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Specific Fluorescence Detection of Lithium Ion with 2,9-Disubstituted 1,10-Phenanthroline Derivatives

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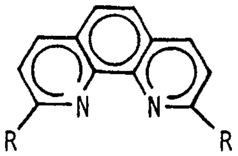
The fluorescence intensity of 2,9-di-n-butyl-1,10-phenanthroline was drastically enhanced in the presence of lithium ion, but not sodium, potassium, and beryllium ions.

Ionophores which can detect ions quantitatively by the spectrophotometrical methods are attractive because of the possibility of the potentially wide applicaitons.[1,2] In particular, the use of fluorescence for analysis in the presence of metal ions provides great promise as an analytical tool.[3-10] We reported recently on the ion-selective electrodes using 2,9-di-n-butyl-1,10-phenanthroline as a carrier which can exhibit excellent lithium ion-selectivity among alkali and alkaline earth metal ions: the ion selectivity coefficient (log k^{pot}(Li Na)) reached -3.2.[11] During the course of our work, we observed that 1,10-phenanthroline derivatives exhibit some selective behaviors for cations, especially lithium ion, in the fluorescence measurement when exposed to ultraviolet light of wavelength around 300 nm.

In this study we report that the fluorescence emission intensity of 1,10-phenanthroline derivatives drastically increases only in the presence of lithium perchlorate in organic solvents. 2,9-Di-n-butyl-1,10-phenanthroline(1) and 2,9-di-t-butyl-1,10-phenanthroline(2) were obtained in good yields by the reaction of 1,10-phenanthroline with four equimolar n-butyl lithium and t-butyl lithium, respectively.[12] Commercially available 2,9-dimethyl-1,10-phenanthroline(3) was also used for comparison. Fluorescence spectra of organic solution containing 0.1 mM(= mmol dm^{-3}) of phenanthroline derivatives with or without perchlorate of Li^+, Na^+, and K^+, and $BeCl_2$ were observed at 23 °C by a Hitachi F-3000 fluorescence spectrophotometer,[9] where quartz cells (1 cm x 1 cm) were used. Standard deviations of each photometric determination were ± 10% or better.



1 : R = $n-C_4H_9$
2 : R = $t-C_4H_9$
3 : R = CH_3

Figure 1 shows excitation and fluorescence emission spectra of phenanthroline (1) with and without metal ions in acetonitrile. The fluorescence emission intensity of 1 remarkably increased only in the presence of lithium ion when irradiated with excitation wavelength of 298 nm. The spectra in the presence of sodium or potassium ion were almost the same as free 1, as is seen in the figures. In the case of addition of beryllium ion, however, the maximum wavelength of fluorescence shifted to around 420 nm, whereas it was the same as that in the presence of sodium or potassium ion when measured in other solvents, e.g., chloroform and dioxane. Thus, it should be noted that acetonitrile solution of phenanthroline(1) only in the presence of lithium ion is strongly fluorescent, and the increase of the fluorescence emission intensity in the presence of lithium ion was about 12-fold compared with that of free phenanthroline(1). In addition, the excitation spectrum does not interfere with the emission spectrum seriously because their spectral overlapping is very small.

