Bull. Chem. Soc. Jpn., 63, 1349—1353 (1990)

Fluorescence Behaviors of 3,3-Bis(8-quinolyloxymethyl)oxetane: Effects of Solvents, Carrier-Concentration, and Metal Ions on the Fluorescence Intensity

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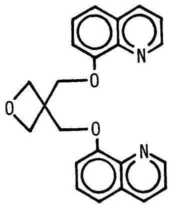
(Received October 7, 1989)

The effects of solvents, the concentration of 3,3-bis(8-quinolyloxymethyl)oxetane (**1**), and the presence of metal ions on the fluorescence intensity of **1** have been investigated. The fluorescence intensity of **1** considerably increased when measured in chloroform, acetonitrile, or dioxane, though resulting in a comparably small increase when measured in ethyl acetate, toluene, or ethylene glycol. When acetone was used as the solvent, the fluorescence spectrum was hardly observed. When the concentration of **1** was adjusted to near 0.1 mmol dm^{-3}, the intensity became maximum in each solvent used, except for acetone. It was observed that the fluorescence intensity of **1** rapidly decreased in a concentration range over 0.1 mmol dm^{-3}. Furthermore, when metal ions were added into an organic solution such as acetonitrile, dioxane, or chloroform containing **1**, the maximum increase in the fluorescence intensity was observed in the presence of lithium salt, whereas the intensity hardly changed in the presence of both potassium and sodium ions, compared with that of **1** in the absence of any metal ion. The presence of magnesium and barium ions also hardly brought about an increase of the intensity. On the other hand, heavy metal ions, such as silver(I) and copper(II), were observed to results in a slight decrease.

Much attention has been increasingly paid to lithium-ion detection, not only using ion-selective electrodes based on neutral carriers,[1—8] but also by spectrophotometric methods,[9,10] which can afford to be an available tool, because lithium-ion detection has become important in biological and environmental systems.[11—14]

We have recently reported that 1,3-bis(8-quinolyloxy)propane derivatives are potential fluorescent ionophores for lithium-ion detection in acetonitrile.[15,16] That is, their fluorescence intensity can increase remarkably in the presence of lithium perchlorate, whereas it hardly increases in the presence of sodium or potassium ions. Furthermore, a linear relationship between the fluorescence intensity and the concentration of lithium ions within the limited range was found; it was demonstrated that a quantitative determination of lithium ions is possible in acetonitrile.[16] Besides, it has been confirmed that the intensity strongly depends on the structure of 1,3-bis(8-quinolyloxy)propane derivatives, and 3,3-bis(8-quinolyloxymethyl)oxetane (**1**) exhibits one of the largest increases of fluorescence intensity in the presence of lithium ions among the ionophores investigated.



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In this study we report on the effects of solvents, the concentration of **1**, and the kind of metal salts on the fluorescence intensity. According to the litherature,[9,10] there are a number of ionophores in which either the electron or fluorescence spctrum can be changed by the addition of metal ions. In particular, many studies on macrocyclic ionophores, which can exhibit a hypochromic and/or bathochromic change in the electron spectrum when metal ions are added, have been reported so far,[8] whereas there are not so many ionophores which can exhibit a remarkable and selective change in the fluorescence spectrum.[17—20] Above all, the fluorescence behaviors of noncyclic polyethers have scarecely been reported.[21—23] We have also investigated the behavior of noncyclic ionophore (**1**) synthesized in the fluorescence spectrum.

