

Possibility of conformation control of Michler's ketone encapsulated into sol–gel matrices

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Abstract

The fluorescence spectra of Michler's ketone (4,4'-bis(dimethylamino)benzophenone) with varying composition of starting chemicals of silicon alkoxides and solvents have been observed during various stages of the sol–gel reaction. Among the reaction systems, the fluorescence spectra in the systems including phenyl and methyl substituted alkoxysilanes or chloroform as a starting reactant showed an explicitly broad and red-shifted TICT (twisted intramolecular charge transfer)-like fluorescence, though the shift was not large compared with that observed in solution. The results showed that a possibility to control flexible conformation of Michler's ketone in rigid environment.

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1. Introduction

The fluorescent or non-fluorescent character of the electronic state of aromatic carbonyl compounds that contain nonbonding (n) electrons is strongly dependent on the solvent properties. The changes have been explained by the existence of close lying $n-\pi^*$ and $\pi-\pi^*$ levels in both the singlet and triplet states [1–3]. The increase in the solvent polarity raises the $n-\pi^*$ energy level and lowers the $\pi-\pi^*$ energy level. Therefore, aromatic carbonyl compounds are non-fluorescent in non-polar solvents and fluorescent in polar solvents as the results of the level inversion. In addition, the fluorescence of molecules having geometrical flexibility shows complicated behavior.

Michler's ketone [MK, 4,4'-bis(dimethylamino)benzophenone] has a flexible geometry around two carbonyl carbon-phenyl bonds. The fluorescence of MK depends on the solvent characteristics [4–8]. In hydrocarbon solvents such as cyclohexane, MK shows a very weak $\pi-\pi^*$ fluorescence. In polar protic solvents such as ethanol, the fluorescence peak locates at around 450 nm originating from

an intramolecular charge-transfer (ICT) state having planar conformation. In polar aprotic solvents such as acetonitrile, the peak is seen at around 520 nm originating from a twisted intramolecular charge transfer (TICT) state. These peak wavelengths for the ICT and TICT fluorescences depend on the character of the solvents. High value of the degree of anisotropy of the fluorescence spectrum of MK in ethanol at room temperature indicated that MK molecule has an unusually short lifetime of the excited singlet state [9]. These characteristic differences of the fluorescence peak and the photophysical and photochemical processes of MK in solutions depend on not only their geometrical and electronic properties of MK but also the physicochemical properties of matrices around the entrapped MK molecules [4–9]. The dependence is also expected in rigid matrices [10]. Therefore, it is important to examine fluorescence behavior of MK in different environmental conditions in order to attain conformation control of MK in various circumstances. Under controlled conditions of the MK geometry, we would expect to control the clear change of the MK fluorescence. In this paper, we will report on the fluorescence spectrum of MK in various stages during the sol–gel processes with varying composition of starting chemicals of silicon alkoxides and solvents. Especially, we focus on the possibility for confor-

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mation control of MK in matrices prepared by the sol–gel method [10–16].

2. Experimental

MK (Aldrich) was purified by repeated recrystallizations from a water–ethanol mixture. Methanol, ethanol, propanol, butanol, octanol, acetonitrile, chloroform, cyclohexane, and HCl supplied by Wako (S. S. G., JIS S, or Luminasol grade), TEOS (tetraethyl orthosilicate), TMOS (tetramethyl orthosilicate), MTES (methyltriethoxysilane), MTMS (methyltrimethoxysilane), and PTES (phenyltriethoxysilane) from Shin-Etsu Chemicals Co. Ltd. were used without further purification. Water was deionized and distilled.

2.2×10^{-4} M ($M = \text{mol dm}^{-3}$) or 1.0×10^{-4} M solutions of MK in methanol, ethanol and chloroform solvents were prepared. Chloroform was used in order to reduce the hydrogen-bonding effect between MK molecules and surrounding solvents. The composition of starting solutions of the sol–gel reaction systems is shown in Table 1. The concentration of MK in individual starting reaction systems was adjusted to 1.0×10^{-5} M for system A and $2.8\text{--}3.3 \times 10^{-5}$ M for systems B and C. The molar ratio of alkoxides (TMOS + MTMS): methanol:water in system A was 1:1:2. The solutions were stirred during the gradual addition, and stirred thoroughly for further 10 min. In order to observe continuous fluorescence spectra, 3 cm^3 of the mixed solutions were poured into individual plastic cells. The procedures were all carried out under a nitrogen atmosphere. The cells were covered with a thin polymer film having three pinholes and allowed to undergo the sol–gel–xerogel transitions at room temperature (300 K) under dark conditions.

