Photophysical property of the J-aggregate thin film of an oxacyanine dye prepared by the spin-coating method and enhancement of its photostability by use of polydimethylsilane

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ABSTRACT

The J-aggregate thin film of an oxacyanine dye has been prepared by the spin-coating method on a quartz plate and its photophysical property has been studied. Coherent size of the J-aggregate was estimated to be ca. 4–7 by means of the fluorescence radiative lifetime. Photostability of the J-aggregate thin film and J-aggregate/poly(dimethylsilane) composite thin film has also been examined. Poly(dimethylsilane) vacuum deposited on the J-aggregate thin film was found to markedly enhance the photostability. This stabilization mechanism has been discussed in terms of the electron transfer from poly(dimethylsilane).

1. Introduction

Cyanine dye thin films spin-coated on a polycarbonate substrate are used as recording layers of optical disks because of their high absorptivity, high reflectivity and wide wavelength-selectivity [1]. Recently, development of the optical disks with higher capacity has been desired and much attention has been paid for the dyes having an absorption band in the short-wavelength region. Monomethine oxacyanine dyes exhibit absorption spectra in the wavelength region of 350–400 nm but with a rather low molar absorptivity. The J-aggregate band of cyanine dyes has a higher molar absorptivity than those of the corresponding dye, and is considered to be more suitable to the use for the recording dye. Therefore, it is desirable to develop J-aggregate thin films of monomethine cyanine dyes having an intense absorption band in the short-wavelength region. Yonezawa et al. [2,3] studied the preparation of J-aggregate thin films of N,N′-dioctadecyloxacyanine perchlorate (O–H–H) by use of the LB method. However, the J-aggregate thin film of oxacyanine dye has not been prepared by the spin-coating method, which is conveniently employed to prepare the recording dye layer. In this study, we have examined the preparation of the J-aggregate thin film of a monomethine oxacyanine dye by means of the spin-coating method.

Cyanine dyes are known to be readily photodegraded, and the improvement of its photostability has been an important subject for many researchers [4–7] to develop the recording dye. Koizumi et al. [8] studied oxidative and reductive photodegradation of dye molecules in liquid phase. The oxidative photodegradation process can be summarized as shown in Scheme 1. Upon photo-irradiation, an excited singlet-state dye molecule (^{1}Dye*) is produced, and then by the intersystem crossing (ISC) process its triplet-state molecule (^{3}Dye*) forms. Subsequently, the energy transfer from ^{3}Dye* to the ground-state oxygen (^{3}O$_2$) takes place to form singlet oxygen (^{1}O$_2$). The ^{1}O$_2$ attacks on a dye molecule to induce oxidation. ^{3}Dye* may also transfer an electron to an acceptor (dye and/or ^{3}O$_2$) to form the radical cation (Dye$^{\bullet+}$) of the dye molecule. Thus, ^{3}Dye* is considered to be mainly responsible for the photodegradation involving oxygen. An electron transfer process from ^{1}Dye* to an electron acceptor is also pointed out as another photodegradation process to give Dye$^{\bullet+}$.

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Improvement of the photostability has been achieved by adding a $^1O_2$ quencher such as diimmonium salts [3,4] or metal complexes [6]. Nakazumi et al. [6] employed nickel complex as the $^1O_2$ quencher, and found out that nickel complex enhanced the photostability of cyanine dyes. Morishima et al. [7] proposed a different approach to improve the photostability of indodicarbocyanine dyes; they made use of the electron transfer mechanism. They employed tetracyanoquinodimethane derivatives as a quencher and confirmed that the degradation rate of the dye was effectively reduced. However, these compounds have a disadvantage in the wavelength-selectivity in the shorter wavelength region because of their light absorption.

We succeeded in preparing stable J-aggregate thin films of thiacarbocyanine dyes as 5-chloro-2-[[5-chloro-3-(3-sulfopropyl)-2(3H)-benzothiazolylidene]methyl]-3-(3-sulfopropyl) benzothiazolium hydroxide potassium salt (C–H–Cl) on a polycarbonate and quartz plate by means of the spin-coating technique and studied their photophysical properties [9]. In J-aggregate thin films the formation quantum yield of the triplet state of J-aggregate ($^3J^*$) was found out to be remarkably reduced, indicating that $^1O_2$ is not responsible for the photodegradation of the J-aggregate thin films. Thus, photodegradation of the J-aggregates was ascribable to the electron transfer from the excited singlet-state of J-aggregate ($^1J^*$) to an electron acceptor (counter ion and/or $^3O_2$) to give the radical cation as shown in the dotted-frame in Scheme 1 (in this case Dye means the J-aggregate).

Polysilanes have unique optical and electronic properties associated with the delocalization of σ-electrons of Si–Si main chain and have been expected to be available for micro-electronics, semi-conductors and integrated optics [10,11]. Diaz and Miller [12,13] prepared thin films of various polysilanes such as poly(dimethylsilane) (PDMS) and poly(di-n-hexyl)silane, and studied the oxidation potential. They determined that the oxidation potential of PDMS is 1.0 V vs. SCE. Since the oxidation potential of a monomethine oxacyanine dye on AgBr was determined to be 1.59 V vs. SCE by Tani et al. [14], PDMS is considered to be available for the electron donor to the radical cation of J-aggregate, and as a result for the suppression of the photodegradation.