Results and Discussion

1. Effect of Solvents on the Fluorescence Intensity in the Absence of Any Metal Ion.

The fluorescence spectra of 3,3-bis(8-quinolyloxymethyl)oxetane (**1**) were measured in the absence of metal ions in several solvents in order to investigate the effect of solvents on fluorescence. Dioxane, toluene, chloroform, ethyl acetate, acetone, acetonitrile, and ethylene glycol were used as solvents with different dielectric constants. Figure 1 shows the relative magnitudes of the fluorescence intensity of 0.1 mM (0.1 mmol dm^{-3}) of **1** in each solvent. Plots of the fluorescence intensity toward the dielectric constants of each solvent used are shown in Fig. 2. As indicated in these figures, there seems to be no relationship between the fluorescence intensity of **1** and the magnitude of the dielectric constants of the solvents. In acetone the fluorescence of **1** is completely quenched in a way different from the other solvents. On the other hand, in a protic solvent, ethylene glycol, the maximum fluorescence wavelength appears at 404 nm and shows about 20-nm red shift, compared with that in the other solvents.

The fluorescence spectrum was then measured while

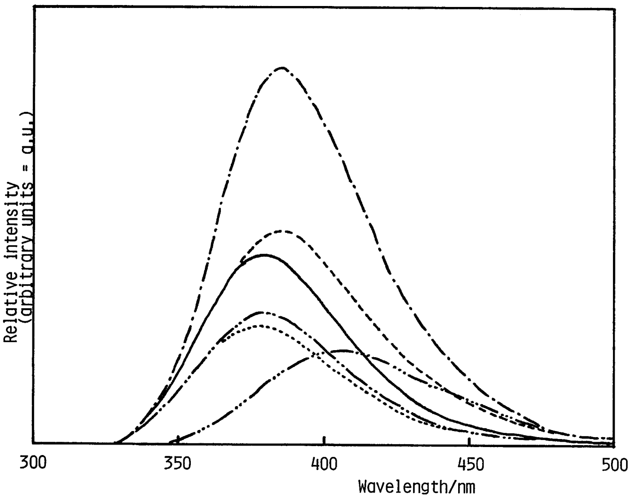

Fig. 1. The influence of solvents on the fluorescence spectrum of **1** (0.1 mmol dm^{-3}). Excitation wavelength 311 nm, 23 °C. Emission maximum: 385 nm in CHCl$_3$ (—·—·—), 384 nm in MeCN (------), 378 nm in dioxane (———), 380 nm in ethyl acetate (—··—··—), 378 nm in toluene (·········), and 404 nm in ethylene glycol (—···—···—). Ionophore **1** has no emission spectrum in acetone.

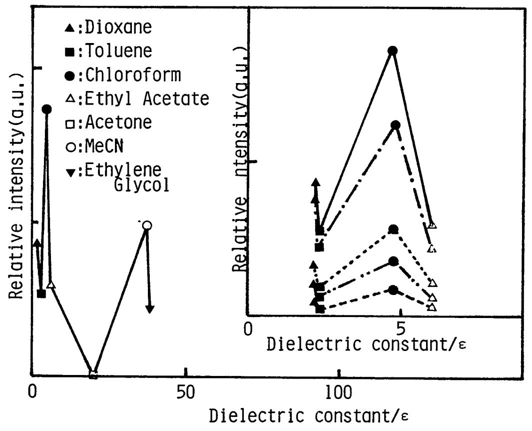

Fig. 2. Plots of the relative fluorescence intensity of **1** vs. the dielectric constants of each solvent. Concentration of **1**, —··—··—: 0.01 mmol dm^{-3} (=mM), —·—·—: 0.05 mM, ———: 0.1 mM, ·········: 0.5 mM, ------: 1.0 mM. Dielectric constants, dioxane 2.21, toluene 2.379, chloroform 4.806, ethyl acetate 6.02, acetone 20.7, acetonitrile 37.5, ethylene glycol 37.7.

changing the concentration from 0.01 mM of **1** in these solvents. Figure 3 shows plots of the maximum fluorescence intensity against each concentration of **1** in chloroform. The fluorescence intensity apparently has a maximum at a certain concentration of **1**. The same phenomenon was observed in the other solvents, except for acetone. In acetone the fluorescence spectrum was not observed at all over the entire range of the concentration. Figure 4 shows plots of the maximum fluorescence intensity in each solvent

