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Molecular forms and fluorescence processes of 9-aminoacridine in thin sol–gel films

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ABSTRACT

Molecular aggregation and fluorescence processes of 9-aminoacridine (9AA) in thin silica gel films have been investigated by the steady state and time-resolved fluorescence measurements. The monomer of 9AA was the preferential species in the sol–gel reaction systems of tetraethylorthosilicate until the gelation occurred. The 9AA molecules formed the dimer or higher aggregates just after preparing the dip-coated thin film from the sol–gel system. The extent of the aggregation decreased in the film prepared from the system in which the reaction further proceeded. This result indicates that the aggregation in the prepared film was gradually prevented by the steric hindrance of the SiO_2 network with the progress of the sol–gel reaction. The fluorescence properties of 9AA revealed the behavior of the molecules due to the change in the physicochemical environment in the matrix.

1. Introduction

Organic–inorganic hybrid materials consisting of an organic dye and inorganic matrix are expected to be utilized for optical devices such as photo memories [1,2] and photovoltaic cells [3–5]. Glass and ceramics are prepared using the sol–gel reaction of metal alkoxides, which proceeds via hydrolysis and polycondensation reactions [6–8]. This method enables the organic–inorganic hybridization by mixing the organic compounds into the starting solution. The dip-coating with the sol–gel system is a useful way to easily provide such highly functional materials to the inactive plate surface [6–10]. The molecular-order physicochemical properties of the system should vary according to the progress of the reaction. The variations are interesting and important for understanding the fundamental chemical reactions. The absorption and fluorescence spectral measurements elucidate the behavior of the organic molecules in the sol–gel reaction system [11–14]. We previously investigated the relationships between the physicochemical changes during the sol–gel–xerogel transitions and the spectroscopic properties of the organic molecules: 1-naphthol [15–19], benzoquinolines [20,21], and thymol blue [22,23].

Some aromatic dye molecules are easily aggregated and change their photochemical properties. There are many reports of the aggregation of rhodamine dyes and their absorption and fluorescence properties in the sol–gel reaction system [24–27]. One report indicated that the aggregation of rhodamine 6G was prevented in the spin-coated films by the sol–gel reaction [24].

In our previous paper, one monomer and two dimers (H- and J-types) are clearly and simultaneously resolved in the absorption spectra of rhodamine B (RB) in the sol–gel reaction of tetraethylorthosilicate [25]. Furthermore, the thin films containing RB were prepared from the sol–gel reaction system as a function of time after mixing of the reaction systems [26]. The absorption and fluorescence spectra of RB in the individual films were observed as a function of time after the preparation of the thin films. The monomer, H-dimer, and J-dimer of RB were resolved from the absorption spectra of the films, and the monomer and J-dimer of the fluorescent species were resolved from the fluorescence spectra. The relative amounts of the three chemical species of RB existing in the films were estimated by the spectral analysis. The RB molecules in the sol–gel film aggregated just after dip-coating until the SiO_2 network was almost formed. The dimerization in the prepared film was gradually prevented with the reaction progress of the sol–gel system used for the dip-coating. In addition to RB [25–27], methylene blue [28] also tended to be separately encapsulated into the pores of the sol–gel reaction systems of silicon alkoxide as the reaction proceeded.

The aggregation behavior of the excimer-emitting dye is also important for investigating in the sol–gel system [29–33]. The excimer of 9-aminoacridine hydrochloride (9AAHCl) is formed from its dimer in the excited state and emits a fluorescence at room temperature, whereas the dimer directly emits the fluorescence at

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low temperature [29–32]. In this study, the change in the molecular form of the 9-aminoacridine (9AA) species in the thin sol–gel film was investigated as a function of the reaction time by steady state and time-resolved fluorescence spectroscopy. We report the molecular aggregation forms and fluorescence processes of the 9AA species in the films.