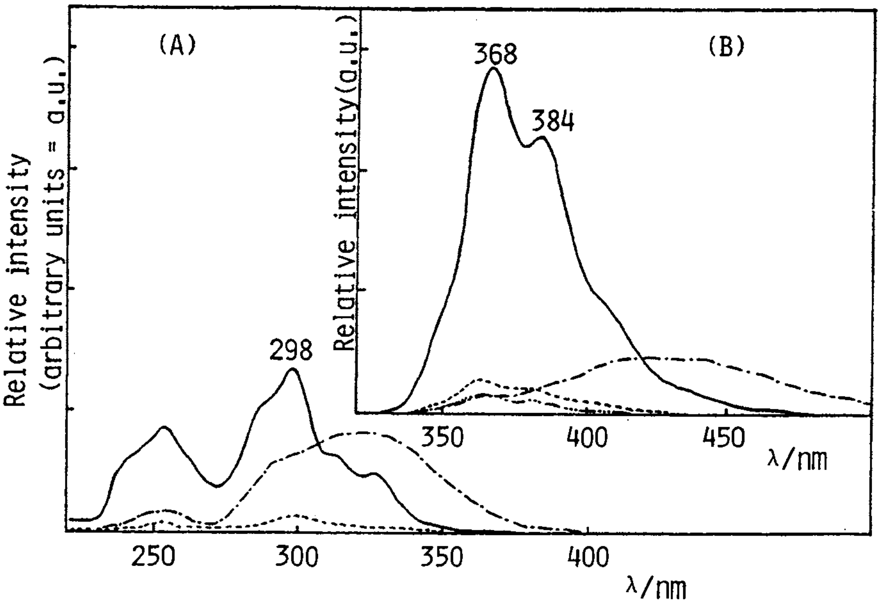


Fig. 1. Effect of the addition of metal ions(0.5 mM) on the fluorescence spectra of 1(0.1 mM) in MeCN: (A) Excitation spectra, ------: 1, 1 + Na^+, and 1 + K^+, ——— : 1 + Li^+, —·—·—: 1 + Be^{2+}; (B) Emission spectra excited at 298 nm(23 °C), ------: 1 and 1 + Na^+, ———: 1 + Li^+, —·—·—: 1 + Be^{2+}, —··—: 1 + K^+.

On the other hand, 2,9-di-t-butyl-1,10-phenanthroline(2) provided the slight increase of fluorescence emission intensity even in the presence of lithium ion as shown in Fig. 2, while the fluorescent change of 2,9-dimethyl derivative(3) due to addition of lithium ion is apparently smaller than that of 1(Fig. 3). This means that 2,9-substituents on 1,10-phenanthrolines play an important role in the increase of fluorescence intensity when phenanthroline derivatives form 2 : 1 complex with lithium ion. The composition of the complex was confirmed by elemental analysis for its crystal and also by the spectrophotomeric titration in the solution. The effect of 2,9-substituents on the fluorescence intensity has the same tendency as that in the ion-selective electrodes.[11)]

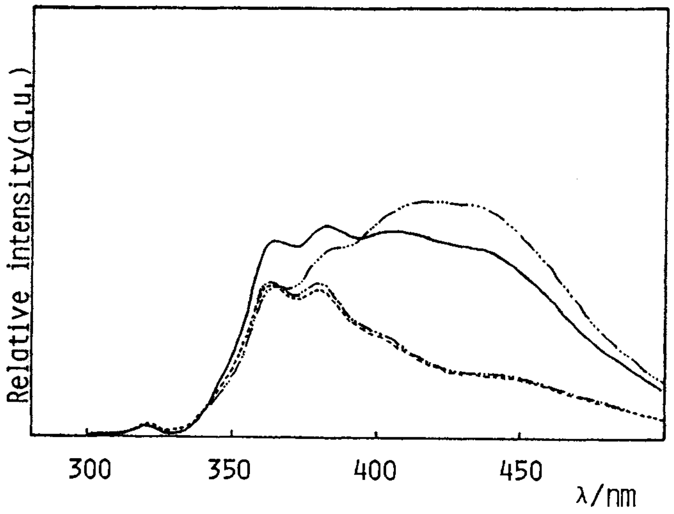


Fig. 2. Effect of the addition of metal ions (0.5 mM) on the fluorescence emission spectra of 2(0.1 mM) in MeCN; -----: 2, ———: 2 + Li^+, —··—: 2 + Na^+, —···—: 2 + K^+. Excitation: 291 nm, 23 °C.