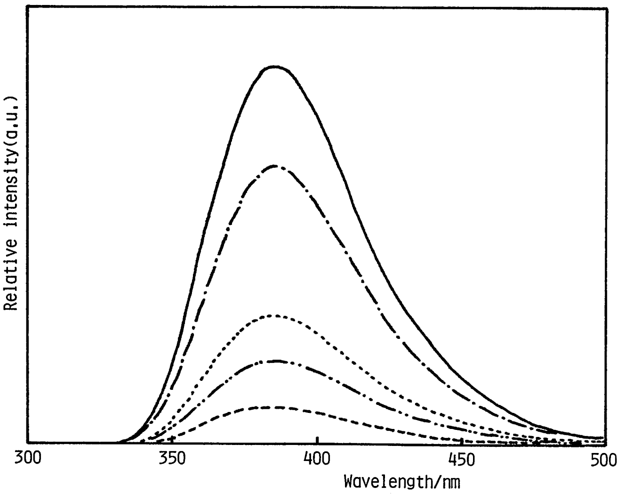

Fig. 3. Effect of the concentration of **1** on the fluorescence spectrum in chloroform. Excitation wavelength 311 nm, 23 °C. —··—··—: 0.01 mmol dm^{-3} (=mM), —·—·—: 0.05 mM, ———: 0.1 mM, ·········: 0.5 mM, ------: 1.0 mM.

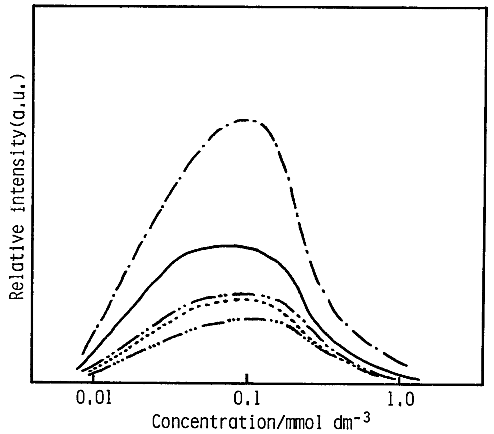

Fig. 4. Effects of the concentration of **1** and the solvent on the maximum fluorescence intensity of **1**. —·—·—: chloroform, ———: dioxane, —··—··—: ethyl acetate, ·········: toluene, —···—···—: ethylene glycol.

against the concentration of **1**. The fluorescence intensity gradually increases in the range between 0.01 and 0.1 mM of the concentration and becomes maximum at a concentration near 0.1 mM. Then, the intensity rapidly decreases in the range over 0.1 mM because of quenching; the spectrum can hardly be observed at 0.1 mM in each solvent. Thus, the fluorescence spectrum is apparently affected to a great extent by the concentration of **1**. Therefore, suitable solvents for fluorometry should be selected and the optimum concentration arranged in fluorescence measurements. The concentration of **1** should be kept constant for a quantitative comparison. Then, the concentration below 0.1 mM of **1** was used in the