2. Experimental

2.1. Materials

An organic dye, 9AAHCl (Aldrich, reagent grade), was purified by three recrystallizations from water. Ethanol, hydrochloric acid, and TEOS (Wako Chemicals, JIS S grade) were used without further purification. The water was deionized and distilled using a Yamato WG23 distiller. Slide glasses for use as the substrate (Matsunami S-1126) were washed with neutral detergents, soaked in a 0.1 M (M = mol dm^{-3}) HCl aqueous solution for 1 h, washed with water and finally dried at room temperature. The slide glasses were used for the UV–vis absorption and fluorescence measurements. A KBr single crystal plate (GL Science GC-KBr) was used as the substrate for the FTIR measurement.

2.2. Sample preparation

9AAHCl was dissolved in ethanol at 2.5×10^{-2} M for the sol–gel reaction. The starting solutions of the sol–gel systems contained 12.0 cm^3 of 9AAHCl in an ethanol solution, 8.0 cm^3 of TEOS, and a 3.0 cm^3 of 1.0×10^{-2} M HCl aqueous solution as the catalyst. The solutions were stirred during the addition, thoroughly stirred for an additional 5 min, and then poured into individual polypropylene vials (50 ml). The vials were closed with a holed cover and kept in a thermostated oven at 35 °C. The thin sol–gel films were prepared by dipping and withdrawing the substrates six times from the sol–gel solution at a speed of 10 mm min^{-1} at room temperature. The dip-coated thin films were made as a function of the reaction time of the prepared solutions. The thickness of the dried dip-coated film was estimated to be ca. 400 nm from their cross section using a field emission scanning electron microscope (Hitachi S-4100).

The steam treatment and heating effects on the fluorescence and FTIR spectra of the thin sol–gel films were investigated. Water was heated to 90 °C and the film samples were exposed to its steam for 1 and 5 min. The other film sample was heated and dried at 100 °C for 5 min.

2.3. Spectral measurements

The UV–vis absorption spectra and fluorescence spectra were observed using a Shimadzu UV-2500 spectrophotometer and a Shimadzu RF-5300 fluorescence spectrophotometer, respectively.

The Ti:Sapphire femtosecond pulse laser and streak scope spectroscopic system were used for the time-resolved fluorescence measurements. The laser system (Clark MXR CPA 2001) generates laser pulses of 150 fs duration (FWHM) with an energy of 750 μJ at 750 nm at a repetition rate of 1 kHz. The second harmonics of the laser pulses (375 nm) was used for the excitation. The fluorescence signal was monitored using a streak scope system (Hamamatsu Photonics C4780).

The FTIR spectra were observed using a Shimadzu FTIR-8300 spectrophotometer.

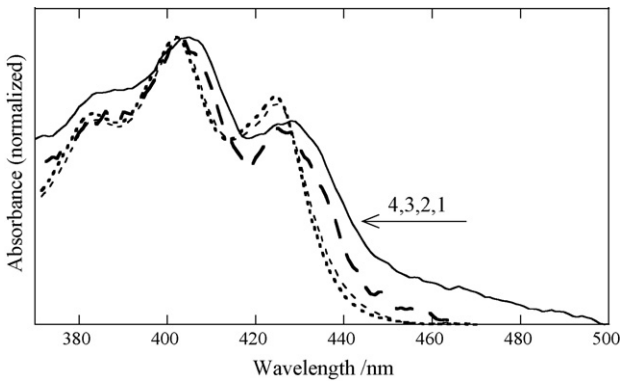

Fig. 1. Absorption spectra of 9-aminoacridine species in the thin films prepared from the sol–gel system reacted for (1) 0 min, (2) 5 min, (3) 1 day, and (4) 7 days.

3. Results and discussion

3.1. Absorption and fluorescence spectra of 9-aminoacridine species in thin sol–gel films

The absorption spectra of the 9AA species were observed in a fluid sol along with the progress of the sol–gel reaction until the gelation occurred. It took 8 days for the gelation in this system. There was little change in the spectrum during the progress of the sol–gel reaction. This spectrum has peaks at 385, 402, and 425 nm and is similar to that observed in ethanol. This spectral behavior indicates that the monomer of 9AA with an ammonium group (monoprotonated species, 9AAH$^+$ [34]) was the preferential species in the system until gelation occurred. There was not a significant change in the concentration of the dye in the system. 9AA species are hard to form the dimer in ethanol compared to in water. The aggregates of the 9AA species were scarcely observed under the present conditions. The effective pH value of the sol–gel reaction systems does not significantly change during the entire sol–gel transition. The pH value was found to be equivalent to ca. 4–6 in water by using the absorption spectrum of thymol blue [22,23]. Consequently, the pH change only slightly influences the molecular forms of the 9AA species during the reaction. The fluorescence spectra of this system were not normally observed due to a strong concentration quenching.

