Effects of diamine bridge length and substituents on the spectral properties of *N*,*N*′-bis(α-substituted salicylidene)diamines in solution

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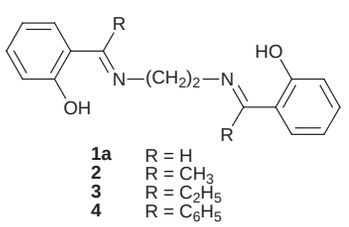
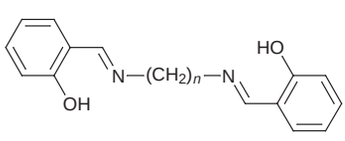
Absorption and fluorescence spectra of thirteen *N*,*N*′-bis(α-substituted salicylidene)diamines in solution were investigated with the intention of investigating the role of the substituent and diamine bridge length on their optical properties. The fluorescence efficiency was improved by an increase in the electron-donating property of the substituents on the azomethine carbon accompanied by an increase of the n→π* transition absorption. However, the effect did not occur for the substituents on the azomethine nitrogen, in which no drastic changes in fluorescence efficiency could be observed. Through the investigation of the diamine bridge length effects, it was found that a diamine Schiff base seems to form neither an inter- nor an intramolecular dimer with any peculiar fluorescence in the solution even if it has a long methylene bridge. It was also suggested that the diamine Schiff base has a third fluorescence species in the excited state, which might be a pre-keto form, the existence of which is strongly affected by the hydrogen bond strength between the hydroxy and azomethine groups.

Introduction

Diamine Schiff bases such as *N*,*N*′-bis(salicylidene)ethylenediamine are quite familiar as tetradentate ligands in metal complexes.[1–3] They are different from monoamine Schiff bases in having two chromophores bridged by a methylene chain in a molecule, and thus the mutual interactions between the chromophores appears to affect their chemical and physical properties. It has been often reported that monoamine Schiff bases show strong fluorescence through the proton transfer between the hydroxy and azomethine groups in the chromophore.[4,5] Therefore, interesting optical properties derived from the interaction between the two chromophores in the diamine Schiff bases could be expected.



1a R = H
2 R = CH_3
3 R = C_2H_5
4 R = C_6H_5



1a	*n* = 2	**1f**	*n* = 7
1b	*n* = 3	**1g**	*n* = 8
1c	*n* = 4	**1h**	*n* = 9
1d	*n* = 5	**1i**	*n* = 10
1e	*n* = 6	**1j**	*n* = 12

Fig. 1 Molecular structure of *N*,*N*′-bis(α-substituted salicylidene)-ethylenediamines and *N*,*N*′-bis(salicylidene)diamines.

In a previous study, we have found that *N*,*N*′-bis(salicylidene)-butane-1,4-diamine and its analogues showed very strong fluorescence in the solid state under ultraviolet irradiation.[6] In particular, their fluorescence intensities were extremely influenced by the length of the bridge between the two chromophores. The relationship between the bridge length and fluorescence intensity was quite unusual and seemed to have no special rules. Thus, it is of interest to investigate the origin of fluorescence for diamine Schiff bases. In this work, we synthesized thirteen *N*,*N*′-bis(α-substituted salicylidene)diamines and examined their absorption, excitation and fluorescence properties in solution with the purpose of obtaining information about the influence of bridge length on their optical properties. The solvent and substituent effects on the fluorescence intensity were also investigated to obtain fundamental information about the factors responsible for their optical properties.

Results and discussion

Effect of the solvents

The chemical structures of the thirteen *N*,*N*′-bis(α-substituted salicylidene)diamines synthesized are shown in Fig. 1. There are two series for the compounds; one is for the investigation of the substituent effects (**1a**, **2**–**4**) and the other is for the investigation of diamine bridge length effects (**1a**–**1j**). Their optical properties were examined in solution.

