

# Chelation of spironaphthoxazine with zinc ions and its photochromic behavior during the sol–gel–xerogel transitions of alkyl silicon alkoxide

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## Abstract

The isomerization and zinc-chelation of spironaphthoxazine (SNO) during the course of the sol–gel–xerogel transitions of the tetraethylorthosilicate (TEOS) system and the mixture systems of TEOS and octyltriethoxysilane (OcTES) have been investigated by measuring the fluorescence and excitation spectra as a function of time. The influence of the hydrophobic octyl groups on the spectroscopic behavior of SNO in the TEOS and TEOS–OcTES systems containing zinc ions have been discussed. A fluorescence spectrum at around 430 nm, observed just after the preparation of the TEOS system, was similar to that of SNO observed in protic highly-polar solvents due to the presence of the ethanol solvent in the system. A weak fluorescence spectrum was observed at around 400 nm just after the preparation of the TEOS–OcTES systems. This spectrum corresponded to that of SNO in low-polar solvents due to the hydrophobicity of OcTES. The fluorescence spectra in both systems were gradually red-shifted to around 450 nm along with the progress of the sol–gel transition, indicating that SNO (ring-closed form) interacts with silanol groups generated by the hydrolysis of the alkoxides. A spectrum due to the zinc complex of the SNO-derivative, merocyanine (MC, ring-open form), also appeared at around 540 nm during the initial stage of the sol–gel–xerogel transitions (around the gelation point) for both systems. SNO molecules and zinc ions were concentrated in prestructural pores and easily interacted with each other. The fluorescence intensity of the complex in the TEOS–OcTES systems, however, was remarkably lower than that in the TEOS system due to the hydrophobicity of the system. Depending on changes in the polarity and volume of the space containing the species, the complex fluorescence intensity increased and decreased. In the TEOS–OcTES systems, the non-complex band was blue-shifted around the gelation point since the polymerization of the silanol groups preferentially occurred and the polarity decreased in the system containing hydrophobic groups. In the gel of the TEOS system and the sol of the TEOS–OcTES system, a photochromic reaction was observed, i.e., SNO formed the MC–Zn complex during UV irradiation, whereas a change was hardly observed during visible irradiation. In the xerogel of the TEOS system and in the gel and xerogel of the TEOS–OcTES system, a reversible photochromic reaction was observed, i.e., the MC–Zn complex was associated and dissociated by UV and visible irradiation, respectively.

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**Keywords:** Chelation; Spironaphthoxazine; Fluorescence; Sol–gel method; Photochromism

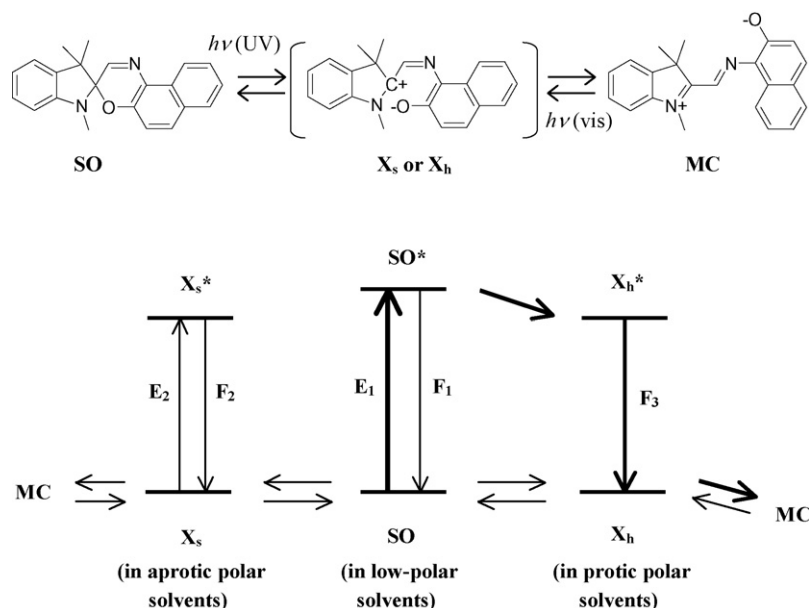
## 1. Introduction

The photochromism of organic compounds in solid matrices is an important phenomenon to provide a photochemical technique for development of electronic devices such as photo-quantum memory [1–4]. However, it is difficult to produce large single crystals of organic photochromic compounds and control their photoreaction [5,6]. Some solid systems have been easily prepared by incorporating such photochromic compounds

into polymers [7–11] and clay minerals [12–19]. For effective photochromism, one needs to control the isomerization and photochemical properties of the molecules in order to perform fast photo switching. Therefore, it is important to study the reactions of such organic molecules in narrow spaces where their motion is restricted.

Spirooxazines (SOs) exhibit the well-known photochromic reaction of photo-induced interconversion between the original colorless form and the colored merocyanine (MC) form [2,4]. The MC easily coordinates to specific metal ions (e.g.,  $Zn^{2+}$ ) in solution, and forms fluorescent and non-fluorescent MC–M complexes, the former is stable to heat and visible light while the latter is unstable [20,21].

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Scheme 1. Molecular forms and fluorescence processes of SNO species in solvents.

We previously reported the details of the fluorescence and excitation spectra of SO in various solvents [22]. Two types of fluorescent intermediate species ( $X_s$  and  $X_h$ ) were intervened between SO and MC by cleavage of the spiro C–O bond, as shown in Scheme 1 [13,23]. In low-polar solvents such as benzene, upon the excitation of SO ( $E_1$ ) the 390 nm fluorescence ( $F_1$ ) was normally emitted from its excited state ( $\text{SO}^*$ ). In aprotic polar solvents such as acetonitrile, part of the SO molecules were transformed into a non-planar, strongly solvated species ( $X_s$ ). The transition from the species  $X_s$  to  $X_s^*$  ( $E_2$ ) is followed by the 450 nm fluorescent emission ( $F_2$ ). In protic polar solvents such as ethanol and water, part of the SO molecules are normally excited to  $\text{SO}^*$  ( $E_1$ ) to produce the hydrogen-bonded species ( $X_h^*$ ) by the C–O bond breakage in the excited states, followed by the 430 nm fluorescent transition to  $X_h$  ( $F_3$ ). The species  $X_h$  was immediately transformed into SO or MC in the ground state. The fluorescence of the MC–Zn complex is observed at around 540 nm by UV irradiation to SO and  $\text{Zn}^{2+}$  in aprotic polar solvent such as acetone and acetonitrile.

