Chromogenic 1,10-Phenanthroline for Determination of Lithium Ion

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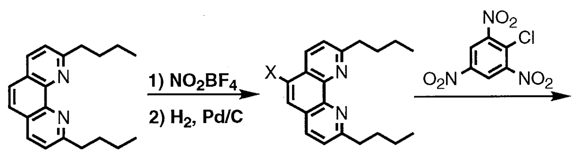
A new chromogenic 1,10-phenanthroline bearing picrylamino residue displays a striking lithium ion-selective shift in maximum absorbance in the presence of base upon addition of lithium ions; upon lithium complexation the color of solution changes from pale yellow to brownish red, the color density being dependent on lithium ion concentration.

A number of chromophores for alkali and alkaline earth metal ions have been reported.[1-4] Most of them are a combination of highly preorganaized cyclic ion sensing moieties and chromogenic moieties. We have reported the 1,10-phenanthroline derivatives which exhibit very high selectivity of Li^+ over other alkali and alkaline earth metal ions as sensing agents for ion-selective electrodes,[5] fluorophores,[6] and carriers in liquid membrane systems.[7]

In this paper we present, 1) the preparation of 1,10-phenanthroline derivative having picrylamine as a chromogenic group, and 2) the selective change in color of the solution of prepared chromophore in the presence of base upon addition of Li^+. 2,9-Dibutyl-1,10-phenanthroline(**1**) was treated with nitronium tetrafluoroborate in acetonitrile to give 2,9-dibutyl-5-nitro-1,10-phenanthroline(**2**). Compound **2** was then reduced with H_2 and 10% Pd/C in ethanol to give 5-amino-2,9-dibutyl-1,10-phenanthroline(**3**) which was reacted with picryl chloride to afford chromogenic phenanthroline(**4**).[8] For comparison, compound without the phenanthroline moiety (**5**) was also prepared. However, attempts for nitration of **1** with HNO_3 and fuming H_2SO_4,[9] with HNO_3 and H_2SO_4,[10] or with acetyl nitrate[11] failed to give any nitrated product.

Wavelength maxima (λ_{max}) and molar absorptivities (ε) of the acid and base forms of chromogenic compounds **4** and **5** are recorded in Table 1. To suppress ionization of the N-H bond and thereby obtain the spectrum for HL (the nonionized ligands) the absorbance was determined in 1,4-dioxane containing 4.6×10^{-2} mol/dm^{-3} HCl. The full ionization of the N-H bond was ensured by use of 1,4-dioxane containing 2.7×10^{-4} mol/dm^{-3} tetramethylammonium hydroxide to obtain the L^- form. The chromophore system of compound **4** exhibited an absorption maximum for the acid form at 359 nm which upon full ionization shifted bathochromically to 440 nm with an increase in the molar absorptivity.



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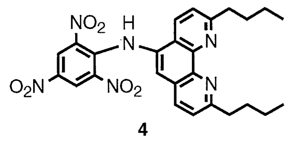
2: X= NO_2
3: X= NH_2



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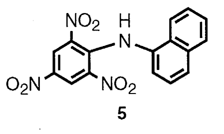

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Table 1. UV-vis spectral characteristics of chromogenic compounds **4** and **5**

Compd	[HL] λ_{max}/nm ($\varepsilon \times 10^{-4}$)	[L$^-$] λ_{max}/nm ($\varepsilon \times 10^{-4}$)
4	294 (2.6)	279 (2.9)
	359 (1.5)	440 (2.6)
5	354 (1.2)	440 (2.2)

Conditions: [HL] = 5×10^{-5} mol/dm^{-3},
[$MClO_4$] = 1×10^{-3} mol/dm^{-3}
in 1,4-dioxane / H_2O(40 / 1 v/v) with
1.2×10^{-3} mol/dm^{-3} $NH_2C(CH_2OH)_3$.

For investigation of the effect of the addition of metal ions upon the optical response of the ligand, alkali metal ion solutions were added to 1,4-dioxane solutions of **4** in the presence of 1.2×10^{-3} mol/dm^{-3} tris(hydroxymethyl)aminomethane. Phenanthroline derivative **4** exhibits very high selectivity for Li^+ over Na^+ and K^+ (Figure 1), while spectrophotometric change was not observed upon addition of metal ions to solution of **5**. Additionally, spectrophotometric changes were not observed upon addition of Mg^{2+} or Ca^{2+} to solutions of **4**.

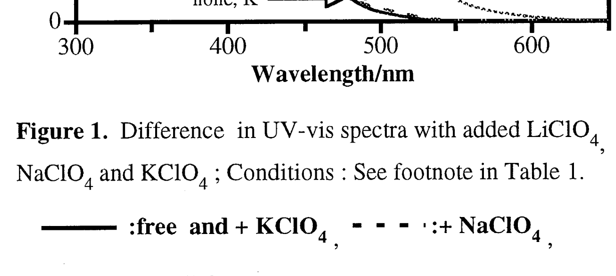

Figure 1. Difference in UV-vis spectra with added $LiClO_4$, $NaClO_4$ and $KClO_4$; Conditions : See footnote in Table 1.