Fig. 2 shows the absorption, fluorescence and excitation spectra of *N*,*N*′-bis(salicylidene)butane-1,4-diamine (**1c**) in chloroform. Three major bands appeared at 255, 320 and 410 nm in the absorption spectrum (solid line). According to the literature[7] these bands can be assigned as follows. The absorption band at 255 nm is most probably related to the π→π* transition of the aromatic chromophore. The band at 320 nm is assigned to the π→π* transition of the azomethine group. The band at 410 nm is the n→π* transition involving the pro-

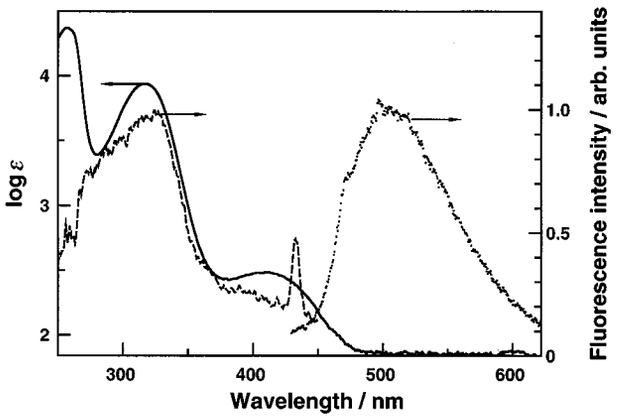
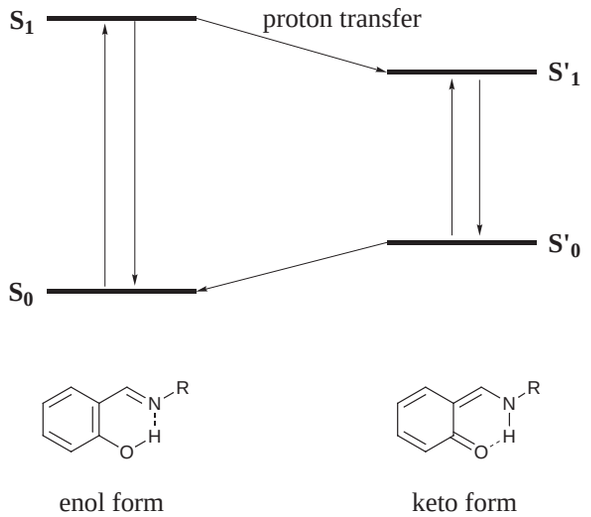


Fig. 2 Absorption (solid line), fluorescence (dotted line) and excitation (broken line) spectra of **1c** at a concentration of 1×10^{-4} mol dm^{-3} in chloroform. Fluorescence spectrum was observed by 410 nm excitation.



Scheme 1 Excited-state intramolecular proton transfer (ESIPT).

motion of a lone pair electron on the nitrogen atom to the antibonding π-orbital associated with the azomethine group.

The fluorescence spectrum (dotted line) of **1c** in chloroform, which was obtained by 410 nm excitation, shows a broad and strong peak at 510 nm. No phosphorescence was observed for the present system. A weak shoulder around 460 nm can be attributed to the Raman scattering of chloroform because peak shifts without drastic intensity changes could be observed for the band by changing the excitation wavelength.[8] The observed fluorescence peak wavelengths were not altered by varying the excitation wavelength between 255 and 410 nm although their intensities changed.

The excitation spectrum of **1c** in chloroform probed at 510 nm (broken line) shows peaks at 320 and 410 nm. A sharp peak at 440 nm originates in the Raman scattering. The observed spectral pattern corresponds well to that of the absorption spectrum.

In order to examine the existence of an intermolecular interaction between the chromophores in solution, the concentration dependence of the spectra of **1c** was investigated between 1×10^{-6} and 8×10^{-4} mol dm^{-3} in chloroform. It is expected that this concentration range would not cause any serious changes in the molecular structure and conformation of the Schiff base itself. Although prepared samples were highly soluble in the organic solvents to concentrations of higher than 1×10^{-2} mol dm^{-3} the concentration dependence of the absorption and fluorescence spectra was examined up to 1×10^{-2} mol dm^{-3}. At 8×10^{-4} mol dm^{-3}, the fluorescence intensity starts to decrease because of the inner filter effect under the present experimental conditions. In the whole concentration region mentioned above, neither shifts of absorption and fluorescence maxima nor new peaks were observed. Furthermore, the molar absorptivity was almost constant for all absorption bands. These facts indicate that extensive aggregation of the Schiff bases does not occur in the ground or in the excited state at least in the concentration range of 1×10^{-6} to 8×10^{-4} mol dm^{-3}. Therefore, all spectral measurements were made at a concentration of 1×10^{-4} mol dm^{-3}.