The sol–gel method enables us to prepare the functional solid materials containing organic and/or organometallic compounds at low temperature. Many investigations of the photochromic behavior of SOs in the systems involving the sol–gel–xerogel transitions have been reported [24–29]. Clarifying the microscopic change in such a system is necessary to control the photoreaction of the compounds. The microscopic properties are, however, very complex, in which the physicochemical properties were investigated by in situ spectroscopic measurements using a molecular probe [30–36].

In our previous studies, we observed the fluorescence photochromic behavior, that is the photo-induced interconversion between  $X_s$  and the MC–Zn complex in the hydrophobic interlayers of montmorillonite clay modified by organic surfactants [12,13] and in the xerogel prepared from silicon alkoxide [23]. The xerogel system also contained the MC–SiOH complex

like the MC–Zn because there were many SiOH groups on the surface of the gel pores in which the organic molecules are encapsulated [23,24,26,29,36]. No interconversion occurred in the surfactant-free montmorillonite. The spaces filled with alkyl groups are suggested to provide a reaction field suitable for the chelation of SNO because of their polarity and volume.

In this study, we observed the isomerization and zinc-interaction of spironaphthoxazine (SNO) and the changes in its fluorescence properties during the sol–gel–xerogel transitions of the silicon alkoxide and alkyl silicon alkoxide systems including SNO and  $\text{Zn}^{2+}$ . The photochemical properties obtained from the fluorescence spectroscopy and reaction due to light irradiation were investigated in order to clarify the influence of the hydrophobicity and polarity in the systems of the sol–gel–xerogel transitions on isomerization and Zn-chelation of SNO.

## 2. Experimental

SNO was synthesized and purified according to a procedure described elsewhere [37]. Ethanol (S grade), tetraethylorthosilicate (TEOS) (S grade), zinc chloride (S grade), and  $5.0 \text{ mol dm}^{-3}$  hydrochloric acid (for volumetric analysis) were purchased from Wako Pure Chemicals, and used without further purification. *n*-Octyltriethoxysilane (OcTES) purchased from Tokyo Kasei Kogyo was used without further purification. Deionized and distilled water was used for preparing the solutions.

An SNO ethanol solution and a zinc chloride ethanol solution were prepared and adjusted to  $1.0 \times 10^{-3}$  and  $1.0 \times 10^{-2} \text{ mol dm}^{-3}$  concentrations, respectively. Hydrochloric acid was diluted with water and adjusted to a concentration of  $1.0 \times 10^{-5} \text{ mol dm}^{-3}$ . The TEOS systems, with (Oc0–Z10 system) and without (Oc0–Z0 system) Zn, and the mixture systems

Table 1  
Compositions of the sol–gel reaction systems

System	TEOS:OcTES <sup>a</sup>	SNO (cm <sup>3</sup> ) <sup>b</sup>	ZnCl <sub>2</sub> (cm <sup>3</sup> ) <sup>c</sup>	Ethanol (cm <sup>3</sup> )	TEOS (cm <sup>3</sup> )	OcTES (cm <sup>3</sup> )	HCl (cm <sup>3</sup> ) <sup>d</sup>
Oc0–Z10	100:0	0.50	0.50	9.00	10.00	0	1.60
Oc0–Z0	100:0	0.50	0	9.50	10.00	0	1.60
Oc50–Z10	50:50	0.50	0.50	9.00	5.00	7.06	1.60
Oc50–Z0	50:50	0.50	0	9.50	5.00	7.06	1.60
Oc75–Z10	25:75	0.50	0.50	9.00	2.50	10.59	1.60

<sup>a</sup> Molar ratio, TEOS: tetraethyl orthosilicate, OcTES: *n*-octyltriethoxysilane.

<sup>b</sup> A  $1.0 \times 10^{-3}$  mol dm<sup>-3</sup> in ethanol solution.

<sup>c</sup> A  $1.0 \times 10^{-2}$  mol dm<sup>-3</sup> in ethanol solution.

<sup>d</sup> A  $1.0 \times 10^{-5}$  mol dm<sup>-3</sup> in aqueous solution.

of TEOS and OcTES, with (Oc50–Z10 and Oc75–Z10 systems) and without (Oc50–Z0 system) Zn, were prepared. The Z10 and Z0 mean that the molar ratios of Zn to SNO included in this solution are 10 and 0, respectively. The Oc0, Oc50, and Oc75 refer to molar ratios of OcTES to the sum of TEOS and OcTES of 0, 50, and 75, respectively. All the TEOS and the TEOS–OcTES systems contain an equal amount of silicon. The compositions of these systems are shown in Table 1. Each solution was stirred for 5 min using a magnetic stirrer. The fluorescence and excitation spectra were measured as a function of time along with the sol–gel–xerogel transitions using a Shimadzu RF-5300PC fluorescence spectrophotometer. The fluorescence spectra were observed upon excitation at 370 and 450 nm, and the excitation spectra were observed at 420, 500, and 540 nm. For the sol, gel, and xerogel samples of the TEOS and TEOS–OcTES systems containing Zn, the changes in the fluorescence spectra by UV (350 ± 10 nm) irradiation for 120 min and visible (450 ± 10 nm) irradiation for 240 min were observed in order to study the photochromic behavior.

### 3. Results and discussion

#### 3.1. Measurements of fluorescence and excitation spectra as a function of reaction time

Fig. 1 shows the fluorescence and excitation spectra of the TEOS system containing Zn (Oc0–Z10 system). The excitation wavelengths for the fluorescence spectra are 370 and 450 nm and the emission wavelength for the excitation spectra is 500 nm. Just after the sample preparation (at day 0), the fluorescence and excitation spectra have peaks at around 430 and 350 nm, respectively, and are similar to those of SO in ethanol. The fluorescence is assigned to the hydrogen-bonded species  $X_h^*$ . As the hydrolysis of the silicon alkoxides occurred, the fluorescence peak was red-shifted due to an increase in the amount of SiOH groups. The gelation of this system occurred at 5 days, when the bands at around 540 and 460 nm assigned to the MC–Zn complex appeared in the fluorescence and excitation spectra, respectively. As the reaction further proceeded, the intensity of the complex bands decreased during evaporation of the solvents from the pores. The bands of the strongly solvated species  $X_s^*$  then appeared at around 450 and 380 nm in the fluorescence and excitation spectra, respectively, because polymerization of the SiOH groups formed the –SiOSi– networks, and the hydrogen-

