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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<sub>2</sub> 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.

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## 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 fluores-

cence 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<sub>2</sub> 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 ( $M = \text{mol dm}^{-3}$ ) 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  $2.5 \times 10^{-2}$  M for the sol–gel reaction. The starting solutions of the sol–gel systems contained 12.0 cm<sup>3</sup> of 9AAHCl in an ethanol solution, 8.0 cm<sup>3</sup> of TEOS, and a 3.0 cm<sup>3</sup> of  $1.0 \times 10^{-2}$  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<sup>-1</sup> 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.

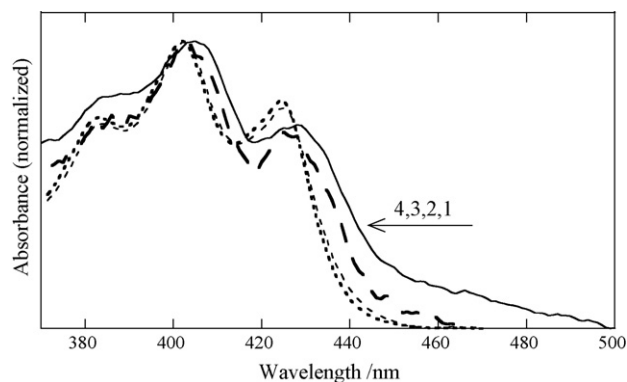


Fig. 1. Absorption spectra of 9-aminoacridine species in the thin films prepared from the sol–gel system reacted for (1) 0 min, (2) 5 min, (3) 1 day, and (4) 7 days.

## 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<sup>+</sup> [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<sup>+</sup>, 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

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