It has been known that proton transfer between the hydroxy and azomethine groups in the Schiff base is dominant, giving strong fluorescence (Scheme 1).[9–11] Thus, the polarity of the solvent must have a serious effect on the optical properties. Here, the effects of solvents on the absorption, fluorescence and excitation spectra of the Schiff base were examined.

Fig. 3(a) shows the absorption spectra of **1c** in several solvents. It is found that the appearance of the absorption bands is influenced by the solvent polarity. For instance, only the π→π* transition bands were observed at 255 and 320 nm in cyclohexane (— - - — - line). Cyclohexane is a non-polar solvent, thus

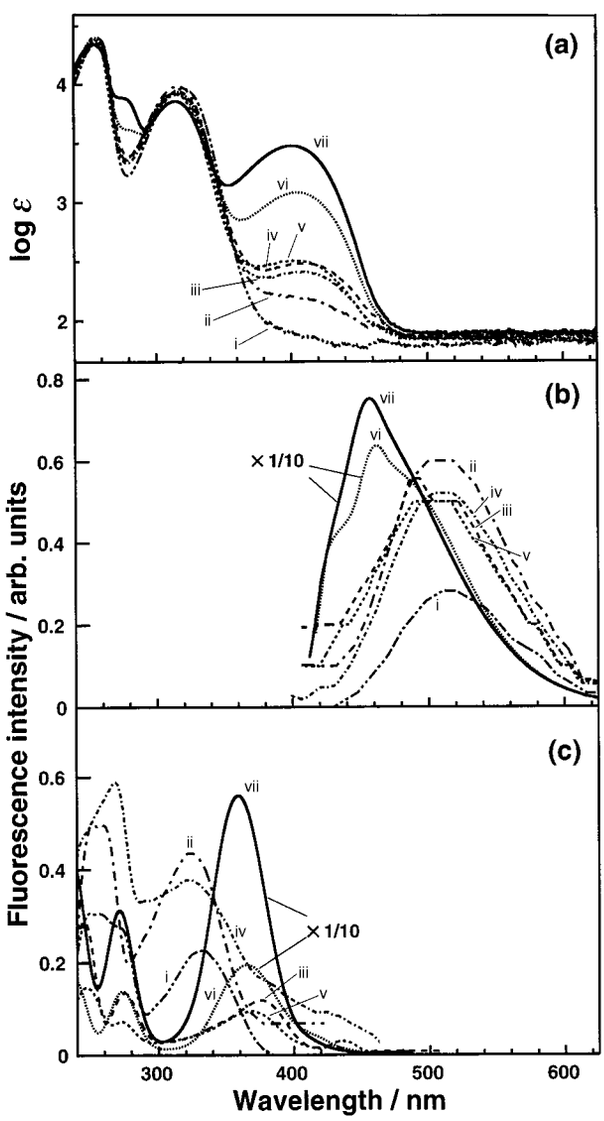


Fig. 3 (a) Absorption, (b) fluorescence and (c) excitation spectra of **1c** at a concentration of 1×10^{-4} mol dm^{-3} in several solvents. i, Cyclohexane; ii, 1,4-dioxane; iii, dichloromethane; iv, chloroform; v, acetonitrile; vi, propan-2-ol; vii, methanol. Excitation wavelength for the fluorescence spectra was 320 nm for the cyclohexane solution, and 410 nm for other solutions.

barely interacts with either the azomethine or the hydroxy groups of the Schiff base, resulting in a weak intramolecular hydrogen bond being formed between the hydroxy and azomethine groups of the Schiff base. This may be related to the result that the n→π* transition band could not be observed in cyclohexane solution. On the other hand, not only the π→π* transition bands but also the n→π* transition band (410 nm) could be observed in polar solvents such as chloroform. The n→π* transition band increased its intensity and was slightly blue shifted with an increase in the polarity of the solvents, although the π→π* transition bands were almost independent of the solvent's polarity. Furthermore, a new band appeared at 280 nm in alcohol, which had the highest polarity of the solvents used. This new band is probably associated with the phenolic chromophore, because the intramolecular hydrogen bond is usually broken in the alcohol solution.[7]

Fig. 3(b) shows the fluorescence spectra of **1c** obtained by the excitation wavelength of 410 nm in several solvents except for cyclohexane. Light absorption of **1c** at 410 nm in cyclohexane was extremely small, thus the 320 nm excitation wavelength was used for the fluorescence measurements of the cyclohexane solution. A broad fluorescence peak appeared at *ca.* 510 nm in the various solutions, except for alcohol. The alcohol solution brought about much stronger fluorescence than the other solutions, but the fluorescence peak appeared at 450 nm. Polar solvents tended to give stronger fluorescence than non-polar solvents. The spectral patterns were independent of the excitation wavelength of 255, 320 or 410 nm for all samples.