In this study, we have applied the spin-coating method to the preparation of the J-aggregate thin film of a monomethine oxacyanine dye, and studied the photophysical property and photostability. We have also prepared a composite thin film by the deposition of PDMS on the J-aggregate thin film to examine whether PDMS is available or not for the suppression of the photodegradation. Coherent size of J-aggregates was studied by means of the absorption bandwidth (full width at half maximum) and fluorescence radiative lifetime.
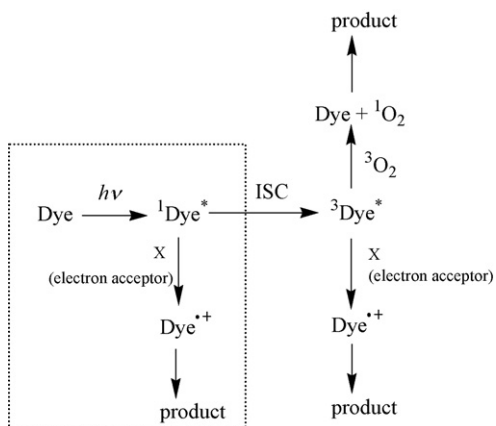
2. Experimental

5-Chloro-2-[[5-chloro-3-(3-sulfopropyl)-2(3H)-benzoxazolylidene]methyl]-3-(3-sulfopropyl)benzoxazolium triethylammonium salt (O–H–Cl) and 5-chloro-2-[[5-chloro-3-(3-sulfopropyl)-2(3H)-benzothiazolylidene]methyl]-3-(3-sulfopropyl)benzothiazolium hydroxide potassium salt (C–H–Cl) were obtained from Hayashibara Biochemistry Research Institute Co., Ltd. Poly(dimethylsilane) (PDMS, average molecular weight: 2×10^3) was obtained from Wako Pure Chem. Ind., Ltd. Molecular structures of these compounds are shown in Scheme 2. Ethanol (Wako Pure Chem. Ind., Ltd. Spectrochem. Anal.) and 2,2,3,3-tetrafluoro-1-propanol (TFP: Tokyo Chem. Co., Ltd. GR >99%) were used as received. Polyvinyl alcohol (PVA) film was kindly provided by Polatechno Co., Ltd. Poly(diallyldimethylammonium chloride) (PDDA) aqueous solution (20 wt%) was obtained from Aldrich Chem. Co. and used after the dilution to 1.0 wt% with water (Millipore Milli-Q). A quartz plate was used as a substrate. The J-aggregate/PDMS composite thin film was prepared by the vacuum deposition of PDMS for 40 min on the J-aggregate thin film using a vacuum deposition system (ULVAC, Inc., VPC-260F) at 5×10^{-3} Pa. The thickness of PDMS thin film was determined to be ca. 600 nm by use of Keyence VF-7500 optical surface morphology measurement microscope. However, we were not able to measure the thickness of J-aggregate thin film, so that we estimated the thickness as follows. The J-aggregate thin film prepared on a 25 mm × 25 mm quartz plate was dissolved into a certain amount of water and the absorption of the solution was measured. Using the Beer–Lambert law, the number of molecules on a substrate was calculated by use of its molar absorptivity in water (96000 M^{-1} cm^{-1}). While, the number of molecules that occupied a layer was estimated by use of the size of the dye molecule calculated by the PM3 method. The number of layers was calculated by dividing the number of molecules on a substrate by that of a layer. As a result, the number

Scheme 1. Photodegradation processes of the dye molecule in solution.
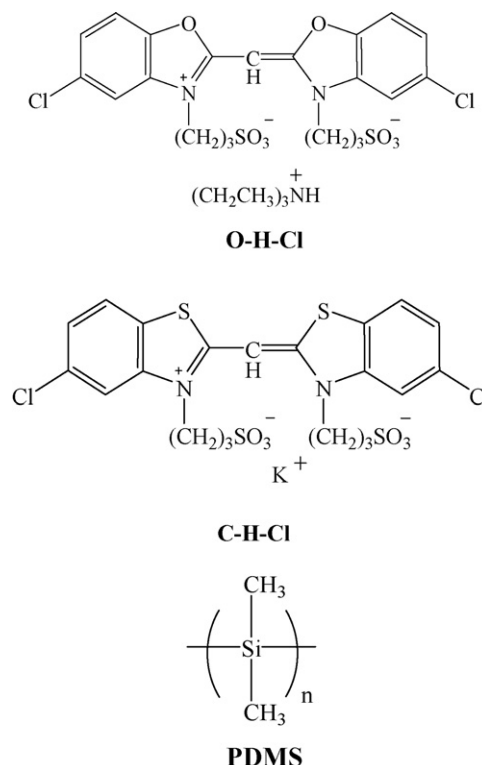
Scheme 2. Molecular structures of O–H–Cl and PDMS.

of layers was determined to be about 50 and the thickness of the film was roughly estimated to be 50 nm.