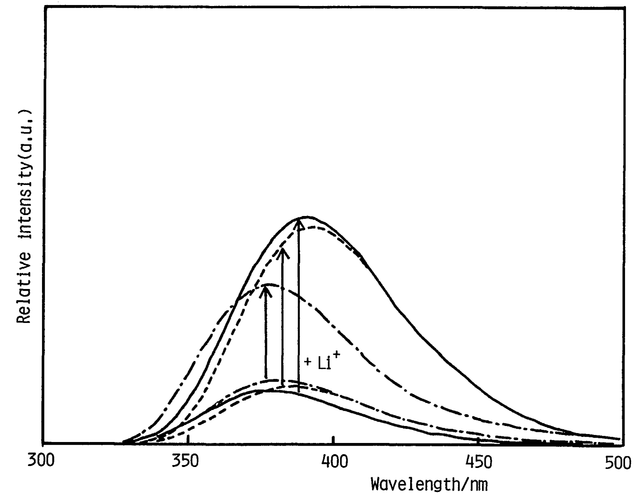

Fig. 5. Influence of the addition of lithium perchlorate (10 mmol dm^{-3}) on the fluorescence spectrum of **1** (0.01 mmol dm^{-3}) in each solvent. Excitation wavelength 306 nm, 23 °C. Emission maximum in the presence of lithium perchlorate: 391 nm in dioxane (———), 392 nm in MeCN (------), and 378 nm in $CHCl_3$ (—·—·—). Lithium perchlorate is partially insoluble in dioxane and $CHCl_3$. Emission maximum in the absence of lithium perchlorate: 378 nm in dioxane (———), 385 nm in MeCN (------), and 382 nm in $CHCl_3$ (—·—·—).

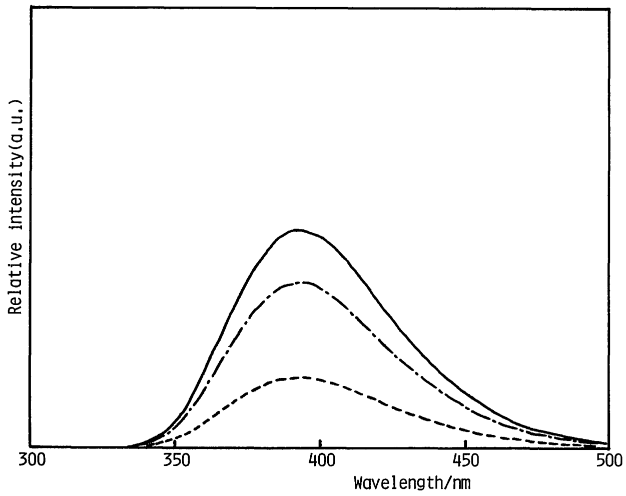

Fig. 6. Influence of the counter anions of lithium ion on the fluorescence intensity of **1** (0.01 mmol dm^{-3}) in MeCN. Excitation wavelength 306 nm, 23 °C. ———: $LiClO_4$ (Emission maximum 392 nm), —·—·—: LiCl (Emission maximum 393 nm), and ------: LiI (Emission maximum 393 nm).

measurement of the fluorescence spectrum under the presence of metal ions.

2. Effects of Solvents on the Fluorescence Intensity in the Presence of Lithium Perchlorate. As shown in Fig. 1, 3,3-bis(8-quinolyloxymethyl)oxetane (**1**) exhibits a comparably large fluorescence intensity in chloroform, acetonitrile, and dioxane. The fluorescence spectra were therefore measured in the presence of lithium perchlorate by using these three solvents. When a one-thousand-fold amount of lithium perchlorate (10 mM) toward 0.01 mM of **1** was added, it was not completely dissolved in the solvents, except in acetonitrile. Then, the fluorescence spectrum of a saturated solution of chloroform or dioxane was measured. Figure 5 shows the spectra of 00.1 mM of **1** in each solvent. Though the maximum fluorescence wavelengths of **1** are slightly different due to the solvent used, in every case the intensity increased 3- to 4-fold more than that without lithium perchlorate. In both acetonitrile and dioxane the intensities are almost the same, while in chloroform it becomes a slightly smaller. Apparently, the ratio of the fluorescence intensity due to the presence of lithium perchlorate increases in the following order: chloroform < acetonitrile < dioxane.

Next, the effect of the counter anion of lithium ion on the fluorescence spectra of **1** was investigated. Figure 6 shows the fluorescence spectra in acetonitrile when chloride and iodide ions were used as counter anions instead of perchlorate ions. When a one-thousand-fold amount (42 mg, 1.0 mmol) of LiCl toward 0.01 mM of **1** was added into 100 ml of the solution, chloride salt was not completely soluble and the supernatant solution was used for the fluorescence measurement: a solution containing 6 mM of LiI. The magnitude of the fluorescence intensity was: $LiClO_4 > LiCl > LiI$.