Fig. 3(c) shows the excitation spectra of **1c** in several solvents at each fluorescence maximum. The spectral patterns in the aprotic solvents were similar to those of the corresponding absorption spectra. On the other hand, the spectral pattern in the alcohol solution was quite different from those in the other solvents; the excitation peaks appeared at 280 and 350 nm. While the 280 nm band is compatible with an absorption band due to the phenolic chromophore, the 350 nm band is in conflict with the absorption spectra.

If the solvent can compete with the hydrogen atom of the hydroxy group in forming a hydrogen bond with the nitrogen lone pair, it would be expected that the intramolecular hydrogen bond tends to be weakened in polar solvents such as alcohol. Previously, Charette *et al.* have observed 280 and 350 nm bands in the absorption spectra of the *N*-salicylidenepropan-2-amine in acid solution, and suggested that these originated from its protonated form.[12] Sharm *et al.* reported that the acid dissociation constant pK_a of a Schiff base was 15.4 in the excited state and 8.51 in the ground state, indicating that Schiff bases could easily accept protic solvents in the excited state.[13] From these facts, it can be considered that the Schiff base in a protic solvent such as alcohol becomes solvated, and the structure or conformation around the azomethine groups might cause a big change by the strong interaction between the azomethine nitrogen and alcohol molecule. The fluorescence species for the excited state in alcohol seems to be different from that in an aprotic solvent.

From the observed results, it can be considered that the solvents that can strongly interact with the azomethine or hydroxy group bring about strong fluorescence of the compound. Fig. 4 shows normalized fluorescence intensity with the molar absorptivity plotted against the orientation polarizability $f(\varepsilon, n)$ of the solvent.[14–16] As is shown in Fig. 4, fluorescence efficiency is not dependent on the polarity of the solvent except for alcohol. Alcohol gave high fluorescence efficiency only in the case of 320 nm excitation. However, as is described above, protonation can occur in protic solvents and induce changes of fluorescence species in the excited states. Thus, it is not appropriate to compare the fluorescence efficiency in alcohol with other solutions. Consequently, it can be said that the fluorescence intensity of **1c** is simply dependent upon the molar absorptivities which vary depending on the polarity of the solvent.

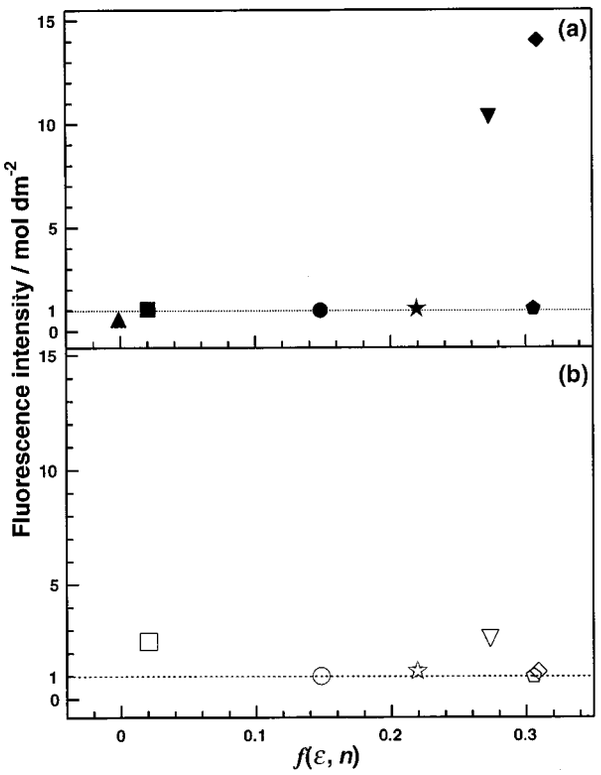


Fig. 4 Fluorescence intensities normalized with the absorptivity *vs.* the oriented polarizability $f(\varepsilon, n)$ of several solvents. (a) 320 nm excitation, (b) 410 nm excitation. Triangle: cyclohexane, square: 1,4-dioxane, star: dichloromethane, circle: chloroform, pentagon: acetonitrile, inverted triangle: propan-2-ol, diamond: methanol. $f(\varepsilon, n) = \left(\frac{\varepsilon - 1}{2\varepsilon + 1} - \frac{n^2 - 1}{2n^2 + 1}\right)$, ε = relative permittivity, n = refractive index. Fluorescence intensity compared with **1c** in chloroform.