UV–vis absorption spectra were recorded on a Hitachi U-3300 spectrophotometer. Fluorescence emission and excitation spectra were measured by using a Hitachi F4500 fluorescence spectrophotometer. Fluorescence decay profiles were determined by the time-correlated single photon counting technique using an Edinburgh FL900 CDT fluorescence photometer system in the nanosecond time-region or a femtosecond laser system (Spectra Physics mode-locked Ti; sapphire laser; Tsunami) combined with a detector microchannel plate photomultiplier tube system (Hamamatsu, R3809U-51) in the picosecond time-region. Fluorescence decay profiles were analyzed by deconvolution procedures using a double exponential function, $I(t) = \alpha_1 \exp(-t/\tau_1) + \alpha_2 \exp(-t/\tau_2)$, where α_i and τ_i are the initial fluorescence intensity and lifetime of the ith component, respectively. By use of these values, the weighted mean lifetime of the J-aggregate thin film was determined as to be $\alpha_1\tau_1 + \alpha_2\tau_2$ [9,15–19]. Fluorescence quantum yield (Φ_f) in TFP solution was determined relative to that of anthracene ($\Phi_f = 0.30$) [20]. The Φ_f value of J-aggregate thin films and the composite thin films were determined by the photoluminescence method using a Hamamatsu absolute PL quantum yield measurement system DynaSpect C9920-02 system, which is made up of an excitation light source (150 W xenon lamp), a monochromator, an integrating sphere and a multi-channel spectrometer. Absorption and fluorescence spectra, and fluorescence lifetime and quantum yields were also measured in PVA film. Phosphorescence emission and excitation spectra of O–H–Cl in ethanol and the J-aggregate thin film were determined on a Hitachi F4500 fluorescence spectrophotometer in phosphorescence mode at 77 K. A 300 W xenon short arc lamp (Ushio, UXL-300) was used as an irradiation light source, and light at the wavelength of the absorption maximum of J-aggregate thin films was selected by a monochromator (JASCO, CT-10). The photo-irradiation was carried out under argon or oxygen to examine the photodegradation of the J-aggregate and the composite thin films. Absorbances at the band maxima of these thin films were measured before and after photo-irradiation.

3. Results and discussion

3.1. Photophysical property of O–H–Cl in solution

Fig. 1 shows the absorption (full line), fluorescence emission (dotted line) and excitation spectra (broken line) of 5-chloro-2-[[5-chloro-3-(3-sulfopropyl)-2(3H)-benzoxazolylidene] methyl]-3-(3-sulfopropyl)benzoxazolium triethylammonium salt (O–H–Cl) in TFP. An absorption band was observed with maxima at 370 and
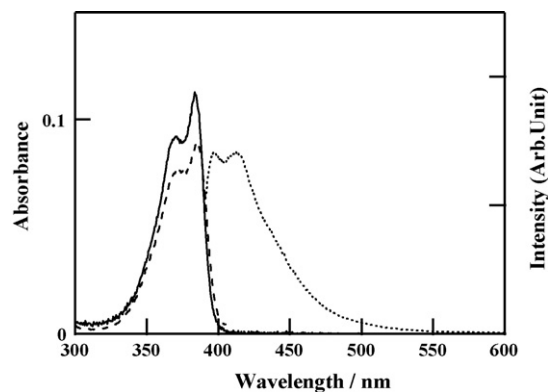

Fig. 1. Absorption (full line), and fluorescence emission (dotted line, excitation at 370 nm) and excitation (broken line, monitored at 415 nm) spectra of O–H–Cl in TFP.

383 nm. Upon the 370-nm light excitation a fluorescence emission band was observed with double peaks at 395 and 412 nm. The excitation spectrum observed by monitoring the fluorescence at 415 nm shows maxima at ca. 370 and 383 nm, in accord with the absorption spectrum. Fluorescence decay profile at 400 nm was measured upon the excitation at 266 nm by means of the time-correlated single photon counting technique and the fluorescence lifetime (τ_f) was determined to be 0.21 ns in TFP. This small τ_f value indicates that the *trans–cis* photoisomerization efficiently takes place [21]. Fluorescence quantum yield (Φ_f) of O–H–Cl in TFP was determined relative to that of anthracene ($\Phi_f = 0.30$) [20], and estimated to be 0.13. Radiative lifetime (τ_f^0), radiative decay rate constant (k_f) and nonradiative decay rate constant (k_{nr}) of the fluorescing state of O–H–Cl in TFP were estimated to be 1.6×10^{-9} s, 6.3×10^8 s^{-1} and 4.2×10^9 s^{-1}, respectively. To suppress the photoisomerization process, O–H–Cl was immersed into a PVA film and τ_f and Φ_f values were determined. The τ_f value in PVA film was 1.9 ns, being 10 times larger than that in TFP and comparable to that (1.6 ns) of the LB film of N,N'-dioctadecyloxyacyanine perchlorate (O–H–H) [22]. The Φ_f value of O–H–Cl in PVA film was determined to be 0.70 ± 0.02. By use of these values, τ_f^0, k_f and k_{nr} of the fluorescing state in PVA film were estimated to be 2.7×10^{-9} s, 3.7×10^8 s^{-1} and 1.6×10^8 s^{-1}, respectively. These photophysical parameters are summarized in Table 1.