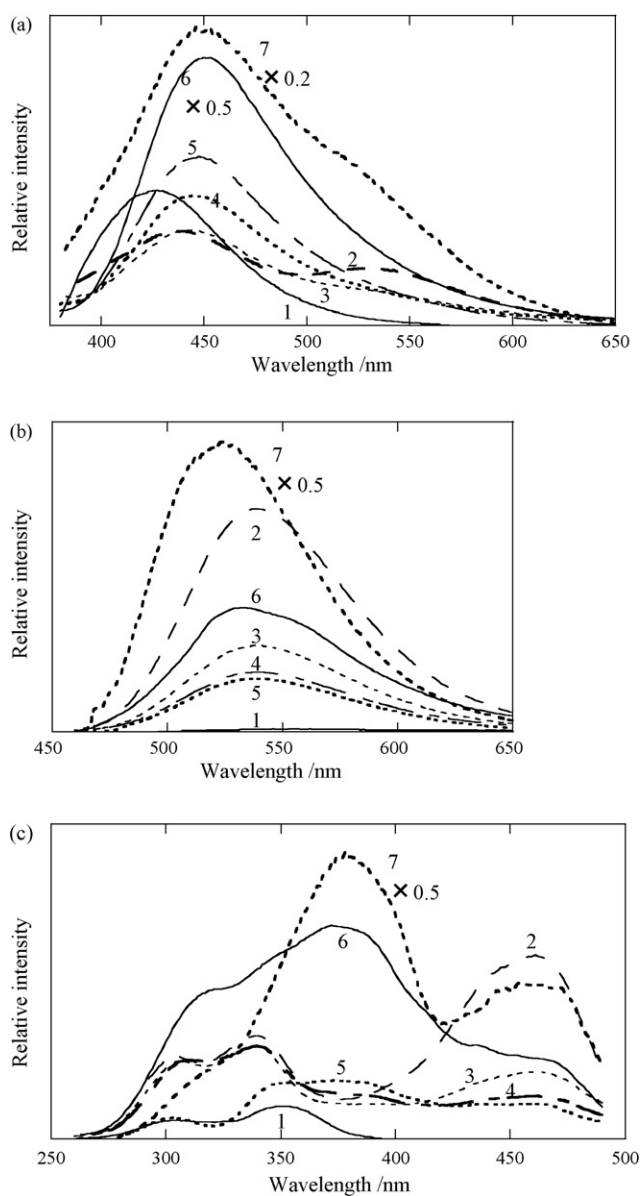


Fig. 1. Changes in (a) and (b) fluorescence and (c) excitation spectra for the Oc0–Z10 system during the sol–gel–xerogel transitions. These spectra were observed (1) just after and (2) 5, (3) 13, (4) 20, (5) 30, (6) 69, and (7) 300 days after the sample preparation. The fluorescence spectra were observed upon excitation at (a) 370 and (b) 450 nm. The excitation spectra were observed at 500 nm.

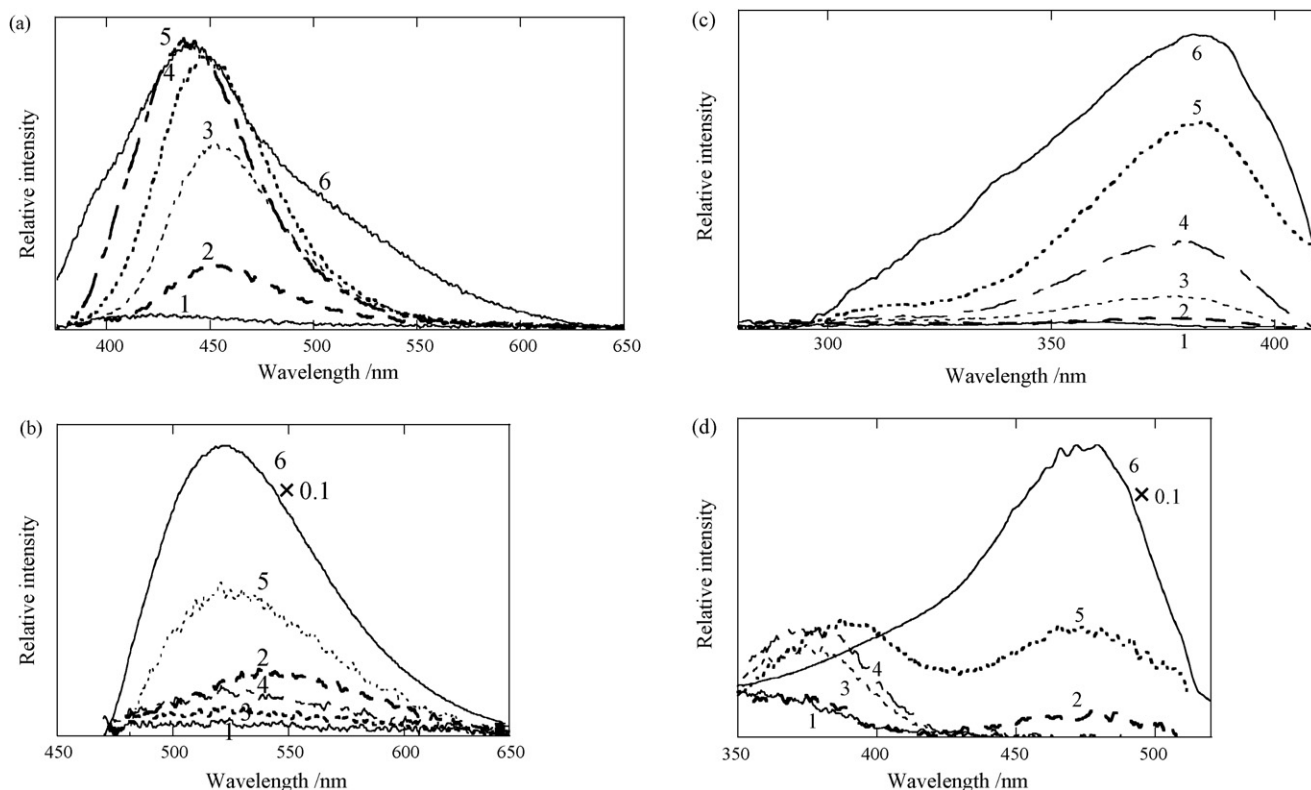


Fig. 2. Changes in (a) and (b) fluorescence and (c) and (d) excitation spectra for the Oc50–Z10 system during the sol–gel–xerogel transitions. These spectra were observed (1) just after and (2) 11, (3) 29, (4) 40, (5) 66, and (6) 300 days after the sample preparation. The fluorescence spectra were observed upon excitation at (a) 370 and (b) 450 nm. The excitation spectra were observed at (c) 420 and (d) 540 nm.

bonding became weaker. After 20 days, the intensity of the MC–Zn complex band increased with the reaction time.

The spectra in the TEOS system without Zn (Oc0–Z0 system) were reported in our previous paper [23]. The spectral behavior was similar to those of the system with Zn except for the following points. In this system, no complex band was found around the gelation time because of the absence of Zn. However, after 300 days, the complex-like bands appeared in the fluorescence spectrum excited at 450 nm and the excitation spectrum observed at 500 nm. We assigned these bands to the MC–SiOH complex, which must also be contained in the Oc0–Zn10 system.