It is difficult to observe the dimer fluorescence spectrum of a highly concentrated solution because of the inner filter effect or the concentration quenching. The preparation of the dip-coated thin film, whose thickness is ca. 400 nm, enabled us to observe the fluorescence spectra of the highly concentrated dye [25–28].

Thin films containing 9AA were prepared from the sol–gel reaction system of TEOS as a function of the reaction time. Fig. 1 shows the absorption spectra of the 9AA species in the individual films. The spectrum of the film prepared just after the preparation of the sol–gel system (0 min) has peaks at around 405 and 430 nm and shoulders at 385–390 and 440–500 nm. The absorption bands at 385–390, 405, and 430 nm and at 440–500 nm are assigned to the J-type dimer and aggregates of 9AAH$^+$, respectively, because they are located at the wavelengths longer than the monomer band [25,26,29–32]. This result indicates that the dimer and higher aggregates were formed just after the preparation of the films although the monomer was the preferential species in the fluid system. With the progress of the sol–gel reaction in the fluid system, these bands were shifted to the shorter wavelength side and became the monomer-like spectrum having peaks at 383, 402, and 425 nm (7 days).

Fig. 2 shows the fluorescence and excitation spectra of the 9AA-containing sol–gel films similar to those shown in Fig. 1. The

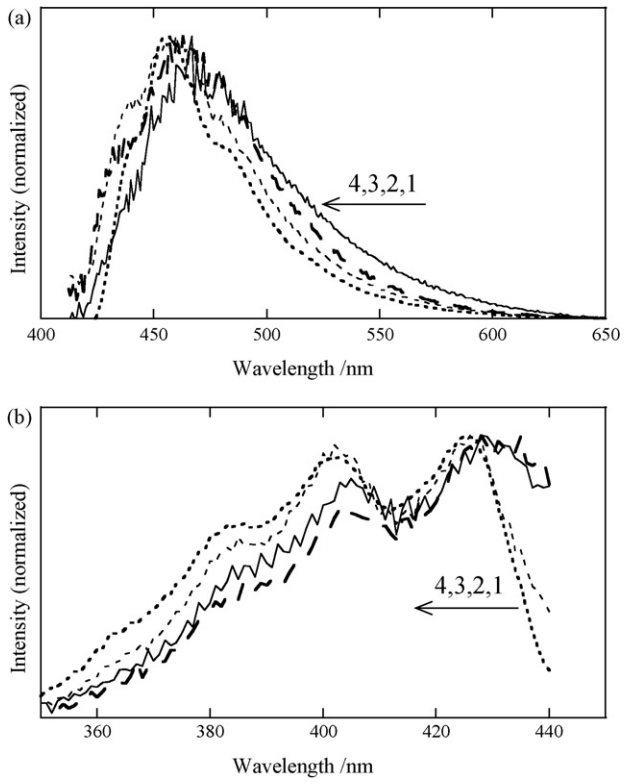

Fig. 2. (a) Fluorescence and (b) excitation spectra of 9-aminoacridine species in the thin films prepared from the sol–gel system reacted for (1) 0 min, (2) 5 min, (3) 1 day, and (4) 7 days. The excitation wavelengths for the fluorescence measurement and the fluorescence wavelength for the excitation measurement are 400 and 530 nm, respectively.