Fig. 2 shows the absorption spectrum (full line) of O–H–Cl observed in ethanol at 77 K, and phosphorescence emission (dotted line) and excitation spectra (broken line) determined in phosphorescence mode. This absorption spectrum is similar to that in TFP except the band sharpness. Upon the 380-nm light excitation

Table 1
Photophysical parameters of O–H–Cl

Samples	τ_f (s)	Φ_f	τ_f^0 (s)	k_f (s^{-1})	k_{nr} (s^{-1})	fwhm (cm^{-1})	N^* Eq. (1)	Eq. (2)
M[a]	210×10^{-12}	0.13 ± 0.02	1.6×10^{-9}	6.3×10^8	4.2×10^9	2290 ± 150		
M[b]	1.9×10^{-9}	0.70 ± 0.02	2.7×10^{-9}	3.7×10^8	1.6×10^8	2610 ± 150		
J[c]	126×10^{-12d}	0.30 ± 0.05	4.2×10^{-10}	2.4×10^9	5.6×10^9	660 ± 120	13 ± 5^e, 15 ± 5^f	3.5 ± 1^g, 6.5 ± 1^h
J/PDMS[i]	108×10^{-12d}	0.25 ± 0.03	4.3×10^{-10}	2.3×10^9	6.9×10^9			

[a] O–H–Cl in TFP.
[b] O–H–Cl in PVA film.
[c] J-aggregate thin film.
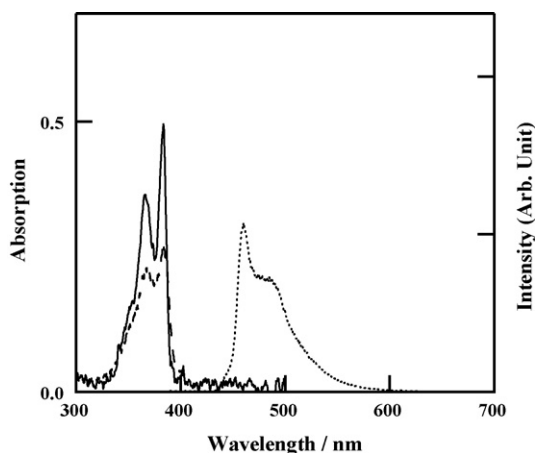[d] Weighted mean fluorescence lifetime (see text).
[e] Determined by use of fwhm in solution.
[f] Determined by use of fwhm in PVA film.
[g] Determined by use of fluorescence radiative lifetime in solution.
[h] Determined by use of fluorescence radiative lifetime in PVA film.
[i] J-aggregate/PDMS composite thin film.

Fig. 2. Absorption (full line), and phosphorescence emission (dotted line, excitation at 380 nm) and excitation (broken line, monitored at 460 nm) spectra of O–H–Cl in ethanol at 77 K in phosphorescence mode.

a phosphorescence emission band was observed with a peak at 460 nm. The excitation spectrum observed by monitoring the phosphorescence at 460 nm is similar to the absorption spectrum.

3.2. Photophysical property of J-aggregate thin film of O–H–Cl

We examined the preparation of the J-aggregate thin film of O–H–Cl by means of the spin-coating method. Fig. 3 shows the absorption spectrum (full line) of the thin film of O–H–Cl prepared by the spin-coating of its TFP solution and successive spin-coating of PDDA solution. This spectrum exhibits an intense absorption band in the wavelength region longer than that in TFP ($\lambda_{max} = 383$ nm) with a maximum at ca. 410 nm, being similar to that of J-aggregates in the LB film of O–H–H [2,3]. Thus, the J-aggregate thin film of O–H–Cl was successfully prepared on a quartz plate by means of the spin-coating method. This film was stable at least 30 days in the dark room. It is noted that O–H–Cl thin film before the spin-coating of PDDA solution shows an absorption band similar to the J-aggregate thin film, accompanied by a weak band in the absorption region of monomer in TFP.

For the J-aggregate thin film of O–H–Cl a fluorescence emission peak (dotted line) was observed at 414 nm upon the 400-nm light excitation. The excitation spectrum (broken line) was observed with a peak at 410 nm by monitoring the fluorescence at 430 nm.
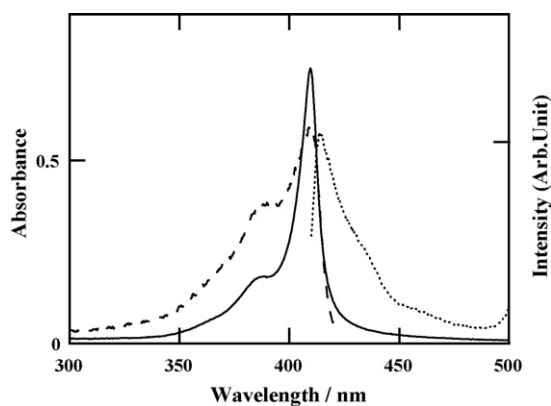
Fig. 3. Absorption (full line), fluorescence emission (dotted line, observed upon 400-nm light excitation) and excitation (broken line, observed by monitoring the fluorescence at 430 nm) spectra of the J-aggregate thin film of O–H–Cl prepared by the spin-coating method with the successive spin-coating of PDDA solution.