——— :free and + $KClO_4$, - - - :+ $NaClO_4$,

··········· :+ $LiClO_4$

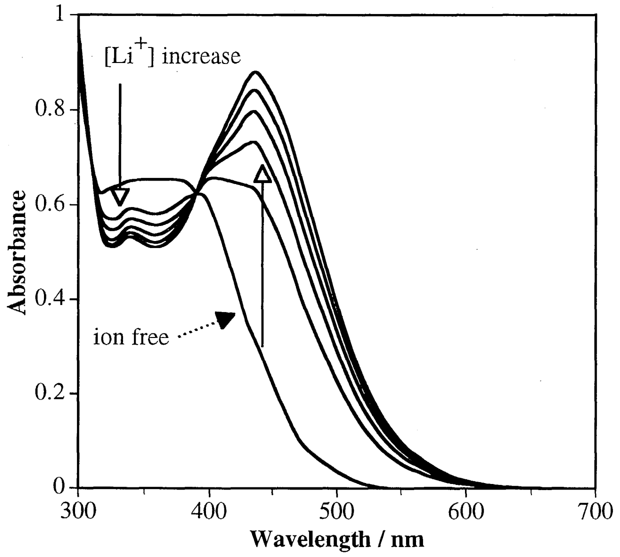

Figure 2. [Li$^+$] response curves for compound **4** [HL] = $5x10^{-5}$ mol/dm^{-3} in 1,4-dioxane / H_2O= 40:1 with $1.2x10^{-3}$mol/dm^{-3} $NH_2C(CH_2OH)_3$, [Li$^+$] =0, 0.48, 0.97, 1.4, 1.9, 2.4mmol/dm^{-3}

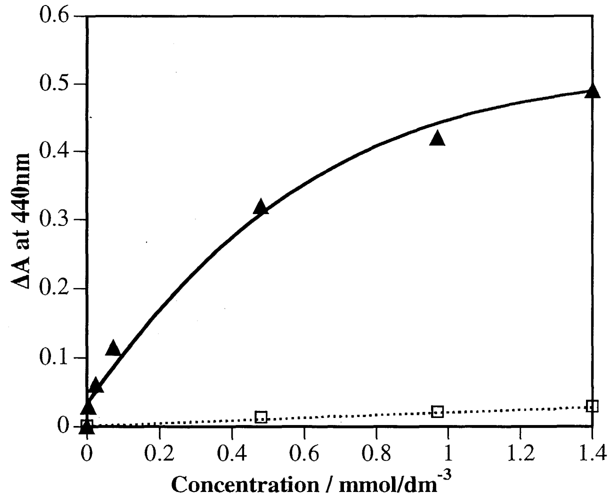

Figure 3. Effect of concentration of alkali metal ions on the absorbance at 440 nm ; Conditions : see Figure 2 ; ——— :$LiClO_4$, ... :$NaClO_4$.

When the metal salts were added in the absense of tris(hydroxymethyl)amine, no significant change in the optical response was observed. Thus, it appears that the base plays the crucial role in generating the response. Deprotonation of the N-H bond is therefore an integral part of the process. The complexation with Li$^+$ makes the N-H proton of **4** more acidic, which allows deprotonation under the experimental conditions.

The optical response curves of **4** for Li$^+$ and the responses for metal ion concentrations are illustrated in Figure 2 and Figure 3, respectively. As is seen in Figure 3, sodium ion has been found to have a lower effect and potassium ion has been found to have no significant effect unless present at concentrations above10^{-3} mol dm^{-3}.

Thus, **4**, which bears acyclic phenanthroline moiety as ion sensing part, showed a very promissing property for use as optical sensing systems for lithium ion. These results suggest that further extension of this system will provide useful information. Compounds such as bridged phenanthrolines [7] may well be superior reagents for lithium ion detection.

References and Notes

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8 Compound **4**: dec. 130°C; ^{1}H-NMR (300 MHz, $CDCl_3$): 1.00 (t, 6H, CH_3), 1.35-2.20 (m, 8H, CH_2-CH_2-CH_2-CH_3), 3.25 (t, 4H, phen-CH_2), 7.45 (d, 2H, phen), 6.67 (d, 2H, phen), 8.10 (d, 2H, phen). Anal. Found: C, 60.20; H, 4.89; N, 15.53 %. Calcd for $C_{26}H_{26}N_6O_6$: C, 60.22; H, 5.05; N, 16.20 %.

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