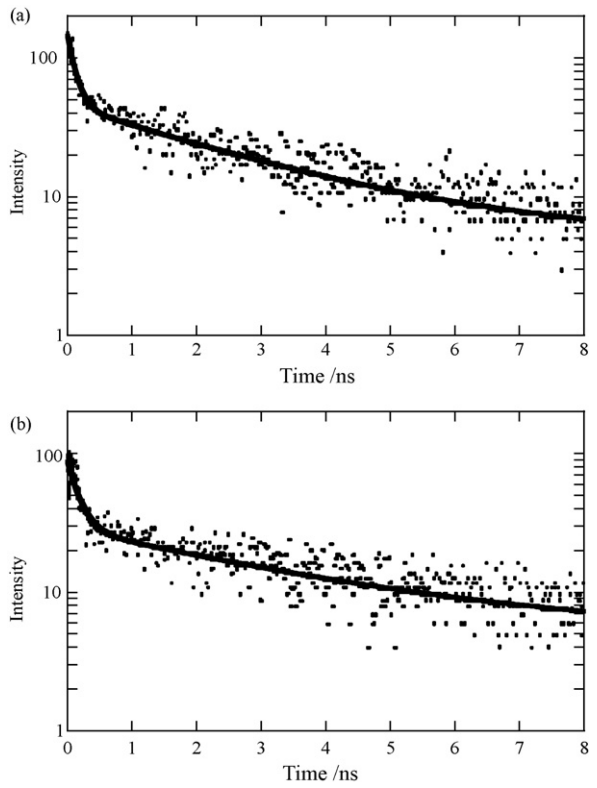

Fig. 3. Fluorescence decay curves of 9-aminoacridine species in the thin film prepared from the unreacted sol–gel system (0-min film). The fluorescence signals were collected in the ranges of (a) 450–500 nm and (b) 500–600 nm and fitted to the double exponential decay curves.

fluorescence spectrum of the film prepared at 0 min exhibits a peak at around 465 nm and shoulders at 430 and 480 nm. This spectrum is not assigned to $9AAH_2^{2+}$ [30,34] due to the acidity in the present system. The 465–480 nm band can be assigned to the J-dimer [29–32]. The fluorescence of the excimers or higher aggregates was not clearly found. The relative intensity of the J-dimer band decreased with the sol–gel reaction time. The fluorescence spectrum of the film prepared at 7 days was that of the monomer having the peak at 456 nm and the shoulders at 440 and 480 nm. The peaks and shapes of the fluorescence excitation spectra of all the films are similar to those of the relevant absorption spectra except the aggregates band, indicating that the fluorescence species of the J-dimer originate from those in the ground state.

3.2. Time-resolved fluorescence measurements of 9-aminoacridine species in thin sol–gel films

Fig. 3 shows the fluorescence decay curves of the 9AA species in the thin sol–gel film prepared at 0 min. The fluorescence signals were collected in the ranges of 450–500 and 500–600 nm and fitted to the double exponential decay curves. The fitting parameters are shown in Table 1. The decay curves consist of two components; i.e., the main component with the shorter lifetimes of 0.11 and 0.13 ns, and the minor component with the longer lifetimes of 2.6 and 3.4 ns. However, these signals were very weak and the some noise was observed. The shorter lifetime can be attributed to the optical background due to light scattering. The longer lifetime component is assigned to the J-dimer as reported for the 9AA microcrystals, 2.3–2.6 ns [32]. The longer lifetime is equivalent to that of the 9AA species in the compacted silica matrix prepared by the sol–gel method, 2.4 ns [33], which can be assigned to the J-dimer. It was reported that the nonfluorescent H-dimer exist in the such sol–gel films in addition to the fluorescent J-dimer [25–27]. The dimmers having both H- and J-characteristics should exist in such heterogeneous solids [25–27,33]. Some 9AA molecules should be densely packed in the limited silica pores. The 9AA concentration in the films is estimated to be >0.1 M. The fluorescence lifetime of the J-dimer in the present study is much shorter than that observed in the low temperature solvent [29,30] because the fluorescent or nonfluorescent aggregates quench the fluorescent species in the pores [32,33,35]. The weakly fluorescent aggregates having both H- and J-characteristics act as quenchers in the sol–gel matrix [33,35]. The absorption band of the aggregates at 440–500 nm overlaps with the fluorescence band of the 9AA species.