The fluorescence decay time-profile was determined by monitoring the emission at 445 nm upon the excitation at 400 nm. This decay time profile could be analyzed by double exponential functions ($I(t) = \alpha_1 \exp(-t/\tau_1) + \alpha_2 \exp(-t/\tau_2)$) [15–19]. The best fitting was obtained with the following parameters: $\alpha_1 = 0.94$, $\tau_1 = 110$ ps, $\alpha_2 = 0.06$ and $\tau_2 = 365$ ps. The weighted mean lifetime was determined to be 126 ± 3 ps, being a little longer than that reported for the LB film of O–H–H (80 ps) [2,3]. The Φ_f value of the J-aggregate thin film of O–H–Cl was determined to be 0.30 ± 0.05, being greater than that of J-aggregate thin film of C–H–Cl [9]. The τ_f^0, k_f and k_{nr} values of the fluorescing state of the J-aggregate thin film were estimated to be 4.2×10^{-10} s, 2.4×10^9 s^{-1} and 5.6×10^9 s^{-1}, respectively. These photophysical parameters are also summarized in Table 1.

We tried to measure the phosphorescence spectrum of the J-aggregate thin film at 77 K by the excitation at the absorption maximum (410 nm), but no phosphorescence was detected, different from the case of O–H–Cl in rigid ethanol solution. This indicates that the formation quantum yield of the triplet state is low in the J-aggregate thin film of O–H–Cl, similar to the case of the J-aggregate thin film of C–H–Cl [9].

3.3. Coherent size of J-aggregates

Coherent size of J-aggregates can be estimated by the following equation (1) [9,24–28]

$$\sqrt{N^*} = \frac{\Delta \nu_{1/2}(M)}{\Delta \nu_{1/2}(J)} \tag{1}$$

where $\Delta \nu_{1/2}(M)$ and $\Delta \nu_{1/2}(J)$ are full width at half maximum (fwhm) of the first absorption bands of the monomer and the J-aggregate thin film, respectively. For O–H–Cl in TFP and in PVA film, $\Delta \nu_{1/2}(M)$ were determined to be 2610 ± 150 cm^{-1} and 2290 ± 150 cm^{-1}, respectively, and $\Delta \nu_{1/2}(J)$ was determined to be 660 ± 120 cm^{-1}. By use of the value in TFP and in PVA film, N^* of the J-aggregate thin film was estimated to be 13 ± 5 and 15 ± 5, respectively, being comparable to those of other cyanine dyes [9,23–27].

Coherent size was also estimated by the following equation

$$\tau_f^0(J) = \frac{1}{N^*} \tau_f^0(M) \tag{2}$$

where $\tau_f^0(M)$ and $\tau_f^0(J)$ are the radiative lifetimes of the monomer and J-aggregate, respectively. For O–H–Cl in TFP and in PVA film, $\tau_f^0(M)$ were determined to be 1.6×10^{-9} s and 2.7×10^{-9} s, respectively, and $\tau_f^0(J)$ was determined to be 4.2×10^{-10} s, and as a result, by use of the value in TFP and in PVA film, N^* of the J-aggregate was estimated to be 3.5 ± 1 and 6.5 ± 2, respectively.

Kuhn and Försterling [28,29] proposed a different way to estimate N^*. They considered that the decrease in excitation energy on going from the monomer to the J-aggregate is given by the sum of bond energies between the N^* coherent dipole oscillators. Therefore, the bond energy for each pair of oscillators is given by $-\Delta E/N^*$, where ΔE is difference in excitation energy between a monomer ($\Delta E(M)$) and J-aggregate ($\Delta E(J)$); $\Delta E = \Delta E(M) - \Delta E(J)$. This energy must agree with the energy kT knocking of this oscillator out of phase by thermal motion, where k and T are Boltzmann constant and absolute temperature, respectively. Therefore, coherent size is given by the following equation [28,29]