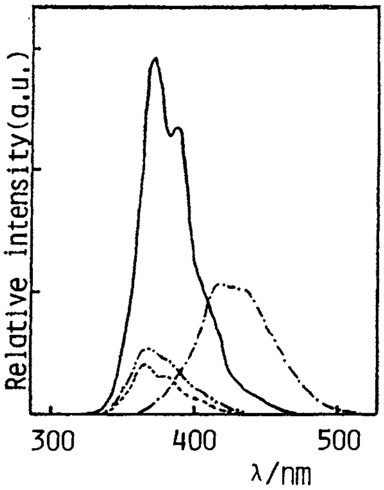


Fig. 3. Effect of the addition of metal ions(0.5 mM) on the fluorescence emission spectra of 3(0.1 mM) in MeCN; ----- : 3 and 3 + K^+, ——— : 3 + Li^+, —·—·—: 3 + Be^{2+}, —··—: 3 + Na^+. Excitation: 292 nm, 23 °C.

Then, the effect of ion concentration on the fluorescence intensity was investigated, and the results are shown in Fig. 4. The fluorescence intensity of 1 gradually increased by adding more than 10^{-6} M(= mol dm^{-3}) of lithium perchlorate when the ligand was kept at 10^{-4} M, and the intensity became constant in the range more than 10^{-4} M of lithium ion. On the other hand, when sodium perchlorate was added, the fluorescence intensity began to increase over 10^{-2} M of sodium ion. There was hardly the increase of the intensity for potassium perchlorate or beryllium chloride in the whole concentration range studied. It was found that the fluorescence intensity of 1 changed depending on the lithium ion concentration in the range from 10^{-6} M to 10^{-4} M without any interference of the other ions investigated, and it is possible to analyze lithium ion concentration quantitatively within the range. In this study divalent beryllium ion was used for comparison because it has the same electronic configuration($1s^2$) as that of monovalent lithium ion, but beryllium ion exhibited different fluorescent behavior from lithium ion and did not result in the increase of the fluorescence intensity of 1.

As has been described, phenanthroline derivative(1) apparently exhibits the specific fluorescent behavior for lithium ion in organic solvents such as acetonitrile and dioxane, and thus it may be available for the fluorimetric specification of lithium ion; however, measurement in aqueous solution is impossible with the present method as the carriers are insoluble in aqueous solution. Furthermore, according to the preliminary experiments, the fluorescence intensity was significantly influenced by water content in organic solution and thus investigations concerning to the effect of water content are now in progress.

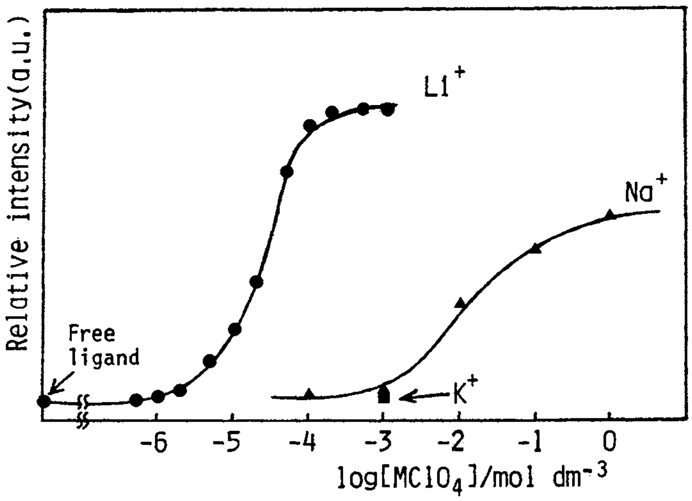


Fig. 4. Plots of fluorescence intensity of 1(0.1 mM) in MeCN vs. logarithmic concentration of perchlorate of alkali metal ions. Excitation at 298 nm, emission recorded at 368 nm, 23 °C. —●— : $LiClO_4$, —▲— : $NaClO_4$, ■ : $KClO_4$.

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