Table 1
Fluorescence decay parameters of 9AA species in the thin sol–gel film prepared at 0 min. The fluorescence decay signals were collected in the ranges of 450–500 and 500–600 nm and fitted to the double exponential decay curves.

Range (nm)	A_1	τ_1 (ns)	A_2	τ_2 (ns)
400–500	0.92	0.11	0.08	2.6
500–600	0.94	0.13	0.06	3.4

Fig. 4 shows the time-resolved fluorescence spectra of the 0-min film in the time range of 0.1–8.6 ns. The spectrum in the 0.1–1.0 ns time range consists of the component decreasing from the shorter wavelength and that having the peak at around 470 nm. The former quickly decays and is hardly seen in the spectra observed after the elapsed time of 1.1 ns. The latter gradually decays in the collected time range. The former and latter should be assigned to the optical background and the J-dimer, respectively, due to the measurements of the fluorescence lifetime and the time-resolved fluorescence spectra. These time-resolved fluorescence analysis

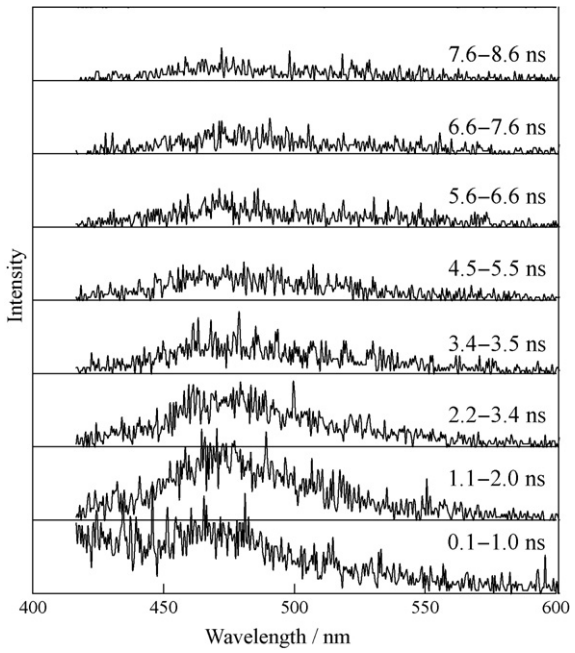

Fig. 4. Time-resolved fluorescence spectra of the 0-min film in the time range of 0.1–8.6 ns.

revealed the superposition of the steady state spectra due to some species.

Fig. 5 shows the fluorescence decay curves of the 9AA species in the thin sol–gel film prepared at 1 day, observed in the ranges of 420–445, 445–470, 478–490, and 520–555 nm and fitted using the double exponential decay curves accompanied with the fitting parameter as shown in Table 2. The fractions of both components

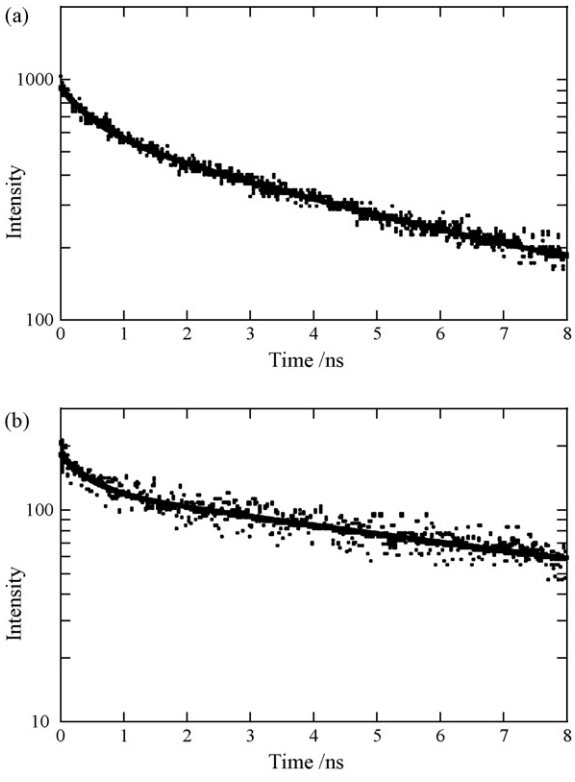

Fig. 5. Fluorescence decay curves of 9-aminoacridine species in the thin film prepared from the sol–gel system reacted for 1 day (1-day film). The fluorescence signals were collected in the ranges of (a) 445–470 nm and (b) 520–555 nm and fitted to the double exponential decay curves.