Effect of the substituent on the azomethine carbon

As the transition bands for the azomethine group seem to be mainly responsible for the fluorescence, a change in the electron density of the azomethine group by several substituents must bring about certain changes in both the absorption and fluorescence. Thus, the substituent effect of the carbon of the azomethine group upon the absorption and fluorescence spectra was examined here.

Fig. 5(a) shows the absorption spectra of *N*,*N*′-bis(α-substituted salicylidene)ethylenediamine in chloroform. Three absorption bands of the π→π* (255 and 320 nm) and n→π* (410 nm) transitions appeared in the respective spectra. While the peak wavelengths and intensities of the π→π* transition bands were almost independent of the substituents, the n→π* transition was sensitive to the substituents. The molar absorptivities of the n→π* transition band of **2**, **3** and **4** were larger than that of **1a**.

Fig. 5(b) shows the fluorescence spectra of *N*,*N*′-bis(α-substituted salicylidene)ethylenediamine in chloroform. The peak at 460 nm is due to Raman scattering of chloroform as mentioned above.[8] **2**, **3** and **4** showed a fluorescence peak at 510 nm which was independent of the excitation wavelength. On the other hand, **1a** gave a fluorescence peak at 510 nm in the case of 255 or 320 nm excitation, but at 450 nm by 410 nm excitation for which the spectral pattern was similar to that of **1c** in the alcohol solution described in the previous section. The excitation spectrum of **1a** at 450 nm was also similar to that of **1c** in the alcohol solution, namely peaks appeared at 280 and 350 nm.

The lone pair electrons on the nitrogen atom can form a

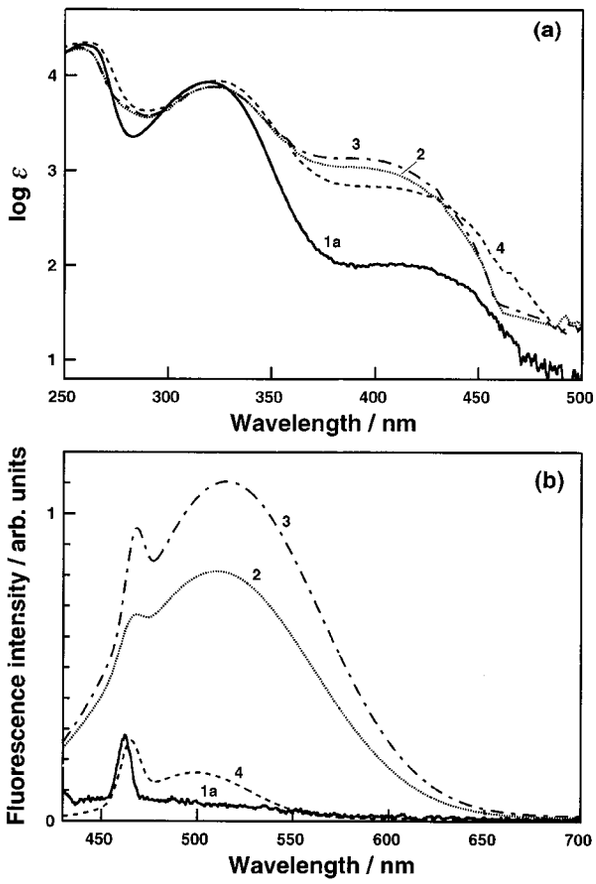


Fig. 5 (a) Absorption and (b) fluorescence spectra of *N,N′*-bis-(α-substituted salicylidene)ethylenediamine at a concentration of 1×10^{-4} mol dm^{-3} in chloroform. Fluorescence spectra were observed by 410 nm excitation.

hydrogen bond with the hydroxy group on the benzene ring in the Schiff base molecule (see Scheme 1), thus the hydrogen bond should be affected by the substituents. This effect was examined through ^{1}H NMR measurements. The chemical shifts of hydroxy protons, δ_{OH}, were observed at 13.2 ppm for **1a**, 15.9 ppm for **2**, 16.1 ppm for **3** and 15.2 ppm for **4**. Previously, it has been reported that δ_{OH} of 2-hydroxyacetophenone, which had a carbonyl group at the *ortho*-position to the hydroxy group, is 12.05 ppm, much larger than that of phenol, 7.54 ppm.[17] This deshielding shift is attributable to the formation of an intramolecular hydrogen bond. Considering this result, we expect that δ_{OH} can be a good measure of the intramolecular hydrogen bond in the Schiff base. The obtained δ_{OH} values for the compounds indicate that the hydrogen bond strength is in the order of **1a** < **4** < **2** < **3**.