Fig. 2 shows the spectra of the TEOS–OcTES system containing Zn (Oc50–Z10 system). The excitation wavelengths for the fluorescence spectra are 370 and 450 nm and the emission wavelengths for the excitation spectra are 420 and 540 nm. At day 0, weak fluorescence was observed, which was assigned to  $X_h^*$ , similar to the TEOS system. At 11 days, when the gelation began, the  $X_s^*$  became the preferential fluorescence species due to the hydrophobicity of the alkyl groups. In addition to this, the fluorescence of the MC–Zn complex was observed, and the amount of the complex was clearly lower in this system than in the Oc0–Z10 system. After 29 days, the fluorescence spectrum was blue-shifted with the reaction time, indicating that the hydrophobicity became higher and the polarity became lower in the spaces containing the SO species. As the reaction further proceeded, the intensity of the complex bands first decreased and then increased after 40 days.

Fig. 3 shows the spectra of the TEOS–OcTES system containing no Zn (Oc50–Z0 system). The excitation wavelength is 370 nm, and the emission wavelength is 420 nm. The spectral behavior in this system was similar to those of the system with Zn except for the observation of no complex. These results indicate that only a slight amount of the MC–SiOH complex is present in the TEOS–OcTES systems whether or not Zn is available.

The OcTES-content dependences of the fluorescence spectra for the systems of the sol–gel–xerogel transitions were observed after formation of the xerogel (300 days after the preparation) as shown in Fig. 4. The excitation wavelengths are 370 and 450 nm. Based on the fluorescence spectra observed upon excitation at 370 nm, the relative intensity of the complex band at around 500–550 nm for the system containing the higher amount of OcTES is weaker, indicating that the hydrophobicity due to the octyl groups prevents the complex formation. The spectra observed by the 450 nm light-excitation also support this result. The complex band intensity became weaker with an increase in the amount of OcTES.

### 3.2. Mechanism of chelation of SNO with zinc ions during the sol–gel–xerogel transitions

The changes in the physicochemical interaction between the SNO species and zinc ions during the sol–gel–xerogel transitions in the TEOS–OcTES system are discussed here and compared with those in the TEOS system [23,38,39]. The changes in



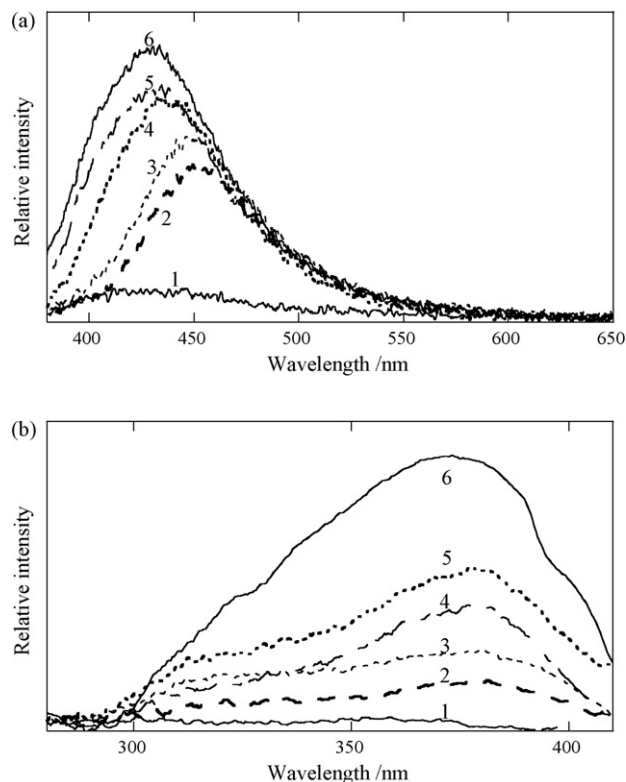


Fig. 3. Changes in (a) fluorescence and (b) excitation spectra for the Oc50–Z10 system during the sol–gel–xerogel transitions. These spectra were observed (1) just after and (2) 11, (3) 29, (4) 40, (5) 66, and (6) 300 days after the sample preparation. The fluorescence spectra were observed upon excitation at 370 nm. The excitation spectra were observed at 420 nm.

configurational relationships between SNO,  $\text{Zn}^{2+}$ , and  $-\text{SiOSi}-$  polymers in the TEOS system are reported on in our previous paper [23]. During the sol state, SNO and  $\text{Zn}^{2+}$  were similarly dispersed in the solvents. In the course of the sol–gel transition, polymerization of the silicon alkoxides proceeded to form the prestructural pores of the sol matrices. SNO and  $\text{Zn}^{2+}$  were encapsulated with solvent and concentrated in such spaces, which were favorable for the formation of the MC–Zn complex. A higher amount of the complex was formed in the Oc0–Z10 system than in the hydrophobic Oc50–Z10 system because it is difficult for SNO to exist as MC in low-polar media. As the solvent evaporated and the amount of SiOH groups decreased during the polymerization, the MC–Zn complex was dissociated into  $\text{X}_s$  and  $\text{Zn}^{2+}$  within the pores of the gel matrices. This is because SNO was adsorbed onto the pore surface and a percentage of  $\text{Zn}^{2+}$  ions are thought to be cross-linked within the silica networks due to isomorphous replacement of Si by Zn. Tetrahedral zinc oxide species were highly dispersed and isolated in the  $\text{ZnO}-\text{SiO}_2$  systems containing a low Zn loading amount, as in the present systems (Zn:Si = 1:1000) [40]. During the dry gel to xerogel transition, the MC–Zn complex was formed again by the concentration in the decreased pore volume. In the high-polar TEOS systems, the MC–SiOH complex was also formed. However, in the TEOS–OcTES systems, SNO cannot interact with the SiOH groups on the surface of the pores filled with the alkyl groups.