$$-\frac{\Delta E}{N^*} = kT \tag{3}$$

In this study, the kT value is 4.11×10^{-21} J ($T = 298$ K). The $\Delta E(M)$ and $\Delta E(J)$ were estimated by use of 0–0 transition energy obtained from the overlap of the first absorption band and fluorescence band as to be 5.09×10^{-19} J (390 nm) and 4.81×10^{-19} J (412 nm), respectively.
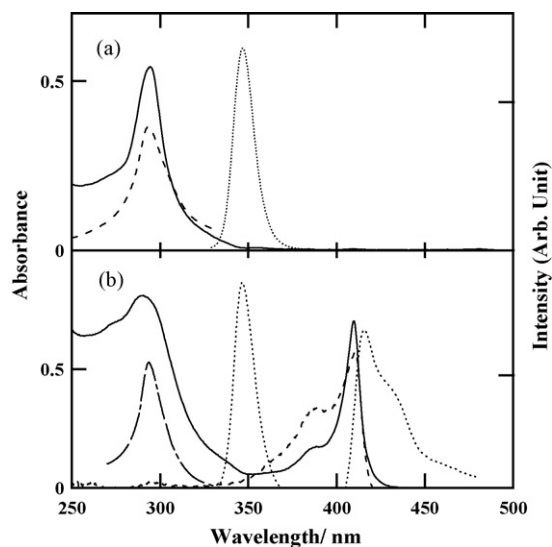
Fig. 4. Absorption (full line), fluorescence emission (dotted line, observed upon 295-nm light excitation) and excitation (broken line, observed by monitoring the fluorescence at 345 nm) spectra of PDMS thin film (a), and absorption (full line), emission (dotted line, observed upon 295-nm and 400-nm light excitation) and excitation (broken line, observed by monitoring the fluorescence at 430 nm) spectra of J-aggregate thin film of the J-aggregate/PDMS composite thin film (b).

Thus, ΔE was determined to be 0.28×10^{-19} J, and N^* was estimated to be 6.8, suggesting that the N^* obtained from radiative lifetime is more plausible than that from fwhm.

3.4. Photophysical property of the composite thin film

Fig. 4a shows the absorption (full line), emission (dotted line) and excitation spectra (broken line) of poly(dimethylsilane)(PDMS) thin film prepared on a quartz plate by vacuum deposition. An absorption maximum was observed at 295 nm and an emission peak was observed at 345 nm upon the 295-nm light excitation. The excitation spectrum was observed with a peak at 295 nm by monitoring the fluorescence at 345 nm. This absorption spectrum is ascribable to the H-aggregate of PDMS [30].

Fig. 4b shows the absorption spectrum (full line) of the composite thin film prepared by the vacuum deposition of PDMS on the J-aggregate thin film of O–H–Cl (J-aggregate/PDMS thin film). There are two absorption bands with a maximum at 295 and 410 nm, being ascribable to PDMS and the J-aggregate of O–H–Cl, respectively, although the 295-nm band of PDMS is somewhat perturbed. The 410-nm absorption band is essentially the same as that of the J-aggregate thin film, indicating that the lowest excited electronic state of the J-aggregate is not perturbed by PDMS. Upon the excitation of the J-aggregate band at 390 nm an emission band was observed with a maximum at 414 nm. Upon the excitation of PDMS band at 295 nm two emission peaks were observed at 345 nm (the fluorescence band of PDMS) and 414 nm (the fluorescence band of the J-aggregate). The excitation spectrum (dashed line) observed by monitoring the fluorescence at 345 nm (PDMS band) shows maxima at 295 nm. The excitation spectrum (broken line) was observed with a peak at 410 nm by monitoring the fluorescence at 430 nm (the fluorescence of J-aggregate), but essentially no excitation spectrum of PDMS was observed. These results indicate that the energy transfer from PDMS to the J-aggregate scarcely takes place and vice versa. The fluorescence decay time profile at 430 nm was determined upon the excitation at 400 nm (J-aggregate band) and was analyzed by double exponential function as in the case of the J-aggregate thin film [9,15–19]. The best fitting was
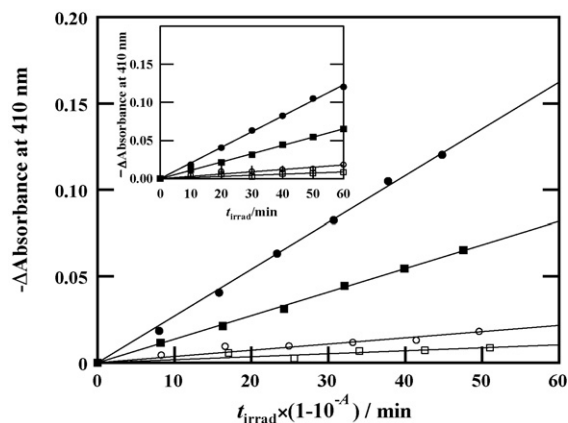
Fig. 5. Decrease in maximum absorbance at 410 nm of J-aggregate thin film (circle) of O–H–Cl and J-aggregate/PDMS composite thin film (square) vs. $t_{irrad} \times (1-10^{-A})$ under Ar (open) and O_2 (closed). Inset shows the decrease in maximum absorbance against the irradiation time (t_{irrad}).