The fluorescence intensity of these compounds increases as the molar absorptivity increases, as can be seen in Fig. 5. In order to examine the efficiency of the fluorescence, relative fluorescence intensities normalized by the molar absorptivity were plotted against the δ_{OH} value, see Fig. 6. It is found that not only the fluorescence intensity increases but the fluorescence efficiency is also improved for **2**, **3** and **4** as the δ_{OH} value shifts to lower field, that is, as the hydrogen bond strengthens. It has been reported that the keto form fluoresces strongly but the enol form fluoresces weakly.[9–11] Then, if the keto form is more stabilized than the enol form, especially at the transition state, the Schiff bases would strongly fluoresce. As the electron density on the nitrogen atoms is increased by the substituent electron-donating groups, the population of the keto form at the transition state would increase, resulting in an improvement of the fluorescence efficiency of the fluorescence.

On the other hand, **1a** gave a different fluorescence spectrum, and thus seems to be an exceptional case in the series. It has

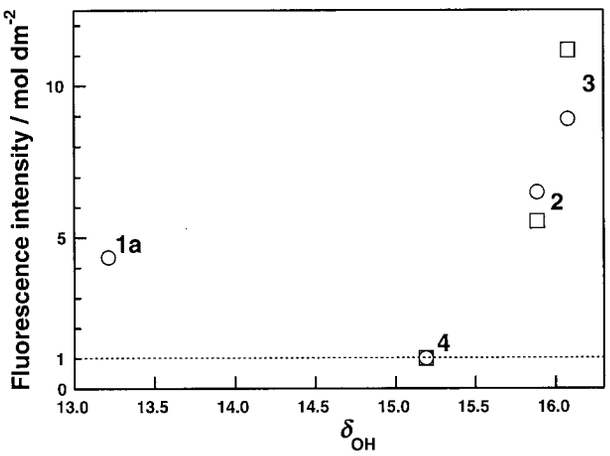


Fig. 6 Relationships between fluorescence intensity and the chemical shift of the hydroxy group (δ_{OH}). ○ is the case of the 320 nm excitation, □ is the 410 nm excitation. Fluorescence intensity was normalized by the molar absorptivity. Fluorescence intensity compared with **4**.

been reported that the fluorescence peak of 2-(2′-hydroxyphenyl)benzothiazole appears at 410 nm for its enol form and at 510 nm for its keto form.[18] According to the ^{1}H NMR measurement, the intramolecular hydrogen bonding ability of **1a** was weaker than other Schiff bases. As is mentioned above, **1a** and **1c** in the alcohol solution give similar fluorescence spectra with a 450 nm peak and excitation spectra with 280 and 350 nm peaks. In both cases, proton transfer from the enol to the keto form is more difficult than for the other compounds. However, it was reported that the enol form of the Schiff base shows only very weak fluorescence,[4,9,10] and the observed 450 nm fluorescence for **1a** is also different from the reported 410 nm fluorescence for the enol form. Thus, it can be considered that there is a third fluorescence species in the excited state, which is neither the usual keto form nor the enol form but is probably a pre-keto form suggested by Barbara *et al.*[19]

Effect of the diamine bridge length

As reported in the previous paper, unusual fluorescence behavior depending on the diamine bridge length could be observed in the solid state.[6] It seemed to be due to structural effects of the Schiff bases such as inter- or intramolecular interaction between chromophores. In order to investigate the effects, a series of Schiff bases with several bridge lengths were prepared, and their absorption and fluorescence spectra in the chloroform solution were investigated.

Fig. 7(a) shows the absorption spectra of diamine Schiff bases with several bridge lengths. Three absorption bands of the π→π* (255 and 320 nm) and n→π* (410 nm) transitions appeared in each spectrum. The absorption peak wavelengths are almost the same for all the samples used here. While the peak intensities of the π→π* transition bands are almost independent of the length of diamine bridge, that of the n→π* transition band becomes stronger as the bridge length becomes longer.