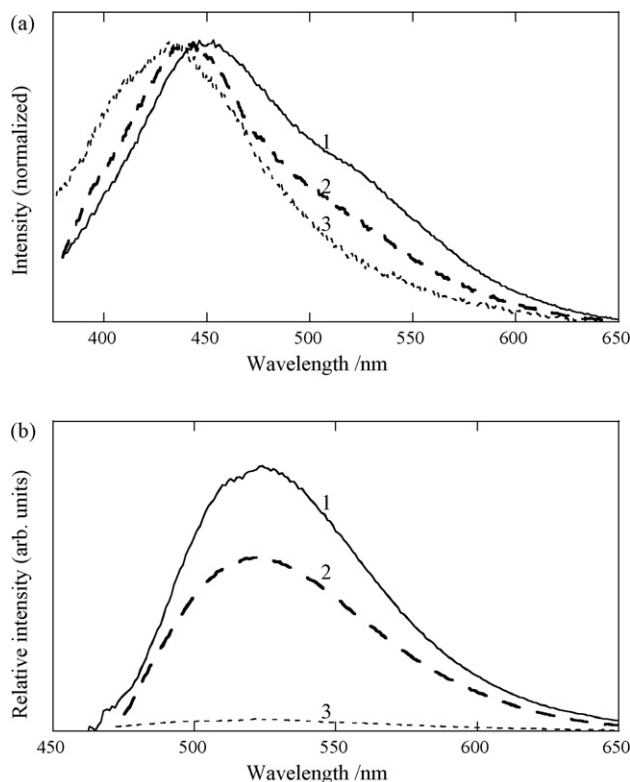
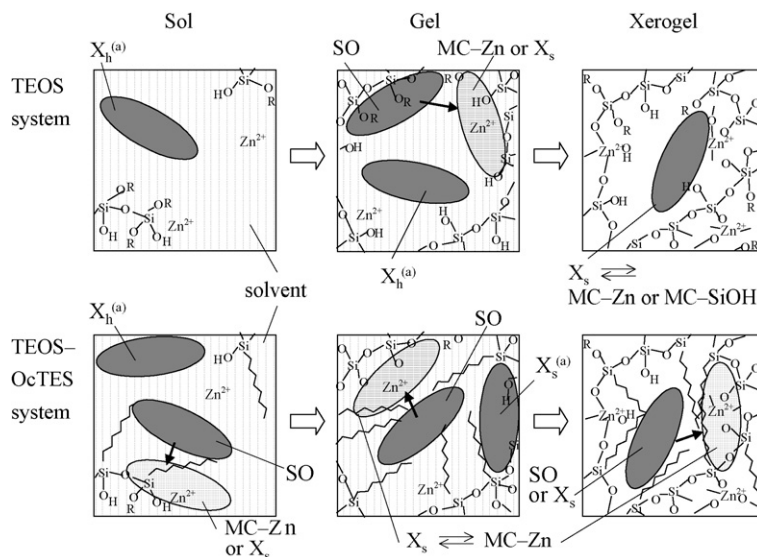


Fig. 4. OcTES-content dependences of fluorescence spectra for (1) Oc0–Z10, (2) Oc50–Z10, and (3) Oc75–Z10 systems observed after formation of the xerogel (300 days after). The spectra were observed upon excitation at (a) 450 and (b) 370 nm.

### 3.3. Observation of spectral changes by light irradiation

Changes in the fluorescence spectra by UV and visible irradiation were investigated in order to examine the influence of the alkyl groups and the progress of the sol–gel–xerogel transitions on the photochromic behavior of the TEOS and TEOS–OcTES systems containing Zn. Scheme 2 illustrates the changes in configurational relationships between SNO,  $\text{Zn}^{2+}$ , and  $-\text{SiOSi}-$  polymers and the photochromic behavior of the SNO species during the sol–gel–xerogel transitions in the TEOS and TEOS–OcTES systems. However, the MC–Zn and MC–SiOH species formed prior to UV irradiation is omitted.

A minor change was observed in the sol sample of the Oc0–Z10 system during UV and visible irradiation similar to that in protic polar solvents due to the strong hydrogen-bonding interaction between SNO and solvent molecules. In the gel sample of the Oc0–Z10 system, the apparent spectral changes were observed only during UV irradiation. Fig. 5 shows the difference fluorescence and excitation spectra between the original spectra of the Oc0–Z10 gel sample and those observed after UV irradiation. Therefore, the positive and negative values denote the increase and decrease of the fluorescence intensity, respectively. The fluorescence spectral band at around 400 nm decreased and those at around 450 and 540 nm increased in intensity. The excitation spectral bands at around 300 and 330 nm decreased and that at around 380 nm increased in intensity. The fluorescence spectral change at around 400 nm and the excitation spectral



Scheme 2. Illustration of changes in configurational relationships between SNO,  $Zn^{2+}$ , and  $-SiOSi-$  polymers and photochromic behavior of the SNO species during the sol-gel-xerogel transitions in the TEOS and TEOS-OcTES systems. The bold arrows indicate the change of the interaction sites with the SNO species upon UV irradiation. The MC-Zn or MC-SiOH species formed prior to UV irradiation is omitted. (a) Main species unchanged during UV light irradiation.

changes at around 300 and 330 nm indicate a decrease in the amount of the SO species. The SO fluorescence decrease resulted from a low amount of SNO at the low-polar sites consisting of  $-SiOSi-$  networks before irradiation, whereas the  $X_h$  was the preferential species in the system. The fluorescence spectral

change at around 460–470 nm and the excitation spectral change at around 380 nm indicate an increase in the amount of the  $X_s$  species. The fluorescence spectral change at around 540 nm and the excitation spectral change at around 460–470 nm indicate an increase in the amount of the MC-Zn species. The SO species in the gel samples was transformed into  $X_s$  and the MC-Zn by UV irradiation. This behavior indicates that the SNO came to interact with the relatively polar site containing high amounts of the  $-SiOSi-$  network and  $Zn^{2+}$ , and some amount of the SiOH groups. However, the reverse reaction was not observed since  $X_s$  and the MC-Zn were more stable than SO in the polar spaces of the TEOS system. The MC-SiOH species must not be readily formed in the gel sample since no spectral change by UV irradiation was observed in the gel of the TEOS system without Zn. The formation of the MC-SiOH species requires the stronger interaction between the SNO species and SiOH groups in narrow spaces such as the pores of the xerogel. The major species  $X_h$  in the gel sample was not readily changed by UV irradiation due to its strong hydrogen-bonding with solvent molecules and the SiOH groups.