obtained with the following parameters; $\alpha_1 = 0.94$, $\tau_1 = 92 \times 10^{-12}$ s, $\alpha_2 = 0.06$ and $\tau_2 = 314 \times 10^{-12}$ s. The weighted mean lifetime (τ_f) was determined to be 108 ± 3 ps, being shorter by ca. 17% than that of the J-aggregate thin film (126 ps). The Φ_f value of the J-aggregate of the composite thin film was determined to be 0.25 ± 0.03, being smaller by ca. 17% than that of the J-aggregate thin film (0.30 ± 0.05). These results indicate that τ_f^0 value is invariant in the J-aggregate and the J-aggregate/PDMS thin films, and fluorescence of J-aggregates in the composite thin film is quenched by PDMS by 17%. The τ_f^0, k_f and k_{nr} values of the fluorescing state of the J-aggregate thin film were estimated to be 4.3×10^{-10} s, 2.3×10^9 s^{-1} and 6.9×10^9 s^{-1}, respectively. These photophysical parameters are summarized in Table 1. In conclusion, the interaction between the J-aggregate and PDMS is weak but the J-aggregate excited-state is slightly quenched by PDMS in the J-aggregate/PDMS composite thin film.

3.5. Photodegradation of J-aggregate thin film and J-aggregate/PDMS composite thin film

To study the photodegradation of the J-aggregate thin film, we examined the absorption spectral change induced by photo-irradiation of the J-aggregate thin film and J-aggregate/PDMS composite thin film. Inset of Fig. 5 shows the absorbance change ($-\Delta$absorbance) upon the 410-nm light irradiation against the irradiation time (t_{irrad}).

Quantity of degraded dye ([degraded Dye]) is written in terms of total number of absorbed photons (N_{photon}) and an efficiency of the dye to degrade upon absorption of a photon (photodegradation efficiency: PDE) as follows:

$$[\text{degraded Dye}] \propto \text{PDE} \times N_{photon} \tag{4}$$

and N_{photon} is given by the following equation

$$N_{photon} \propto I(1-10^{-A}) \times t_{irrad} \tag{5}$$

where A and I are absorbance of J-aggregate thin film at the wavelength of the incident light and light intensity, respectively. When [degraded Dye] is small, this quantity is proportional to $-\Delta$absorbance; [degraded Dye] $\propto -\Delta$absorbance. As a result,

$$-\Delta\text{absorbance} \propto \text{PDE} \times (1-10^{-A}) \times t_{irrad} \tag{6}$$

Therefore, when $-\Delta$absorbance is plotted against $(1-10^{-A}) \times t_{irrad}$, a linear relationship is expected, and the slope of the line gives the value of PDE. Fig. 5 shows plots of $-\Delta$absorbance of

the J-aggregate thin film (circle) and J-aggregate/PDMS composite thin film (square) under argon (open) and oxygen (closed) against $(1-10^{-A}) \times t_{irrad}$. For these plots linear relationships are observed between $-\Delta$absorbance and $(1-10^{-A}) \times t_{irrad}$ both under argon and oxygen. For the J-aggregate thin film the best fitting was obtained with slopes of $(0.4 \pm 0.03) \times 10^{-3}$ min^{-1} and $(2.80 \pm 0.05) \times 10^{-3}$ min^{-1} under argon and oxygen, respectively. PDE of the J-aggregate thin film under oxygen is ca. 7 times higher than that under argon. For the J-aggregate/PDMS composite thin film, the slope was determined to be $(0.20 \pm 0.03) \times 10^{-3}$ min^{-1} and $(1.40 \pm 0.02) \times 10^{-3}$ min^{-1} under argon and oxygen, respectively. Thus, PDE of the composite thin film both under argon and oxygen are a half of those of the J-aggregate thin films, indicating that PDMS reduced the PDE by ca. 50%. This also means that the screening effect of PDMS from oxygen is not the main factor in the reduction of the photodegradation of the J-aggregate thin film. Since the Φ_f value of the J-aggregate in the composite thin film was smaller by ca. 17% than that in the J-aggregate thin film, the fluorescence quenching is considered to be responsible for the reduction of the photodegradation by at most ca. 34%. Therefore, the main process of the stabilization may be ascribed to the electron transfer from PDMS to the radical cation of the J-aggregate ($J^{\bullet+}$); PDMS may play a role as an electron donor.

Kawasaki et al. [31] reported that the oxidation potential of the J-aggregate film (0.85 V vs. SCE) of C–H–Cl is a little smaller than that of the monomer (0.96 V vs. SCE). The oxidation potential of the J-aggregate of O–H–Cl may be also considered to be close to that of the monomer. Tani et al. [14] also reported that the oxidation potential of 3,3′-diethyloxacyanine iodide (monomethine oxacyanine) on AgBr was 1.59 V vs. SCE, and for the J-aggregate of O–H–Cl a value close to this is expected. The oxidation potential of PDMS was reported to be 1.0 V vs. SCE by Diaz et al. [12,13]. Therefore, the oxidation potential of these thin films on a quartz plate is expected to be in the order of C–H–Cl < PDMS < O–H–Cl, and PDMS is considered to play a role as an electron donor in the O–H–Cl/PDMS system but not in the C–H–Cl/PDMS system.

