triplet lifetime of Pr-I should be different from those of Et-ClO₄ and Et-F because of the heavy atom effect induced by the counterion (halogen atom). Thus, the decay time profile of singlet molecular oxygen may depend on the counterion. To confirm this, decay time profiles of singlet molecular oxygen were measured for Et-I, Et-ClO₄, and Et-F spin-coated on PC. Contrary to our expectation, the observed lifetime for Pr-I is the same as those for Et-I, Et-ClO₄, and Et-F within the experimental error, indicating that the lifetime of singlet molecular oxygen does not reflect that of the triplet carbocyanine dye. Also the triplet lifetime of Pr-I should depend on the concentration of oxygen and therefore the observed lifetime of the singlet molecular oxygen is expected to depend on concentration of oxygen. The lifetime under air, however, is the same as that under oxygen (33 ± 5 μ s) within the experimental error. This also supports that the lifetime of the singlet molecular oxygen does not reflect that of the triplet carbocyanine dye. The lifetime of singlet molecular oxygen observed (33 ± 5 μ s) is similar to intrinsic lifetimes of singlet molecular oxygen in poly(methyl methacrylate) (~ 20 to 25 μ s) and in polystyrene (~ 17 to 21 μ s) reported by Clough et al.⁵⁹ Thus, we can conclude that the observed lifetime of singlet molecular oxygen in PC is intrinsic. From the values of the diffusion coefficient and lifetime of singlet molecular oxygen, we can estimate the propagation distance of singlet molecular oxygen from the interface between the dye thin film and PC into PC by Fick's law. The diffusion coefficient of molecular oxygen was reported to be 5.5×10^{-8} cm² s⁻¹ in polycarbonate at 25 °C,⁷⁹ and it was estimated that half of the singlet molecular oxygen survived at 33 μ s after the laser excitation surpassed 0.4 μ m.

The amount of singlet molecular oxygen diffused into PC is proportional to the emission intensity immediately after the laser excitation. At present, the emission quantum yield of singlet molecular oxygen in PC is not known and therefore absolute number of the singlet molecular oxygen could not be estimated from the emission intensity. Thus, we estimated the relative amount of singlet molecular oxygen diffused into PC (ϕ_{Δ}^{rel}) by comparing the emission intensity at 1270 nm immediately after the laser excitation. The value of ϕ_{Δ}^{rel} is normalized to that of Et-ClO₄ and is summarized in Table 1. The value of ϕ_{Δ}^{rel} is in the following order: Pr-I (1.6 ± 0.2) = Et-I (1.6 ± 0.2) > Et-ClO₄ (1.0) > Et-F (0.8 ± 0.2). The value of ϕ_{Δ}^{rel} does not depend on substituents on the 1 and 1' positions but on the counterion, suggesting that the formation of singlet molecular oxygen at the interface between the dye thin film and PC is enhanced by the heavy atom effect. However, as mentioned above, the triplet carbocyanine dye could not be observed by the nanosecond transient absorption and therefore the quantum yield of intersystem crossing could not be determined.

Reactivity of Carbocyanine Dyes in the Film State with Singlet Molecular Oxygen. Photodegradation induced by

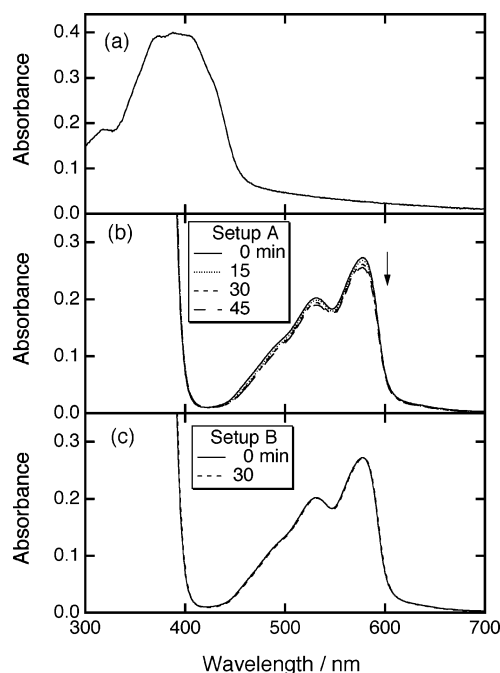


Figure 7. Absorption spectrum of perinaphthenone spin-coated on a quartz plate (a) and absorption spectral changes of Et-CIO₄ spin-coated on a polycarbonate plate by the irradiation in the experimental setups A (b) and B (c) shown in Figure 2.