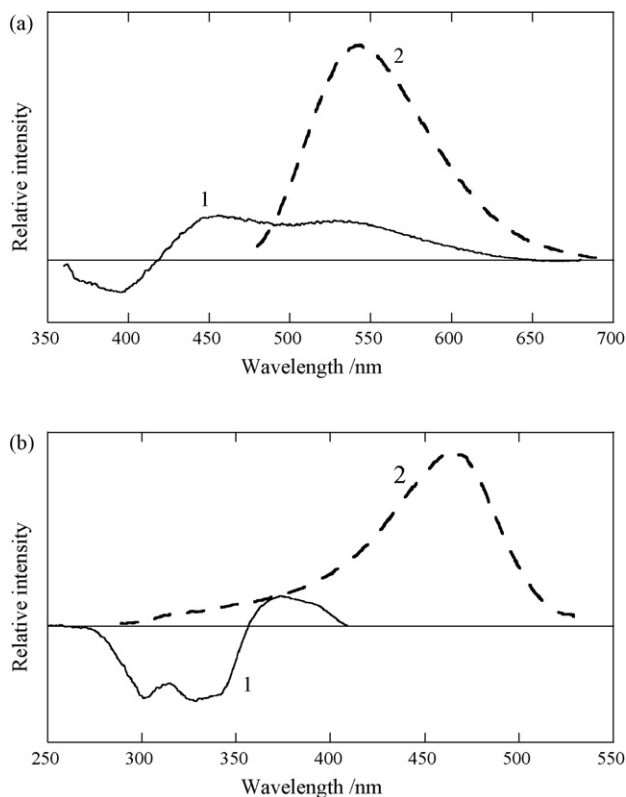


Fig. 5. Difference (a) fluorescence and (b) excitation spectra between the original spectra of the Oc0-Z10 gel sample and those observed after 350 nm irradiation. The fluorescence spectra were observed upon excitation at (1) 370 and (2) 450 nm. The excitation spectra were observed at (1) 420 and (2) 540 nm.

In the xerogel sample of the Oc0-Z10 system, the reversible interconversion between  $X_s$  and the MC-Zn or the MC-SiOH was observed during UV and visible irradiation as reported in a previous paper [23]. Fig. 6 shows the difference fluorescence and excitation spectra between the original spectra of the xerogel sample of Oc0-Z10 and those observed after UV and visible irradiation. The fluorescence spectral band at around 450 nm decreased and that at around 540 nm increased in their intensities during UV irradiation. The excitation spectral bands at around 300 and 330 nm decreased and that at around 440–450 nm increased in their intensities during UV irradiation. These reverse processes were observed during visible irradiation. This sample has a moderately polar environment in which  $X_s$  and the MC-Zn or the MC-SiOH exist in their stable states. The electrophilicity of  $Zn^{2+}$  is weakened by its incorporation

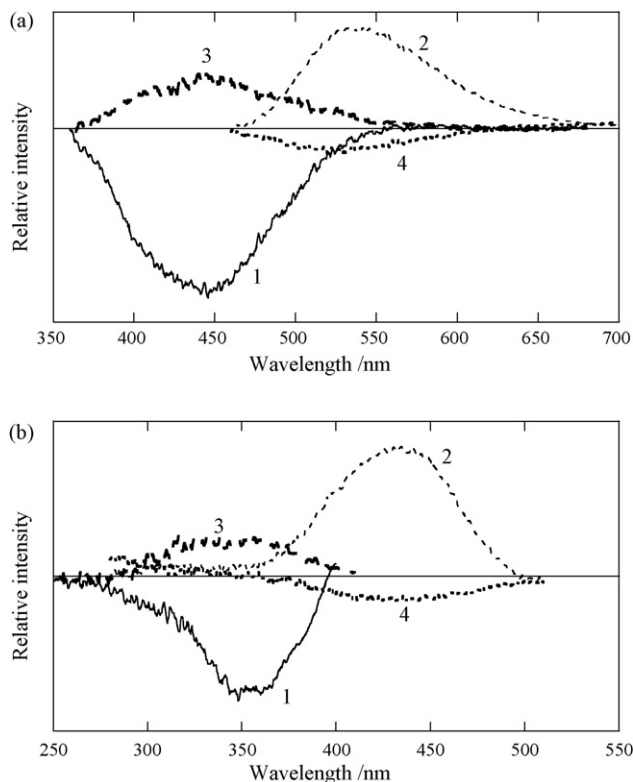


Fig. 6. Difference (a) fluorescence and (b) excitation spectra between the original spectra of the xerogel sample from the Oc0–Z10 system and those observed after (1 and 2) 350 and (3 and 4) 450 nm irradiation. The fluorescence spectra were observed upon excitation at (1 and 3) 370 and (2 and 4) 450 nm. The excitation spectra were observed at (1 and 3) 420 and (2 and 4) 540 nm.

into the silica network. The  $Zn^{2+}$  is postulated to appropriately interact with the excited species  $X_s^*$ , which promotes the ring-opening reaction to produce the MC, and then forms the complex with the resulting MC. Furthermore, the dissociation of the complex and the ring-closure reaction of the resulting MC can also proceed during visible irradiation. This is because  $X_s$  or MC interacts with the cross-linked  $Zn^{2+}$  more weakly than  $Zn^{2+}$  dissolved in a solvent, which exhibits the uncontrollable chelation.

In the sol sample of the TEOS–OcTES systems, the apparent spectral changes were observed during only UV irradiation similar to that in the gel sample of the TEOS system. The fluorescence spectral changes indicate the decrease in the amount of SO species and the increase in the amounts of  $X_s$  and the MC–Zn species. The SO fluorescence decrease indicates that initially a small amount of SNO was at the low-polar environment due to the octyl groups. The fluorescence of  $X_s$  and the MC–Zn results from the relatively polar environment affording weak hydrogen-bonding due to the ethanol, octyl groups, and the –SiOSi– polymers. The reverse reaction was not observed since  $X_s$  and the MC–Zn were more stable than SO in the polar spaces. Although the  $X_h$  was the preferential species in the system, a small amount of SO was found to play a role in the spectral changes.

In the gel sample of the Oc75–Z10 system, two different photochromic reactions were observed during UV and visible

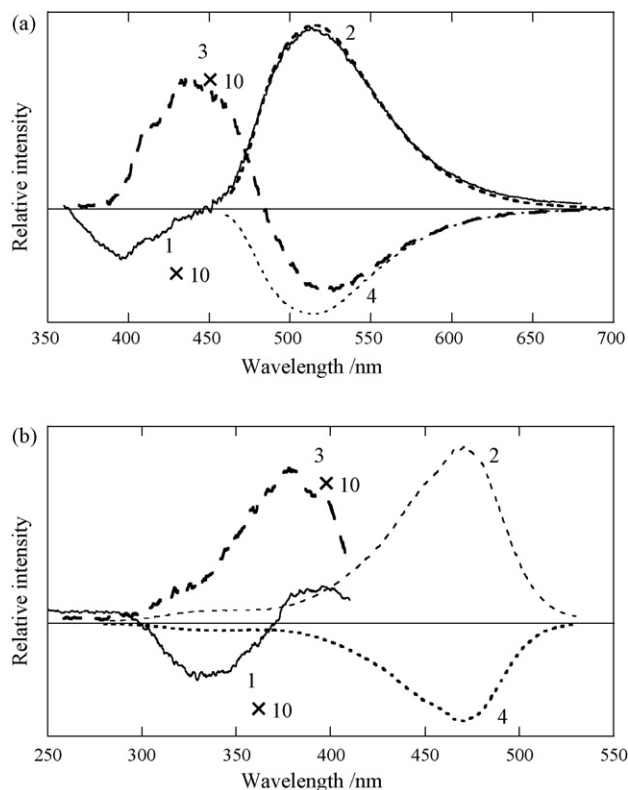


Fig. 7. Difference (a) fluorescence and (b) excitation spectra between the original spectra of the gel sample from the Oc75–Z10 system and those observed after (1 and 2) 350 and (3 and 4) 450 nm irradiation. The fluorescence spectra were observed upon excitation at (1 and 3) 370 and (2 and 4) 450 nm. The excitation spectra were observed at (1 and 3) 420 and (2 and 4) 540 nm.