Methanol was used as the solvent to adapt for the silicon methoxides to prepare the system A. On the other hand, the system B included ethanol because of well-mixing with chloroform and TEOS. We confirmed that the environmental changes in sol–gel reaction systems including ethanol-TEOS and methanol-TMOS were essentially same, although their reaction rates were slightly different. The influence of chloroform on the physicochemical properties in the systems, therefore, can be discussed by comparison between these two systems.

The fluorescence and excitation spectra of the samples were measured using a Shimadzu RF-5000 spectrofluorometer. The data were transferred to a personal computer for processing. Since the concentration in the systems is so high, we cannot show the results for the excitation spectra. The absorption spectra also cannot be obtained throughout the entire sol–gel process due to many cracks of the gel samples. This is because the volume of the systems gradually decreased during the gel to xerogel transition. The volume in the xerogel state usually becomes about one order of magnitude smaller than that of the original sol and the shrink is not uniform. This behavior results in a space between the face of the spectroscopic cell and the system itself.

3. Results and discussion

We had prepared many reaction systems to examine fluorescence change of MK during the sol–gel reaction. Most systems showed only ICT fluorescence, therefore we will show some typical reaction systems which show somewhat different behavior emitting not only the ICT fluorescence but also the possible TICT fluorescence.

Table 1
Chemicals for the systems

System	TMOS:MTMS ^a	Methanol (cm ³)	MK ^b (cm ³)	TMOS (cm ³)	MTMS (cm ³)	HCl ^c (cm ³)	Gelation ^d (days)
A1	10:0	2.24	0.76	10.95	0	2.67	4
A2	8:2	2.26	0.74	8.76	1.93	2.61	8
A3	5:5	2.27	0.73	5.47	4.83	2.51	8
A4	2:8	2.29	0.43	2.19	7.73	2.42	9
A5	0:10	2.30	0.70	0	9.66	2.36	9
		Ethanol (cm ³)	MK ^e (cm ³)	TEOS (cm ³)		HCl ^f (cm ³)	Gelation (days)
B		5.0	5.0	5.0		0.06	11
		Ethanol (cm ³)	MK ^g (cm ³)	PTES ^h (cm ³)		HCl ⁱ (cm ³)	Gelation (days)
C1		5.0	5.0	5.0		2.0	14
C2		5.0	5.0	5.0		3.0	8

^a Molar ratio, TMOS: tetramethyl orthosilicate, MTMS: methyltrimethoxysilane.

^b MK (2.2×10^{-4} mol dm⁻³) in methanol solution.

^c 1.0×10^{-5} mol dm⁻³.

^d The day when the gelation was observed.

^e MK (1.0×10^{-4} mol dm⁻³) in chloroform solution.

^f 1.0 mol dm^{-3} .

^g MK (1.0×10^{-4} mol dm⁻³) in ethanol solution for C1 and chloroform solution for C2.

^h PTES: phenyltriethoxy silane.

ⁱ 1.0×10^{-2} mol dm⁻³.

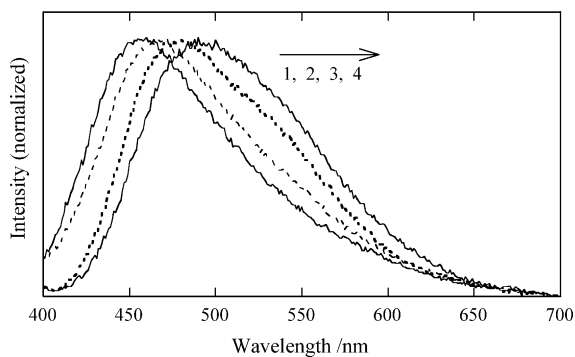


Fig. 1. Fluorescence spectra of MK excited at 370 nm during the sol-gel-xerogel transitions for system A4. (1) Just after the mixing; (2) 7 days; (3) 23 days and (4) 62 days.