singlet molecular oxygen should also depend on the reactivity of carbocyanine dyes in the film state with singlet molecular oxygen. To study the reactivity, singlet molecular oxygen was produced by use of the perinaphthenone thin film as a sensitizer which was prepared by spin-coating on a quartz plate. Perinaphthenone is known to be one of efficient sensitizers in solution ($\phi_{\Delta} > 0.9$),⁷¹ and the sensitizer coated on a glass plate is known to be a clean singlet molecular oxygen generator.⁷² The absorption spectrum of the perinaphthenone in the film state is shown in Figure 7a. Its absorption maximum was observed around 400 nm, where the absorption of the carbocyanine dye thin film is very weak as shown in Figure 7b,c. Therefore, to produce singlet molecular oxygen the perinaphthenone thin film was irradiated with 400-nm light. The carbocyanine dye coated on PC was faced to the perinaphthenone coated on a quartz plate with a small intervening gap (0.5 mm) as shown in Figure 2. The perinaphthenone coated on a quartz plate was irradiated from the backside (setup A) or frontside (setup B). Figure 7b shows the absorption spectral change of Et-CIO₄ on PC induced by irradiation of the perinaphthenone thin film in the setup A. Although the absolute value is small, the absorption decreased upon irradiation. In control experiments (setup B), no spectral change was observed during the irradiation as shown in Figure 7c. These indicate that the decrease in the absorption is meaningful and the degradation of Et-CIO₄ in the film state is induced by the singlet molecular oxygen produced on the surface of the perinaphthenone thin film.

Figure 8 shows the change in the absorbance of Et-CIO₄ at 578 nm in the setup A (full circles) and B (open squares) as a function of the irradiation time. Absorbance change is proportional to the irradiation time, and the slope for the setup A (slope A) was $3.6 \times 10^{-4} \text{ min}^{-1}$. The absolute reaction yield of Et-CIO₄ in the film state with singlet molecular oxygen could not be estimated because it is essentially impossible to estimate absolute number of singlet molecular oxygen reached at the surface of the Et-CIO₄ thin film from the surface of the perinaphthenone thin film. Thus, we estimated the relative

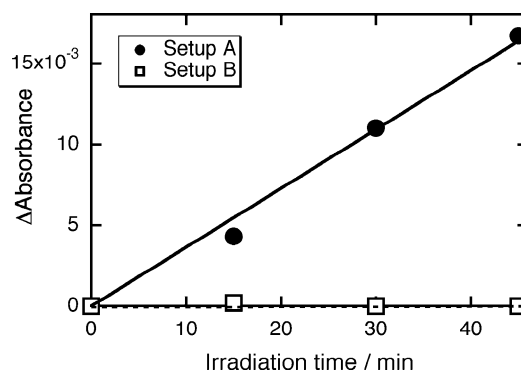


Figure 8. Absorbance changes of Et-CIO₄ spin-coated on a polycarbonate plate observed upon the irradiation in the experimental setups A (full circles) and B (open squares) shown in Figure 2 as a function of the irradiation time.

reactivity ($\phi_{\Delta\text{-cyanine}}^{\text{rel}}$) of carbocyanine dyes in the film state with singlet molecular oxygen by comparing the slope A for these carbocyanine dyes. The value of $\phi_{\Delta\text{-cyanine}}^{\text{rel}}$ is normalized to that of Et-CIO₄ and is in the order Et-CIO₄ (1.0) > Et-F (0.6 \pm 0.1) > Et-I (0.4 \pm 0.1) > Pr-I (0.1 \pm 0.1) (Table 1), indicating that Et-CIO₄ shows relatively high reactivity with singlet molecular oxygen although the formation yield of singlet molecular oxygen is low. Singlet molecular oxygen is quenched by carbocyanine dyes, and therefore, the reactivity of singlet molecular oxygen with carbocyanine dyes may correlate with the quenching rate constant of singlet molecular oxygen by carbocyanine dyes. As mentioned before, k_q in acetonitrile is in the order Et-CIO₄ < Et-I < Et-F < Pr-I and is not necessarily the same order as that of $\phi_{\Delta\text{-cyanine}}^{\text{rel}}$ (Et-CIO₄ > Et-F > Et-I > Pr-I). The difference in the order between k_q and $\phi_{\Delta\text{-cyanine}}^{\text{rel}}$ may be ascribable to the difference between the quenching rate constant in acetonitrile and in the dye thin film. The difference in the order is also ascribable to the fast physical quenching of the singlet molecular oxygen by dyes compared with the chemical quenching.

Effect of Singlet Molecular Oxygen on Photodegradation.

The efficiency of photodegradation induced by singlet molecular oxygen should be proportional to both the formation yield of singlet molecular oxygen and reactivity of carbocyanine dyes in the film state with singlet molecular oxygen ($\phi_{\Delta\text{-cyanine}}$). If the amount of singlet molecular oxygen diffused into PC (ϕ_{Δ}) is assumed to be proportional to the total amount of singlet molecular oxygen produced by irradiation of carbocyanine dyes in the film state, the relative efficiency of photodegradation induced by singlet molecular oxygen ($\Phi_{\text{PD-}\Delta}^{\text{rel}}$) is written as follows:

$$\Phi_{\text{PD-}\Delta}^{\text{rel}} = \phi_{\Delta}^{\text{rel}} \times \phi_{\Delta\text{-cyanine}}^{\text{rel}} \quad (3)$$

The value of $\Phi_{\text{PD-}\Delta}^{\text{rel}}$ is in the following order: Et-CIO₄ (1.0) > Et-I (0.6 \pm 0.2) > Et-F (0.5 \pm 0.2) > Pr-I (0.2 \pm 0.2) (Table 1). Values of $\Phi_{\text{PD-}\Delta}^{\text{rel}}$ well correspond to those of $\Phi_{\text{PD-O}_2}^{\text{rel}}$ (Et-CIO₄ (1.00) > Et-I (0.53 \pm 0.1) > Et-F (0.41 \pm 0.1) > Pr-I (0.15 \pm 0.1)).