irradiation. Fig. 7 shows the difference fluorescence and excitation spectra of the gel sample of Oc75–Z10 observed before and after UV and visible irradiation. The fluorescence spectral band at around 400 nm due to SO decreased and that at around 530 nm due to the MC–Zn increased in their intensities during UV irradiation. The excitation spectral bands at around 330–350 nm due to SO decreased and that at around 460–470 nm due to the MC–Zn increased in their intensities during UV irradiation. Furthermore, the fluorescence and excitation spectral bands due to the MC–Zn decreased and those due to  $X_s$  increased in their intensities during visible irradiation. This sample mainly exhibited a transformation from SO to the MC–Zn during the UV irradiation and that from the MC–Zn to  $X_s$  during visible irradiation. The SO fluorescence decrease indicates that a small amount of SNO was at the low-polar sites consisting of the octyl groups and the –SiOSi– networks before light irradiation. Once the SO interacted with Zn to form the MC–Zn, it was still in the region having a polar environment including the Zn. The MC–Zn cannot invert to SO in this system since SNO prefers a highly-polar environment as shown in the gel sample of the TEOS system and the sol sample of the TEOS–OcTES system. The conversion from the MC–Zn to  $X_s$  indicates that the electrophilicity of  $Zn^{2+}$  was weakened by its interaction with the silica networks. The major species  $X_s$  which originally existed was not readily changed by UV irradiation because it was stabilized in the relatively polar site containing solvent molecules,

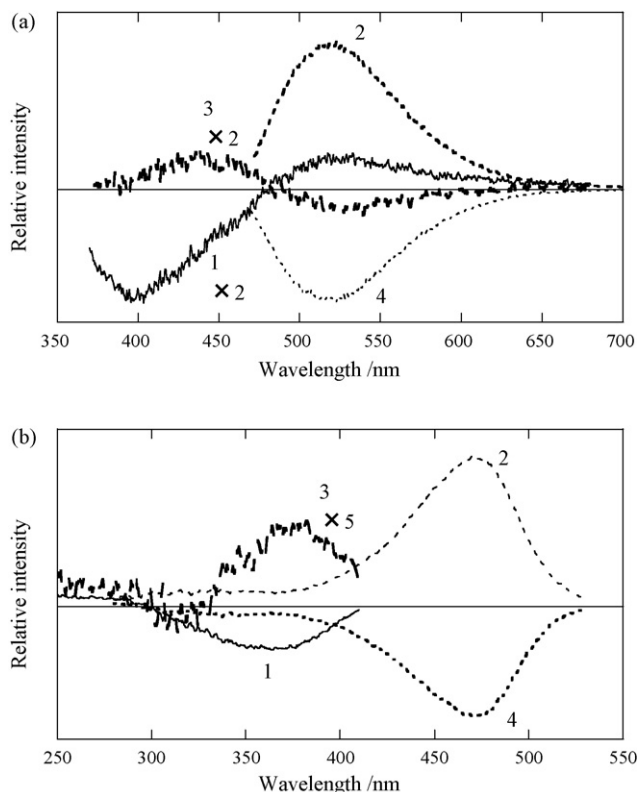


Fig. 8. Difference (a) fluorescence and (b) excitation spectra between the original spectra of the xerogel sample from the Oc75–Z10 system and those observed after (1 and 2) 350 and (3 and 4) 450 nm irradiation. The fluorescence spectra were observed upon excitation at (1 and 3) 370 and (2 and 4) 450 nm. The excitation spectra were observed at (1 and 3) 420 and (2 and 4) 540 nm.

the  $-\text{SiOSi}-$  networks, and octyl groups, and was therefore not able to interact with  $\text{Zn}^{2+}$ .

In the xerogel sample of the Oc75–Z10 system, the photochromic reactions similar to those seen in the gel sample were observed during UV and visible irradiation. Fig. 8 shows the changes in the fluorescence and excitation spectra of the xerogel sample of Oc75–Z10 due to UV and visible irradiation. The main characteristic of the behavior in the xerogel sample that is distinct from in the gel sample is a decrease in the  $X_s$ . This decrease was clearly observed during UV irradiation, manifested as decreases in the fluorescence band at around 450 nm and excitation band at 380 nm located on the low energy side of the respective SO bands. The conversion from  $X_s$  to the MC–Zn, which did not readily occur in the gel sample of the Oc75–Z10 system, was enhanced in the xerogel. These results indicate that a larger amount of the MC–Zn was produced in the xerogel sample than in the gel sample due to the concentration in the decreased pore volume. The hydrophobicity due to the octyl groups controlled the physicochemical properties during all the sol–gel–xerogel transitions in the Oc75–Z10 system.

#### 4. Conclusions

SO and  $\text{Zn}^{2+}$  were homogeneously dispersed in the TEOS and TEOS–OcTES systems just after the preparation. In the TEOS systems, the fluorescence peak was red-shifted due to

progress of the hydrolysis of silicon alkoxides with increases in amount of the SiOH groups and in polarity in the system. In the TEOS–OcTES systems, the solvated species ( $X_s$ ) became the preferential fluorescence species in the initial stage of the sol–gel–xerogel transitions because of aggregation of the hydrophobic alkyl silicon alkoxides. As polymerization of the silicon alkoxides proceeded to some extent, SO and  $\text{Zn}^{2+}$  were encapsulated with solvent in prestructural pores and concentrated at around the gelation time. A larger amount of the MC–Zn complex was formed in the TEOS systems than in the hydrophobic TEOS–OcTES systems because it is difficult for SNO to transform into MC in low-polar media.

In the TEOS systems, the species  $X_s$  was gradually formed after the gelation time because of a decrease in proton-donating ability of the pore surface by polymerization of the SiOH groups. In the TEOS–OcTES systems, the fluorescence peak assigned to the  $X_s$  was blue-shifted after the gelation time because of an increase in hydrophobicity and a decrease in polarity in the pores by aggregation of alkyl groups.