3.1. Fluorescence spectra of system A during the sol-gel-xerogel transitions

The fluorescence peak at starting time in all solutions was located at around 456 nm, indicating the ICT fluorescence of MK because of alcohol solvent. The peak wavelength (λ_{\max}) of the fluorescence spectra of MK during the sol-gel-xerogel transitions is characterized as follows: a rapid red shift at first stage, a gentle red shift and final constant wavelength in rigid matrix. Fig. 1 shows a typical result observed for system A4. The gelation was observed at 9 days. From the starting solution the red shift of the fluorescence was continued and the λ_{\max} was observed at 484 nm at 23 days. After then, the λ_{\max} shifted gradually to the red and reached at ca. 495 nm after 62 days. The spectra observed at 23 and 62 days show a shoulder at around 530 nm. This indicates that there is a contribution from the TICT fluorescence to the total fluorescence. The spectral changes for the other A systems are similar, though the magnitude of the red shift was not the same. Aggregation of MK is unlikely to occur under the present condition because such polar organic molecules tend to be individually encapsulated into the gel pores [11,15]. It is impossible to observe the dimer or excimer emission. Protonation of the diethylamino groups of MK is not also expected to occur in the present systems, considering the acidity in the systems, estimated to range in the effective pH value from 1.65 to 5.25 [17] and pK_b value of *p*-aminobenzophenone, ca. 0.5 [18,19].

Fig. 2 shows the fluorescence spectra at 158 days for four samples except for system A5, which was so turbid due to the phase separation that its spectra could not be measured. It is seen that the spectral shifts depend on the ratio of TMOS:MTMS. The increase of MTMS, resulting in increase of non-polar environment by increase of methyl groups around the entrapped MK, shifts the spectrum to the red. It is also seen that there is a shoulder, assigned to the contribution of the TICT fluorescence, exists at around 530 nm for systems A2, A3, and A4. Increase of the TICT contribution to the systems shifts the spectra to the red. These results indicate that the

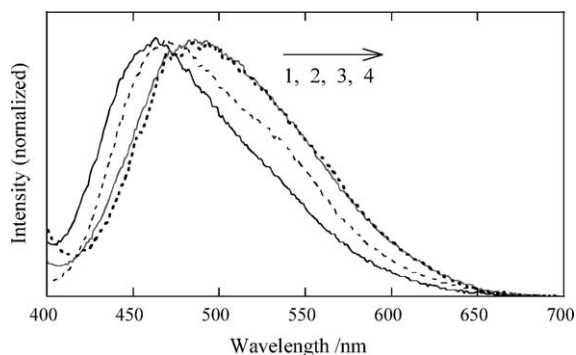


Fig. 2. Fluorescence spectra of MK excited at 370 nm in the xerogel state (at 158 days). (1) System A1; (2) system A2; (3) system A3 and (4) system A4.

whole spectra of MK entrapped in the rigid circumstance of the gel state mainly consist of the two fluorescent components from the ICT and TICT states.

TMOS has four methoxy groups. MTMS has three methoxy groups and one methyl group. This methyl group does not take part in the sol-gel reaction. Therefore, it is expected that A1 has relatively polar property and system A4 has relatively non-polar one among the systems. To examine the effect of the polar and non-polar properties of the matrices around the entrapped MK on the fluorescence spectra of MK during the sol-gel reaction processes, the changes in the peak wavelengths for the individual system as a function of time are shown in Fig. 3. As clearly shown in Fig. 3, the red shift of the fluorescence spectra largely depends on the starting chemical composition. The λ_{\max} for A1 indicates that the contribution from the TICT fluorescence in TMOS rich component is very small through the sol-gel reaction. On the other hand, the contribution from the TICT fluorescence for A3 and A4 is remarkable. These results indicate that excited-state geometry for fluorescent state and contribution from the TICT component for MK can be controlled by the amount of MTMS. Though the results are not shown here, the spectral shift of MK during the sol-gel-xerogel transitions for the TEOS + alcohol and TMOS + alcohol systems was small.