Fig. 7(b) shows the fluorescence spectra of diamine Schiff bases with several bridge lengths, excited at 410 nm. The fluorescence peak was observed at *ca.* 510 nm except for **1a**. As is described above, **1a** shows a fluorescence peak at 450 nm by 410 nm excitation, and seems to be an exceptional case among the series. Fluorescence intensities also increase as the bridge length becomes longer.

Considering the fact that absorption and fluorescence peak wavelength were almost independent of the diamine bridge length, the possibility that the fluorescence results from the intramolecular dimer between the chromophores can be

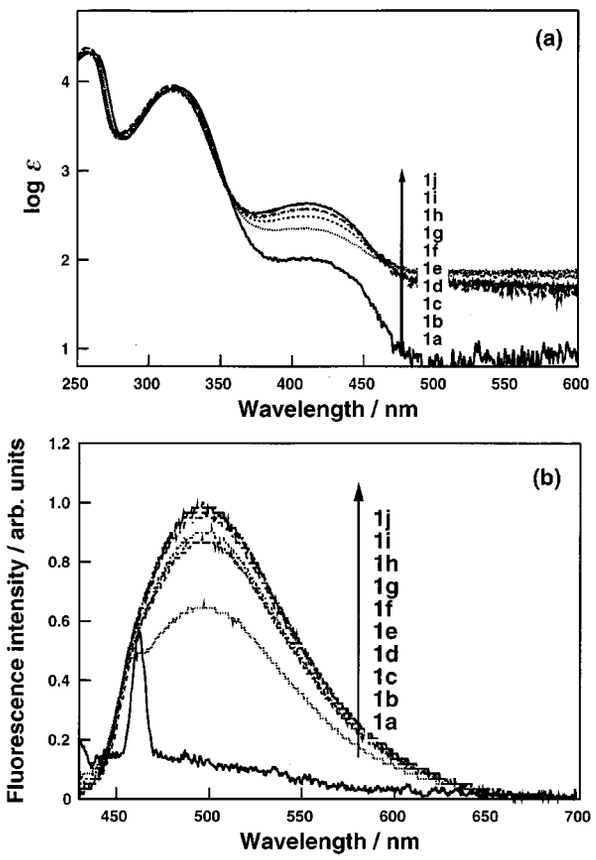


Fig. 7 (a) Absorption and (b) fluorescence spectra of *N*,*N*′-bis(salicylidene)diamines with several bridge lengths at a concentration of 1×10^{-4} mol dm^{-3} in chloroform. Fluorescence spectra were observed by 410 nm excitation.

excluded. The bridge length of 12 methylene units seems to be long enough to form an intramolecular dimer between the chromophores by the alkyl chain twisting if desirable. Therefore, it can be concluded that diamine Schiff bases do not form an intramolecular dimer in the solution even though they have a long methylene bridge.

In order to investigate the fluorescence efficiency of fluorescence, the relative fluorescence intensity normalized with the molar absorptivity was plotted against the diamine bridge length for various compounds in Fig. 8. As is shown in the figure, the fluorescence efficiency of the fluorescence seems to be almost independent of the diamine bridge length for both 320 and 410 nm excitation. It has been known that the basicity of diamines increases with an increase in the number of methylene units between the two amino groups.[20] Then, at least the methylene units should behave as an electron donating substituent on the azomethine group. Actually, the effect seems to be reflected in the absorption spectra as the change of absorptivity of the n→π* transition band. The longer diamine bridge gave the higher electron density on the nitrogen atom, resulting in an increase of the molar absorptivity of the n→π* transition band due to the substituent effect on the azomethine nitrogen. However, the fluorescence efficiency of the fluorescence was not influenced by the diamine bridge length. This is contrary to the results of the substituent effect on the azomethine carbon. Namely, it is found that there is an essential difference in the substituent effect of the azomethine carbon and nitrogen upon the fluorescence although the absorption spectra are not so much influenced by them.