Table 2
Fluorescence decay parameters of 9AA species in the thin sol–gel film prepared at 1 day. The fluorescence decay signals were collected in the ranges of 420–445, 445–470, 478–490, and 520–555 nm and fitted to the double exponential decay curves.

Range (nm)	A_1	τ_1 (ns)	A_2	τ_2 (ns)
420–445	0.48	0.38	0.52	3.7
445–470	0.43	0.59	0.57	3.8
478–490	0.42	0.26	0.58	3.6
520–555	0.46	0.43	0.54	7.5

are almost the same values. The shorter lifetime component can be assigned to the optical background. The longer lifetime component is assigned to the monomer or J-dimer. The lifetime of 3.6–3.8 ns, observed at 420–445, 445–470, and 478–490 nm, is assigned to the monomer and that of 7.5 ns, observed at 520–555 nm is assigned to the J-dimer. The weak J-dimer fluorescence was observed at the wavelengths longer than its peak because its main band was hidden by the strong monomer fluorescence at 420–500 nm. The lifetime of the J-dimer is equivalent to that of the 9AA species in the pre-micellar aggregates of sodium dodecyl sulfate (SDS), 7.1 ns [36]. The monomer and dimer of 9AA species are densely packed in the pre-micellar aggregates, i.e., SDS clusters. In such system, the lifetime of the monomer quenched by the dimer was shorter than that of the dimer [37,38]. The lifetime of the J-dimer in the 1-day film is longer than that in the 0-day film. These results indicate that the aggregates as quenchers decreased in the film prepared from the sol–gel system aged for a longer time. However, the lifetime values of the monomer and J-dimer observed in the present study are much shorter than those in water or organic solvents [29–31,34]. The present results agree with the fact that the lifetime of the J-dimer was longer than that of the monomer [29,30].

Fig. 6 shows the time-resolved fluorescence spectra of the 1-day film in the time range of 0.2–8.5 ns. The spectrum observed in the time range of 0.2–1.0 ns has a peak at around 455 nm and shoulders at around at 430 and 480 nm, originating from the monomer fluorescence. The spectra become broader with the elapsed time after excitation. The spectrum for 7.5–8.5 ns exhibits a peak at around

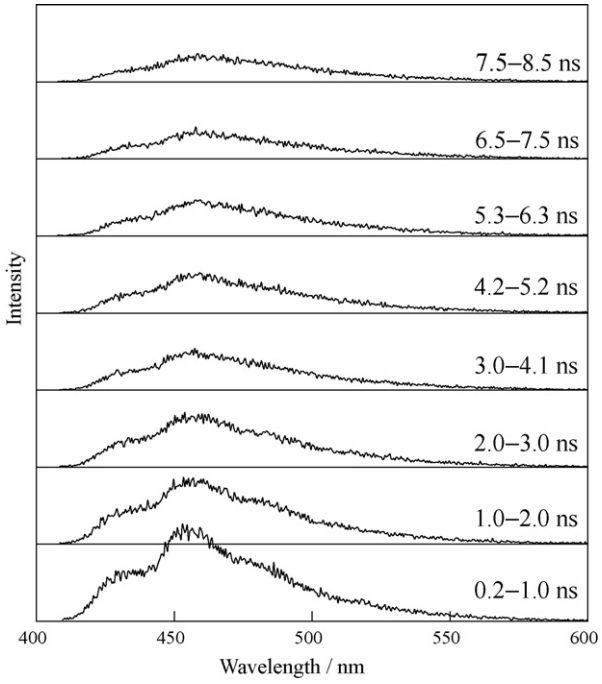

Fig. 6. Time-resolved fluorescence spectra of the 1-day film in the time range of 0.2–8.5 ns.