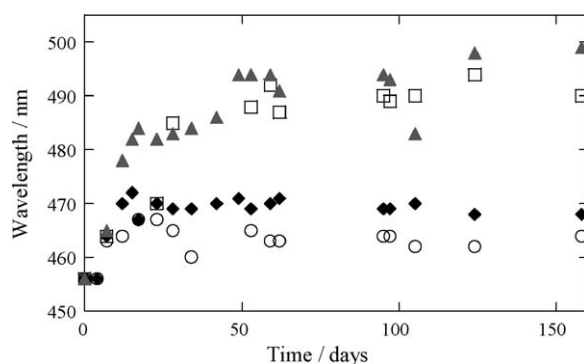


Fig. 3. Changes in peak wavelengths during the sol-gel-xerogel transitions for system A1 (○), system A2 (◆), system A3 (□), and system A4 (▲).

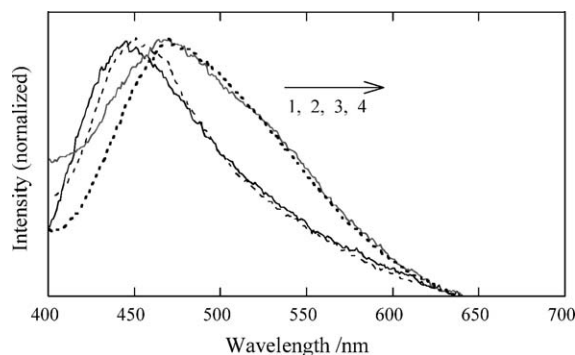


Fig. 4. Fluorescence spectra of MK excited at 340 nm during the sol-gel-xerogel transitions for system B. (1) Just after the mixing; (2) 16 days; (3) 26 days and (4) 113 days.

3.2. Fluorescence spectra of system B during the sol-gel-xerogel transitions

The influence of chloroform on the fluorescence spectra of MK during the sol-gel reaction processes for the system B is shown in Fig. 4. The fluorescence peak observed just after the preparation of the system was located at 444 nm, indicating the ICT fluorescence. The λ_{\max} shifted to the red according to the progress of the reaction. At 113 days, the fluorescence showed the peak at 470 nm, and shoulder at around 530 nm. This result shows that fluorescence states of MK in matrix are composed of the ICT and TICT ones. These results indicate that non-polar chloroform solvent has large effect on the fluorescent state of MK though MK molecules are entrapped in the rigid matrix.

To clarify the effect of chloroform on the fluorescence peak of MK during the sol-gel reaction processes, the changes in the λ_{\max} for the system B are shown in Fig. 5 as a function of time. The red shift of the fluorescence spectra in the first reaction stage was significant. The λ_{\max} at around 470 nm indicates that the main fluorescence state of MK is the ICT state in the gel stage of system B. It was also indicated the contribution from the TICT fluorescence because chloroform reduces the hydrogen-bonding effect between MK molecules and surrounding solvents. These results show that

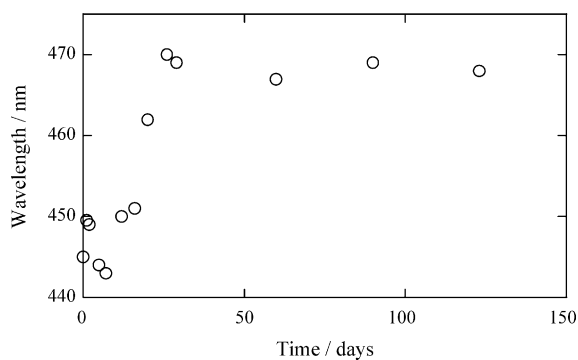


Fig. 5. Change in peak wavelength during the sol-gel-xerogel transitions for system B.