Thus, the fluorescence intensity of **1** increased considerably in the presence of lithium ions in dioxane or chloroform in a similar manner as that in acetonitrile. Besides, the intensity is apparently affected by the kind of counter anions; iodide ions are not suitable for fluorescence measurements because they becomes a quencher of the fluorescence of **1**.

3. Effects of Metal Ions on the Fluorescence. As previously reported, in the fluorescence spectra of oxetane derivative (**1**) in acetonitrile, the addition of lithium ions into the solution can give rise to a specific and drastic increase in the fluorescence intensity, whereas the addition of sodium or potassiumion does not.[15,16] In this study the fluorescence behaviors of **1** were investigated when alkaline earth metal ions, magnesium and barium ions, and heavy metal ions, silver(I) and copper(II), were added into the solution. In order to improve the solubility of the salts of those ions in organic solvents, 4-cyclohexylbutyrate ion was used as a counter anion of each metal ion. However, these salts are not always suitable for measurements in acetonitrile or chloroform because of their generally low solubility in such solvents. The change of the fluorescence intensity in chloroform or acetonitrile is summarized in Table 1. Both the intensity and the

Table 1. Effects of the Metal Ion on the Fluorescence Intensity of **1**

Run	Metal ion	Solvent	Ratio (mol/mol) of Metal:Ligand	Relative fluorescence intensity toward free **1**	
				Peak max/nm	Intensity
1	Mg(II)	$CHCl_3$	10	385	1.0
2	Mg(II)	$CHCl_3$	100	384	0.87
3	Mg(II)	MeCN	160[a]	387	0.76
4	Ba (II)	MeCN	160[a]	386	1.0
5	Ag (I)	MeCN	210[a]	397	0.5
6	Cu (II)	$CHCl_3$	10	385	0.13
7	Cu (II)	$CHCl_3$	100	—	0
8	Cu (II)	MeCN	170[a]	386	0.5

a) Precipitants were formed to some extent when metal salts were added into the solution. The supernatant solution was used for the measurements.

shape of the spectra in the presence of a large amount of magnesium ion (ten-fold amount of **1**) hardly changed in chloroform compared with those of **1** in the absence of any metal ion (run 1). A slight decrease in the intensity was observed when the measuring conditions were changed, as in runs 2 and 3. Though precipitants were observed in acetonitrile when barium salt was added, the intensity did not also change in this case. Thus, no significant change in the spectra was observed upon the addition of alkaline earth metal ions as well as alkali metal ions, except for lithium ions. On the other hand, when 4-cyclohexylbutyrates of Ag(I) and Cu(II) were added into an acetonitrile solution, precipitants yielded and the relative intensity became half that of free **1**. In chloroform, though the addition of Cu(II) did not give any precipitants, the intensity became remarkably small. When a one-hundred-fold amount of Cu(II) salt toward 0.01 mM of **1** was added, it became negligible (run 7). In the electron-absorption spectrum, this sample solution was blue and had a large absorption band at 670 nm, based on d-electron of Cu(II); the second absorption band of the d–d transition (a large shoulder band) appeared at about 360 nm. This absorption band is considered to be able to quench fluorescence because it overlaps both the excitation wavelength (311 nm) and the maximum fluorescence line (380 nm) in the fluorescence spectra.

