Drastic Change in Fluorescence Intensity of Acyclic Polyethers caused by Addition of Lithium Ion

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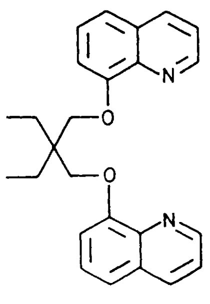
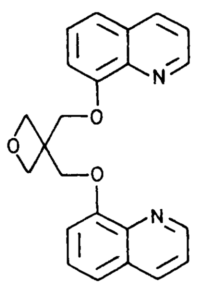
Lithium ion is the only alkali metal ion which drastically enhances the fluorescence intensity of 2,2-diethyl-1,3-bis(8-quinolyloxy)propane and 3,3-bis(8-quinolyloxymethyl)oxetane.

Much attention has been focused on compounds which can selectively recognize lithium ion as carrier for various purposes, *e.g.*, for ion-selective electrodes in the therapy of maniacal psychosis.[1] Although lithium ion has been monitored by flame and atomic absorption analyses and ion-selective electrodes, photometric methods are also attractive since they have some advantages.[2] We recently reported that compounds (**1**) and (**2**) can exhibit excellent lithium ion selectivity as carriers for both ion transport through bulk liquid membranes and ion-selective electrodes.[3,4] We now report the effect of the addition of alkali metal ions on the fluorescence spectra of the acyclic polyethers (**1**)—(**3**) in MeCN.

Figure 1 shows the fluorescence spectrum of (**1**) in the presence or absence of alkali metal perchlorates in MeCN. The fluorescence intensity increased significantly compared to that of free (**1**) only on addition of lithium perchlorate; sodium perchlorate had only a slight effect, and potassium perchlorate hardly any effect at all. In other words, the fluorescence intensity of (**1**) responds specifically to addition of lithium perchlorate. The fluorescence intensity of (**2**) responded similarly, whereas the fluorescence spectrum of (**3**) was not affected by the addition of any alkali metal salt. These results accord with those for ion transport through liquid membranes.[3,4]


(**1**)


(**2**)

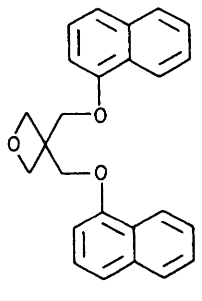

(**3**)

Figure 2 shows a plot of the relative fluorescence intensity of (**1**) at the emission maximum against the concentration of lithium perchlorate in MeCN; a significant dependence was observed, particularly in the concentration range 10^{-5}—10^{-4} M of $LiClO_4$. The intensity is unaffected for $[LiClO_4] > 10^{-3}$ M and $< 10^{-6}$M $LiClO_4$, the intensity for $[LiClO_4] < 10^{-6}$M being almost the same as that for free (**1**).

Although the hypsochromic effect on the absorption spectrum was larger for the complexation of (**1**) with $LiClO_4$ than for other alkali metal ions, the effect on absorption intensity changes with different cation species showed a relatively small variation compared with the emission method.

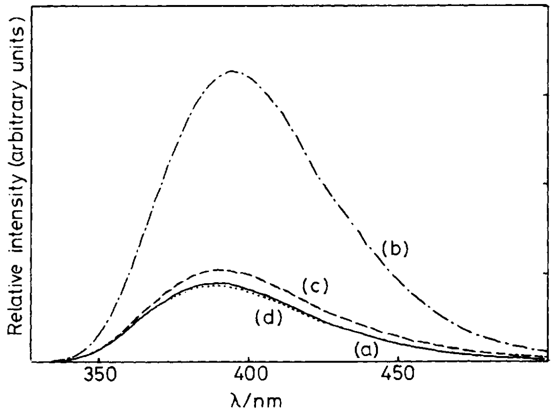


Figure 1. Effect of the addition of 0.1 M alkali metal perchlorates upon the fluorescence spectrum of (**1**) (0.1 mM) in MeCN ($KClO_4$ is partially soluble in MeCN). Excitation wavelength 303 nm, 23 °C. (a) free (**1**), (b) (**1**) + $LiClO_4$, (c) (**1**) + $NaClO_4$, (d) (**1**) + $KClO_4$. Emission maximum: 389 nm for free (**1**) and (**1**) + Na^+ or K^+, 395 nm for (**1**) + Li^+.

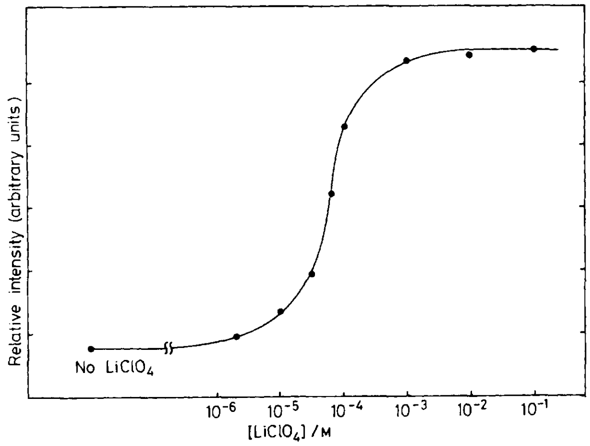


Figure 2. Fluorescence intensity of (**1**) (0.1 mM) in MeCN *vs.* $[LiClO_4]$. Excitation at 303 nm, emission recorded at 395 nm, 23 °C.

Similar effects were also observed in a hydroxylic solvent, MeOH.[5] Thus, compounds (**1**) and (**2**) which exhibit a specific response to lithium ion in the fluorescence spectrum, have the property of 'switching on' of fluorescence by lithium ion recognition and might be expected to be a powerful tool for monitoring lithium ion concentration.

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