We tried to detect the superoxide anion produced by irradiation of carbocyanine dyes in the film state by making use of the chemiluminescence method.⁸⁰ However, chemiluminescence due to the production of the superoxide anion was not observed, suggesting that the formation yield of the superoxide anion is too low to be detected. In the film state, stabilization energy of the superoxide anion is considered to be low compared with solvation energy in the liquid phase. These suggest that photodegradation of carbocyanine dyes in the film

state induced by singlet molecular oxygen is dominant in the whole photodegradation caused by molecular oxygen directly and/or indirectly, although the contribution of photodegradation induced by singlet molecular oxygen could not be estimated.

We also analyzed products formed upon the reaction of Et-ClO₄ in the film state with the singlet molecular oxygen sensitized by the perinaphthenone thin film with GC-MS. Main signals were observed at retention times of 7.1 min ($m/z = 187$), 7.4 min ($m/z = 189$), and 14.2 min ($m/z = 405$). Signals observed at retention times of 7.1 min ($m/z = 187$) and 14.2 min ($m/z = 405$) are the same as those of oxidized products formed by the direct photolysis of Et-ClO₄ under oxygen. These common signals at 7.1 and 14.2 min support that photodegradation of carbocyanine dyes in the film state induced by singlet molecular oxygen is dominant in the whole photodegradation caused by the molecular oxygen directly and/or indirectly. The signal at the retention time of 7.4 min ($m/z = 189$) commonly observed indicates that this is ascribed to the pyrolyzed product or impurity.

In liquid phase (methanol), the contribution of photodegradation induced by singlet molecular oxygen was reported to be only 10–30% for 1-(aryloxy)-2-naphthols.⁴⁰ By irradiation of dicarbocyanine dyes, both singlet molecular oxygen and the superoxide anion were detected in acetonitrile by the spin-trapping technique.⁵⁴ Chen et al. studied the photochemistry of cyanine dyes and carbocyanine dyes in water and reported that the superoxide anion was detected by the spin-trapping technique but singlet molecular oxygen was not detected.⁸ In the liquid phase, the contribution of singlet molecular oxygen on the photodegradation seems to be less important than the superoxide anion for reported systems. In the case of carbocyanine dyes studied, singlet molecular oxygen could not be detected by emission measurements in ethanol (dye concentration is 10^{−6}–10^{−5} M). To examine why singlet molecular oxygen was not detected, we measured the nanosecond transient absorption spectra of carbocyanine dyes in ethanol. The absorption band due to the triplet state was not observed, but that due to the cis form was observed around 550 nm with the lifetime of about 10 μs. This indicates that carbocyanine dyes efficiently give rise to isomer upon excitation, so that singlet molecular oxygen was not observed. However, as mentioned before, singlet molecular oxygen was observed by irradiation of carbocyanine dyes in the film state. The efficiency of photodegradation of carbocyanine dyes in the film state was hundreds times higher than that in solution. In thin film (rigid matrix), the photoisomerization of carbocyanine dyes is considered to be suppressed and the quantum yield of intersystem crossing is expected to be higher than that in ethanol. Therefore, the formation yield of singlet molecular oxygen in the film state is higher than that in ethanol and the photodegradation in solid phase is more efficient than that in solution. Furthermore, fluorescence was not observed for carbocyanine dyes in the film state but was observed in ethanol. It is clear that photodegradation processes of dyes in the film state cannot be inferred from that in solution.

Conclusion

Photodegradation processes of carbocyanine dyes in the film state were studied. We determined the relative efficiency ($\Phi_{PD-O_2}^{rel}$) of the whole photodegradation caused by molecular oxygen directly and/or indirectly. The photodegradation of carbocyanine dyes in the film state was mainly caused by active oxygen species produced in the dye thin film. Singlet molecular oxygen ($^1\Delta_g$) produced at the interface between the dye thin

film and polycarbonate plate was detected by the emission spectroscopy in near-IR region, and its observed lifetime was $33 \pm 5 \mu s$. The relative formation yield (ϕ_{Δ}^{rel}) of singlet molecular oxygen produced at the interface between the dye thin film and polycarbonate plate was determined. The relative reactivity of carbocyanine dyes in the film state ($\phi_{\Delta-cyanine}^{rel}$) was also determined by exploiting a perinaphthenone thin film as a singlet molecular oxygen generator. $\Phi_{PD-O_2}^{rel}$ and $\phi_{\Delta-cyanine}^{rel}$ strongly depend on both substituents on the 1 and 1' positions and the counterion. ϕ_{Δ}^{rel} also depends on the counterion, and the order of ϕ_{Δ}^{rel} is the same as that of the atomic number of halogen atom in the counterion of the carbocyanine dye.

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