As described above, there was no metal ion which could remarkably increase the fluorescence intensity of **1** among four metal ions, unlike the lithium ions. The size of the metal ion-diameter is as follows: Li(I) (1.20 Å) $<$ Mg(II) (1.30 Å) $<$ Cu(II) (1.44 Å) $<$ Na(I) (1.98 Å) $<$ Ag(I) (2.52 Å) $<$ K(I) (2.66 Å) $<$ Ba(II) (2.70 Å). When making an inspection based on the CPK model building, the cavity size enclosed by two nitrogen atoms of the quinoline rings and two ether-oxygen atoms could best fit lithium and magnesium ions. Complexation with divalent magnesium ions might be excluded for the following reasons: 1) a magnesium ion requires six or more coordination numbers for stable complexation, 2) two counter anions seem to be difficult to coordinate to the magnesium ion of the complex at the same time because of the structural torsion based on the quinoline rings,[26] and 3) the hydration energy of magnesium ion is too high to form a stable complex with **1**. It is, therefore, pressumed that metal ions having a larger ion-size than that of the lithium ion could not be incorporated into the pseudocavity, resulting in no responce in the fluorescence spectrum.

So far, a similar increase by metal ions in the fluorescence intensity was observed in fluorescent crown ethers; this was concluded to be a consequence of the rigidification of the molecule due to strong complexation.[18,19] Similarly, in this noncyclic ligand system, it is suspected that a strong interaction exists between the metal ion coordinated and the nitrogen and oxygen atoms of **1** due to a hypsochromic shift in the maximum wavelength upon complexation.

Experimental

Materials. The 3,3-bis(8-quinolyloxymethyl)oxetane (**1**) which was used as a reagent for fluorescence measurements was prepared from the reaction of 3,3-Bis(chloromethyl)-oxetane[27] with two equimolar 8-quinolinol in the presence of potassium *t*-butoxide in *N*,*N*-dimethylformamide (previously reported procedure). Extra-pure grade lithium, sodium, and potassium perchlorates, lithium chloride, and lithium iodide were commercially available from Wako Pure Chemical Ind. Ltd. Also, 4-cyclohexylbutyrates of magnesium(II), barium(II), silver(I), and copper(II) ions were obtained from Dojin Laboratories, Ltd. Solvents for the fluorescence spectra (Uvasol for fluorometry), acetonitrile, chloroform, and dioxane were purchased from Merck Ltd. Extra-pure grade toluene, ethyl acetate, acetone, and ethylene glycol were obtained from Wako Pure Chemical Ind. Ltd. These solvents were used without further purification for measurements of the fluorescence spectra. They were confirmed to be inactive over the entire range of wavelengths measured before use.

Measurements of the Fluorescence Spectra. Each solution of **1** was adjusted in the concentration range from 0.01 to 1.0 mM (=mmol dm^{-3}) by using measuring flasks. An acetonitrile solution of 0.01 mM of **1** containing 10 mM of lithium perchlorate was also adjusted. Since a thousand-fold molar amount of lithium perchlorate was not fully soluble in dioxane or chloroform solutions of 0.01 mM of **1**, a lithium perchlorate saturated solution was used for the fluorescence measurements. An acetonitrile solution of 0.01 mM of **1** containing 6 mM of lithium iodide was adjusted. Since a thousand-fold molar amount of lithium chloride was not fully soluble in acetonitrile solution of 0.01 mM of **1**, the saturated solution was used for the fluorescence measurements. Chloroform solutions of 0.01 mM of **1** containing 0.1 mM and 1.0 mM of 4-cyclohexylbutyrates of Mg(II) or Cu(II) ion were adjusted without precipitation. As soon as 4-cyclohexylbutyrate of magnesium ion (0.35 g, 0.97 mmol), barium ion (0.46 g, 0.97 mmol), silver(I) (0.36 g, 1.3 mmol), or copper(II) (0.41 g, 1.0 mmol) was added into 100 ml of an acetonitrile solution of 0.06 mM of **1**, the precipitants separated out, and the supernatant solution was used for the measurements.

The fluorescence spectra of each solution containing 0.01 mM of **1** with or without metal ion were recorded at 23 °C on a Hitachi F-3000 Fluorescence spectrophotometer. Quartz glass cells (10 mm×10 mm) were used for the measurement. The other detailed conditions are described in the footnotes of each figures and in the table. Standard deviations of each result of determinations were ±10% or better.