The MC–Zn complex was dissociated into  $X_s$  and  $\text{Zn}^{2+}$  during the wet gel–dry gel transition because SNO was adsorbed onto the pore surface and  $\text{Zn}^{2+}$  was progressively cross-linked within the silica networks during solvent evaporation. The MC–Zn complex was formed by contraction in volume of the pore during the dry gel–xerogel transition, and the MC–SiOH complex was also formed in the TEOS systems. In the TEOS–OcTES systems, SNO cannot interact with the SiOH groups on the pore surface, which are filled by the alkyl groups.

In the gel of the TEOS system and the sol of the TEOS–OcTES system, a photochromic reaction was observed, where SNO formed the MC–Zn complex during UV irradiation, whereas little change was observed during visible irradiation. In the xerogel of the TEOS system and in the gel and xerogel of the TEOS–OcTES system, a reversible photochromic reaction was observed as the MC–Zn complex was associated and dissociated by UV and visible irradiation, respectively. The hydrophobicity due to the octyl groups probably controls the physicochemical properties in such gel systems.

#### References

- [1] M. Irie, Chem. Rev. 100 (2000) 1685.
- [2] G. Berkovic, V. Krongauz, V. Weiss, Chem. Rev. 100 (2000) 1741.
- [3] K. Matsuda, M. Irie, J. Photochem. Photobiol. C 5 (2004) 169.
- [4] W. Yuan, L. Sun, H. Tang, Y. Wen, G. Jiang, W. Huang, L. Jiang, Y. Song, H. Tian, D. Zhu, Adv. Mater. 17 (2005) 156.
- [5] K. Amimoto, T. Kawato, J. Photochem. Photobiol. C 6 (2005) 207.
- [6] S.M. Aldoshin, L.A. Nikonova, V.A. Smirnov, G.V. Shilov, N.K. Nagaeva, J. Mol. Struct. 750 (2005) 158.
- [7] A. Romani, G. Chidichimo, P. Formoso, S. Manfredi, G. Favaro, U. Mazzucato, J. Phys. Chem. B 106 (2002) 9490.
- [8] S.-H. Kim, C.-H. Ahn, S.-R. Keum, K. Koh, Dyes Pigm. 65 (2005) 179.
- [9] T. Suzuki, N. Oda, T. Tanaka, H. Shinozaki, J. Mater. Chem. 16 (2006) 1803.
- [10] D. Pisignano, E. Mele, L. Persano, A. Athanassiou, C. Fotakis, R. Cingolani, J. Phys. Chem. B 110 (2006) 4506.
- [11] M. Piech, N.S. Bell, Macromolecules 39 (2006) 915.
- [12] H. Nishikiori, R. Sasai, N. Arai, K. Takagi, Chem. Lett. (2000) 1142.
- [13] H. Nishikiori, R. Sasai, K. Takagi, T. Fujii, Langmuir 22 (2006) 3376.



- [14] P.L. Gentili, U. Costantino, M. Nocchetti, C. Miliani, G. Favara, *J. Mater. Chem.* 12 (2002) 2872.
- [15] R. Sasai, H. Ogiso, I. Shindachi, T. Shichi, K. Takagi, *Tetrahedron* 56 (2000) 6979.
- [16] R. Sasai, H. Itoh, I. Shindachi, T. Shichi, K. Takagi, *Chem. Mater.* 13 (2001) 2012.
- [17] T. Yui, I. Shindachi, R. Sasai, K. Takagi, *Mol. Cryst. Liq. Cryst.* 431 (2005) 321.
- [18] N. Iyi, T. Fujita, C.V. Yelamaggad, F. Lopez Arbeloa, *Appl. Clay Sci.* 19 (2001) 47.
- [19] M. Ogawa, *J. Mater. Chem.* 12 (2002) 3304.
- [20] J. Zhou, F. Zhou, Y. Li, F. Zhang, X. Song, *J. Photochem. Photobiol. A* 92 (1995) 193.
- [21] M.J. Preigh, F. Lin, K.Z. Ismail, S.G. Weber, *J. Chem. Soc., Chem. Commun.* (1995) 2091.
- [22] H. Nishikiori, N. Tanaka, K. Takagi, T. Fujii, *Res. Chem. Intermed.* 29 (2003) 485.
- [23] H. Nishikiori, N. Tanaka, K. Takagi, T. Fujii, *J. Photochem. Photobiol. A* 183 (2006) 53.
- [24] J. Biteau, F. Chaput, J.-P. Boilot, *J. Phys. Chem.* 100 (1996) 9024.
- [25] L. Hou, H. Schmidt, *J. Mater. Sci.* 31 (1996) 3427.
- [26] X. Sun, M. Fan, E.T. Knobbe, *Mol. Cryst. Liq. Cryst.* 297 (1997) 57.
- [27] B. Schaudel, C. Guermeur, C. Sanchez, K. Nakatani, J.A. Delaire, *J. Mater. Chem.* 7 (1997) 61.
- [28] F. Ortica, G. Favaro, *J. Phys. Chem. B* 104 (2000) 12179.
- [29] A. Lafuma, S. Chodorowski-Kimmes, F.X. Quinn, C. Sanchez, *Eur. J. Inorg. Chem.* (2003) 221.
- [30] R. Winter, D.W. Hua, X. Song, W. Mantulin, J. Jonas, *J. Phys. Chem.* 94 (1990) 2706.
- [31] T. Fujii, T. Mabuchi, H. Kitamura, O. Kawauchi, N. Negishi, M. Anpo, *Bull. Chem. Soc. Jpn.* 65 (1992) 720.
- [32] T. Fujii, K. Toriumi, *J. Chem. Soc. Faraday Trans.* 89 (1993) 3437.
- [33] U. Narang, R. Wang, P.N. Prasad, F.V. Bright, *J. Phys. Chem.* 98 (1994) 17.
- [34] K. Matsui, K. Nakazawa, *Bull. Chem. Soc. Jpn.* 70 (1997) 2331.
- [35] B. Dunn, J.I. Zink, *Chem. Mater.* 9 (1997) 2280.
- [36] T. Mabuchi, H. Nishikiori, N. Tanaka, T. Fujii, *J. Sol-Gel Sci. Technol.* 33 (2005) 333.
- [37] N.Y.C. Chu, in: H. Durr, H. Bouas-Laurent (Eds.), *Photochromism: Molecules and Systems*, Elsevier, Amsterdam, 1990, p. 506.
- [38] H. Nishikiori, T. Fujii, *J. Phys. Chem. B* 101 (1997) 3680.
- [39] H. Nishikiori, S. Nagaya, N. Tanaka, A. Katsuki, T. Fujii, *Bull. Chem. Soc. Jpn.* 72 (1999) 915.
- [40] H. Yoshida, T. Shimizu, C. Murata, T. Hattori, *J. Catal.* 220 (2003) 226.