Table 3
Absorption and fluorescence band positions and fluorescence lifetimes of 9AA species in the sol–gel reaction systems of TEOS.

Species	Absorption band position (nm)	Fluorescence band position (nm)	Fluorescence lifetime (ns)
$9AAH^+$ monomer	385, 402, 425	456	17.1 (bulk gel) 3.6–3.8 (1-day film)
$9AAH^+$ J-dimer	385–390, 405, 430	465–480	2.6, 3.4 (0-min film) 7.5 (1-day film)
$9AAH^+$ aggregates	440–500	–	–

470 nm, originating from the J-dimer. These results correspond to those of the fluorescence lifetime.

On the other hand, even the film prepared at 7 days contained some aggregates due to their fluorescence analysis. The bulk gel containing a small amount of 9AA species (2.5×10^{-4} M) exhibited a monomer fluorescence having the lifetime of 17.1 ns, which was close to that in ethanol. This value is similar to the lifetime of $9AAH^+$ in water and organic solvents [29–31,34]. The molecules of 9AA are easy to aggregate in the sol–gel film, resulting from the environment surrounding the molecules affected by the rapid formation of silica networks during the dip-coating [26–28]. The assigned absorption and fluorescence band positions and fluorescence lifetimes of the 9AA species are summarized in Table 3.

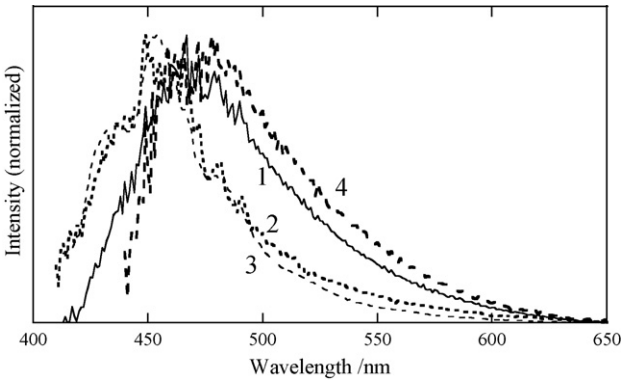

Fig. 7. Fluorescence spectra of 9-aminoacridine species in the 0-min film (1) as-prepared, after (2) 1-min and (3) 5-min steam treatments, and (4) after 5-min heating.

3.3. Aggregation of 9-aminoacridine species in the thin sol–gel films

In acid-catalyzed sol–gel systems in the same manner as this study, the –SiOSi– polymers linearly lengthen and form cross-linked networks along with the progress of the sol–gel reaction [8]. These results lead to the concept of the microscopic configurational relationships between dye molecules and the –SiOSi– polymers in a fluid sol and in the dip-coated films [26].

The monomer 9AA was the preferential species in the systems of the sol–gel reaction of TEOS until gelation occurred. In the fluid system, two or more 9AA molecules can be in a certain structural region (prestructure of the pores) during the initial stage of the sol–gel reaction (long before the gelation point). Separation of the 9AA molecules in such a region gradually increases by growing –SiOSi– networks around the 9AA molecules that increase with the progress of the reaction. The configuration during the final stage of the reaction occurs after the sol–gel reaction proceeded to some extent. On the other hand, preparing a film rapidly produces more networks and condensation in the system. The aggregation of the 9AA molecules in the thin film was promoted just after dip-coating until the formation of the SiO_2 networks in the system proceeds to some extent. The growth of the networks depends on the reaction conditions of the sol–gel system. The distribution of the 9AA molecules in the dip-coated film reflects the situation in the fluid sol in which the film was prepared; the extent of the aggregation of the 9AA molecules in the film depends on the physical restraint in the fluid system. The degree of aggregation decreased with the reaction time of the sol–gel system. Under the reaction conditions, following the evaporation of ethanol and water in the film, and the 9AA species are aggregated and deposited in the pore structure of the film. These results indicate that the solvent evaporation plays an important role in the formation of the dimers or higher aggregates. These phenomena are similar to that of the systems containing rhodamine B and methylene blue [26–28].