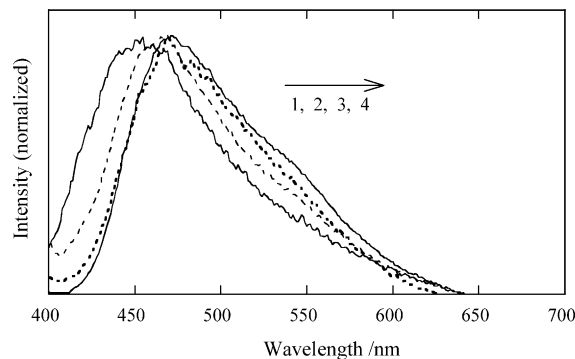


Fig. 6. Fluorescence spectra of MK excited at 370 nm during the sol-gel-xerogel transitions for system C1. (1) Just after the mixing; (2) 14 days; (3) 22 days and (4) 120 days.

a small amount of the twisted MK molecules was entrapped in the relatively large pore of the gel.

3.3. Fluorescence spectra of system C during the sol-gel-xerogel transitions

To confirm the volume effect of substituent of silicon alkoxide on the fluorescence spectra of MK, we have observed the fluorescence spectra of MK in PTES system as a function of time, because the volume of phenyl substituent is large and can be expected to make large pore in the space in which MK molecule will be entrapped. Fig. 6 shows the results for the system C1. The fluorescence peak at starting solution located at around 446 nm. Gelation was observed at 14 days. According to the progress of the sol-gel reaction, the spectral shift to the red was seen. Contrary to our expectation, we could not observe remarkable TICT spectrum of MK through all stages of the sol-gel reaction, though a curtain contribution of the TICT fluorescence at around 530 nm can be seen.

To elucidate the effect of phenyl group on the fluorescence peak of MK during the sol-gel reaction processes, the change in the λ_{\max} for the system C1 is shown in Fig. 7 as a function of time. The red shift of the fluorescence spectra in the first reaction stage was large. The λ_{\max} at around 470 nm indicates that the main fluorescence state of MK is the ICT state in the

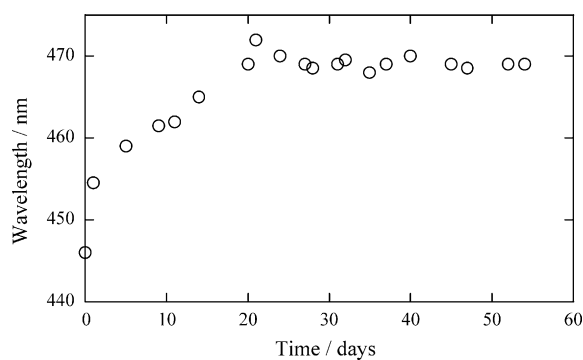


Fig. 7. Change in peak wavelength during the sol-gel-xerogel transitions for system C1.

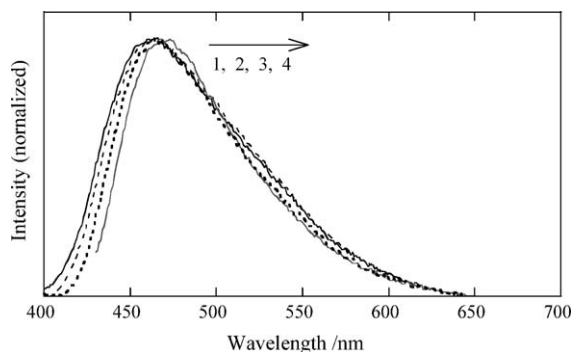


Fig. 8. Excitation wavelength effect on the fluorescence spectra for system C2 observed at 150 days. Excited at (1) 320 nm; (2) 360 nm; (3) 400 nm and (4) 420 nm.

gel stage of PTES. It was also indicated the contribution from the TICT fluorescence. These results show that twisted MK molecules were entrapped in the relatively large pore of the gel.

The effect of excitation wavelength on the fluorescence spectra of MK for the system C2 is shown in Fig. 8. Although the dependence of excitation wavelength on the spectral features is not large, the λ_{max} of the fluorescence is obviously located at longer wavelength side, excited by longer wavelength light. This obvious effect indicates that there are more than two species of MK in the ground state in this rigid matrix.

4. Conclusions

The fluorescence spectra of MK have been observed in various chemicals during the sol–gel–xerogel transitions of the silicone alkoxides. Dual fluorescences originating from

the ICT and TICT states are observed both in not only relatively non-polar circumstance but also the gels having large radius pore. These are more than two ground state geometries of MK in such gel matrices. These results show that the possibility of conformational control of MK entrapped into the sol–gel matrices.

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