Conclusion

Absorption and fluorescence spectra of two series of *N*,*N*′-bis(α-substituted salicylidene)diamines in solution were investi-

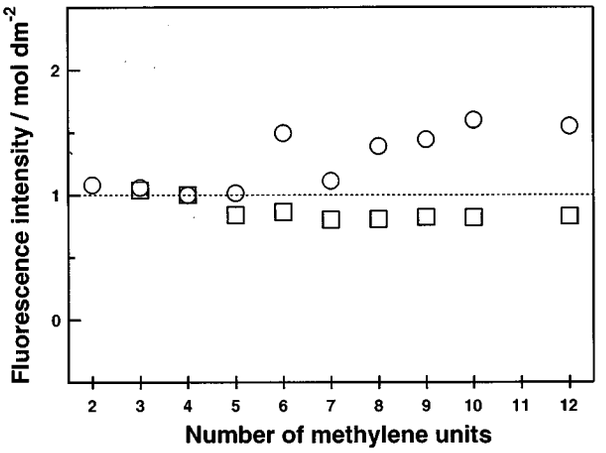


Fig. 8 Relationship between the fluorescence intensity and number of methylene unit of diamine bridge. ○ is the case of the 320 nm excitation, □ is the 410 nm excitation. Fluorescence intensity was normalized by the molar absorptivity. Fluorescence intensity compared with **1c**.

gated. Their optical properties were considerably influenced by the polarity of solvents and substituents on the chromophore. It was shown that the diamine Schiff bases in a protic solvent, such as alcohol, were in a solvated form to give different excitation bands and fluorescence spectra. While substituted groups on the azomethine carbon influenced the fluorescence efficiency of the fluorescence in the solution, those on the azomethine nitrogen did not have any serious effects. Although details about the phenomena are still not clear, it seems to be related to a transition process of excited species concerning the azomethine group. On examining the optical properties of diamine Schiff bases with several bridge lengths in solution, neither inter- nor intramolecular interaction could be observed, despite the diamine bridge being up to twelve methylene units long. It seems to be difficult to form a stacking structure between two chromophores for diamine Schiff bases. From these results, it is suggested that there are at least three fluorescence species of diamine Schiff bases in the excited state: enol, keto and possibly pre-keto forms, of which the lifetimes are closely related to the electron density of the azomethine nitrogen.

These obtained results are not directly related to the unique fluorescence phenomena of solid state diamine Schiff bases observed in our previous study, but seem to be helpful in understanding it, giving fundamental information about their optical properties. Further investigations into the relationship between the fluorescence properties and crystal structures or the lifetimes of excited species are necessary to fully understand the fluorescence phenomena.

Experimental

Materials

Thirteen *N*,*N*′-bis(α-substituted salicylidene)diamines were synthesized using the following procedure. *N*,*N*′-bis(salicylidene)-butane-1,4-diamine (**1c**) was synthesized in the following manner. 0.4 mol of salicylaldehyde in 60 cm^3 of hot ethanol was added to 0.2 mol of butane-1,4-diamine in 50 cm^3 of ethanol. The solution was then stirred for 30 min at 60 °C (water bath), and the yellow microcrystals produced were cooled to room temperature. Recrystallization from ethanol gave yellow plate-like crystals. Other diamine Schiff bases were also synthesized in a similar manner, and recrystallized from ethanol or chloroform to give yellow crystals.

Measurements

The UV-VIS absorption spectra of diamine Schiff bases were recorded on a SHIMADZU UV-3100 spectrophotometer in the wavelength range of 200–1000 nm. Weighed samples were

dissolved in chloroform, methanol, propan-2-ol, acetonitrile, dichloromethane, 1,4-dioxane, and cyclohexane which were distilled before use. Fluorescence spectra of diamine Schiff base compounds were measured with a 1 cm^3 quartz cell using a HITACHI Model 850 fluorescence spectrophotometer at 25 °C. Fluorescence was monitored at a 90° angle to the excitation light. The fluorescence and excitation spectra were not corrected for spectral response. This does not cause serious errors, because the change of fluorescence spectra of the diamine Schiff bases is small for different chain lengths. The relative fluorescence efficiency is defined as the relative fluorescence intensity divided by the absorbance of the sample at the excitation wavelength. In the study of the substituent effect, **4** was selected as the fluorescence efficiency standard with unit fluorescence efficiency, while in the study of the effect of diamine bridge length, **1c** was selected as a standard. ^{1}H NMR spectra were taken on a BRUKER AMX-500 spectrometer operating at 500 MHz, using the sample dissolved in $CDCl_3$ in the presence of tetramethylsilane as the internal reference.

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