References

1) D. Ammann, W. E. Morf, P. Anker, P. C. Meier, E. Pretsch, and W. Simon, *Ion-Selective Electrode Rev.*, **5**, 3 (1983).

2) E. Metzger, D. Ammann, U. Schefer, E. Pretsch, and W. Simon, *Chimia*, **38**, 440 (1984).

3) K. Kimura, H. Yano, S. Kitazawa, and T. Shono, *J. Chem. Soc., Perkin Trans.*, **11**, 1945 (1986).

4) V. P. V. Gadzekpo, G. J. Moody, J. D. R. Thomas, and G. D. Cristian, *Ion-Selective Electrode Rev.*, **8**, 173 (1986).

5) K. Hiratani, T. Okada, and H. Sugihara, *Anal. Chem.*, **59**, 766 (1987).

6) H. Sugihara, T. Okada, and K. Hiratani, *Chem. Lett.*, **1987**, 2391.

7) K. Suzuki, K. Tohda, H. Sasakura, H. Inoue, K. Tatsuta, and T. Shirai, *J. Chem. Soc., Chem. Commun.*, **1987**, 932.

8) M. Takagi and K. Ueno, *Top. Curr. Chem.*, **121**, 37 (1984).

9) H. -G. Löhr and F. Vögtle, *Acc. Chem. Res.*, **18**, 65 (1985).

10) *Chem. Eng. News*, November 9, p26, **1986**.

11) D. J. Cram, R. A. Carmack, and R. C. Helgeson, *J. Am. Chem. Soc.*, **110**, 571 (1988) and references cited therein.

12) M. J. Schou, *J. Psychiatr. Res.*, **6**, 67 (1968).

13) M. Canessa, N. Adragna, H. S. Solomon, T. M. Connolly, and D. C. Tosteson, *N. Engl. J. Med.*, **302**, 772 (1980).

14) D. C. Tosteson, *Sci. Am.*, **244**, 164 (1981).

15) K. Hiratani, *J. Chem. Soc., Chem. Commun.*, **1987**, 960.

16) K. Hiratani, *Analyst*, **113**, 1065 (1988).

17) "Ion-selective Electrodes in Analytical Chemistry," ed by H. Freiser, Plenum Press, New York and London (1978).

18) H. Nishida, Y. Katayama, H. Katsuki, H. Nakamura, M. Takagi, and K. Ueno, *Chem. Lett.*, **1982**, 1853.

19) O. S. Wolfbeis and H. Offenbacher, *Monatsh. Chem.*, **115**, 647 (1984).

20) A. P. de Silva and S. A. de Silva, *J. Chem. Soc., Chem. Commun.*, **1986**, 1709.

21) K. W. Street, Jr. and S. A. Krause, *Anal. Lett.*, **19**, 735 (1986).

22) S. Ghosh, M. Petrin, A. H. Maki, and L. R. Sousa, *J. Chem. Phys.*, **87**, 4315 (1987) and references cited therein.

23) K. Nakashima, Y. Nagaoka, S. Nakatsuji, T. Kaneda, I. Tanigawa, K. Hirose, S. Misumi, and S. Akiyama, *Bull. Chem. Soc. Jpn.*, **60**, 3219 (1987).

24) A. Villiger, W. E. Morf, and W. Simon, *Helv. Chim. Acta*, **66**, 1078 (1983).

25) M. E. Huston, K. W. Haider, and A. W. Czarnik, *J. Am. Chem. Soc.*, **110**, 4460 (1988).

26) K. Ueno, K. Hiratani, K. Taguchi, T. Okada, and H. Sugihara, *Chem. Lett.*, **1987**, 949.

27) T. W. Campbell, *J. Org. Chem.*, **22**, 1029 (1957).