Fig. 7 shows the fluorescence of the 9AA species in the as-prepared 0-min film, after steam treatment for 1 and 5 min, and after heating for 5 min. The film exhibits a broad fluorescence band at 430–600 nm. The fluorescent spectra of the film changed to the monomer-like spectrum after the 1- and 5-min treatments. The spectra observed after the treatment exhibited a peak at around 450 nm and the shoulder at around 430 nm like those of the 1-day film. On the other hand, the J-dimer band at longer than 480 nm was enhanced after heating because the dye aggregation was promoted by shrinkage of the pore volume.

As shown in Fig. 8, the FTIR spectra of these samples exhibit bands due to the O–H stretching (around 3300 cm^{-1}) and bending (around 1650 cm^{-1}) modes of the Si–OH and the adsorbed water and due to the Si–O stretching mode of the Si–O–Si (around 1100 and 790 cm^{-1}) and Si–OH (around 930 cm^{-1}) [39–41]. The absorbance due to the Si–OH is relatively strong in the as-prepared 0-min film, compared to the 1-day film because the polymerization of the alkoxide species progresses less. The relative intensity of the band due to the Si–O–Si increased and those due to Si–OH decreased by the steam treatment. The polymerization of the Si–OH was observed by heating as expected. Hot water promotes the hydrolysis and sequential polymerization of the silicon alkoxide species, resulting in the reorientation of the silica networks. It is suggested that the aggregates of the 9AA species were dissociated and reoriented by the hot water and the change in the silica networks. Steam treatment at 80–100 °C was previously found valid to promote the polymerization of the alkoxide species and the particle

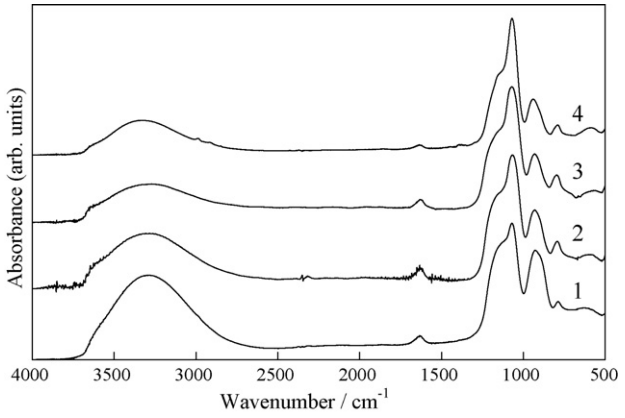

Fig. 8. FTIR spectra of the 0-min film (1) as-prepared, and after (2) 1-min and (3) 5-min steam treatments, and (4) the as-prepared 1-day film.

growth in the sol–gel systems [42–44]. Only heating the samples at such a temperature cannot change the 9AA orientation although it promotes the polymerization of the alkoxide species. In consequence, the dye aggregation was promoted by shrinkage of the pore volume.

4. Conclusions

The steady state and time-resolved fluorescence measurements revealed the molecular aggregation and fluorescence processes of the 9AA species in the thin silica gel films. The monomer 9AA species was the preferential species in the systems of the sol–gel reaction of TEOS. The fluorescent species exhibiting the lifetime of 2.6–3.4 ns assigned to the J-dimer was observed in the film prepared from the as-prepared sol–gel system. The fluorescence components having the lifetime of 3.6–3.8 ns assigned to the monomer and 7.5 ns assigned to the J-dimer were observed in the film prepared from the sol–gel system that reacted for 1 day. These species were quenched by the nonfluorescent aggregates and their lifetime values were shorter than those observed in the homogeneous systems. 9AA molecules formed the dimer or higher aggregates just after preparing the dip-coated thin film from the sol–gel system. The extent of the aggregation decreased in the film prepared from the system in which the reaction further proceeded. This result indicates that the aggregation in the prepared film was gradually prevented by the steric hindrance of the SiO_2 network with the progress of the sol–gel reaction. The relationship between the molecular forms and fluorescence process of 9AA revealed the behavior of the molecules due to the change in the physicochemical environment in the matrix.

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