We examined the photodegradation of the C–H–Cl/PDMS system with the same thickness of PDMS as the O–H–Cl/PDMS system. No stabilization due to PDMS was observed in this case, different from the case of the O–H–Cl/PDMS system. Thus, it is obvious that PDMS does not screen the J-aggregate thin film from oxygen, and the experimental results on the photodegradation of the C–H–Cl/PDMS and O–H–Cl/PDMS systems are reasonably explained by considering the electron transfer from PDMS to $J^{\bullet+}$. As a result, it is concluded that the electron transfer from PDMS to J-aggregate thin film is predominant factor for the stabilization of the O–H–Cl/PDMS system.

4. Summary

The J-aggregate thin film of an oxacyanine dye has been prepared by the spin-coating method on a quartz plate and its photophysical property has been studied. Photostability of the J-aggregate thin film and J-aggregate/PDMS composite thin film has also been examined. PDMS vacuum-deposited on the J-aggregate thin film was found to markedly enhance the photostability. The stabilization of the J-aggregate thin film by PDMS has been explained by considering the electron transfer from PDMS to $J^{\bullet+}$ which is produced upon photo-irradiation.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jphotochem.2008.05.011.

References

[1] T. Ishiguro, E. Hamada, A. Shin, Y. Arai, T. Iwamaru, Electron. Ceram. 18 (1987) 49 (in Japanese).
[2] Y. Yonezawa, A. Yamaguchi, N. Kometani, Phys. Status Solidi (b) 242 (2005) 803.
[3] A. Yamaguchi, Y. Yonezawa, N. Kometani, J. Phys. Chem. B 109 (2005) 1408.
[4] M. Shinkai, K. Namba, Senryo Yakuhin 37 (1992) 185 (in Japanese).
[5] H. Nakazumi, Shikizai 63 (1990) 677 (in Japanese).
[6] H. Nakazumi, E. Hamada, T. Ishiguro, H. Shiozaki, T. Kitao, J. Soc. Dyers Colour 105 (1989) 26.
[7] S. Morishima, K. Wariishi, Y. Inagaki, M. Shibata, T. Ishida, H. Kubo, Jpn. J. Appl. Phys. 38 (1999) 1634.
[8] M. Koizumi, Koukagaku Gairon, Asakura Syoten, Tokyo, (1963), p. 370.
[9] K. Tani, C. Ito, Y. Hanawa, M. Uchida, K. Otaguro, H. Horiuchi, H. Hiratsuka, J. Phys. Chem. B 112 (2008) 836.
[10] R. West, J. Organomet. Chem. 300 (1986) 327.
[11] R.D. Miller, J. Michl, Chem. Rev. 89 (1989) 1359.
[12] A.F. Diaz, M. Baier, G.M. Wallraff, R.D. Miller, J. Electrochem. Soc. 138 (1991) 742.
[13] A.F. Diaz, R.D. Miller, J. Electrochem. Soc. 132 (1985) 834.
[14] T. Tani, S. Kikuchi, K. Honda, Photogr. Sci. Eng. 12 (1968) 80.
[15] R. Adachi, T. Inoue, T. Ogawa, Anal. Sci. 17 (2001) 449.
[16] R. Brunner, A. Bietsch, O. Hollricher, O. Marti, A. Lambacher, Surf. Interface Anal. 25 (1997) 492.
[17] E. Rousseau, M. Van der Auweraer, F.C. De Schryver, Langmuir 16 (2000) 8865.
[18] N. Kometani, H. Nakajima, K. Asami, Y. Yonezawa, O. Kajimoto, J. Phys. Chem. B 104 (2000) 9630.
[19] E. Rousseau, M. Koetse, M. Van der Auweraer, F.C. De Schryver, Photochem. Photobiol. Sci. 1 (2002) 395.
[20] S.L. Murov, I. Carmichael, G.L. Hug, Handbook of Photochemistry, 2nd ed., M. Dekker, New York, 1993, p. 137.
[21] V. Khimenko, A.K. Chibisov, H. Göner, J. Phys. Chem. 101 (1997) 7304.
[22] N. Tamai, H. Matsuo, T. Yamazaki, I. Yammazaki, J. Phys. Chem. 96 (1992) 6550.
[23] K. Kemnitz, K. Yoshihara, T. Tani, J. Phys. Chem. 94 (1990) 3099.
[24] T. Tani, T. Suzumoto, K. Kemnitz, K. Yoshihara, J. Phys. Chem. 96 (1992) 2778.
[25] N. Kometani, H. Nakajima, K. Asami, Y. Yonezawa, O. Kajimoto, Chem. Phys. Lett. 294 (1998) 619.
[26] L. Jeunieau, V. Alin, J.B. Nagy, Langmuir 16 (2000) 597.
[27] E.W. Knapp, Chem. Phys. 85 (1984) 73.
[28] H. Kuhn, H.D. Försterling, Principles of Physical Chemistry, John Wiley & Sons. Inc., New York, 2000, p. 808 (Chapter 23).
[29] T. Kobayashi, J-Aggregates, World Scientific, Singapore, 1996, p. 20, Chapter 1.
[30] Y. Ichino, N. Minami, Chem. Phys. Lett. 343 (2001) 520.
[31] M. Kawasaki, T. Sato, J. Phys. Chem. B 105 (2001) 796.