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Azacrown indoaniline dye as a sensing molecule in optical sensors for the selective detection of Li^+

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Abstract

The complex formation of azacrown indoaniline (**ACIA**) dye **9** with Li^+ and Na^+ was investigated spectrophotometrically. As the polarity of the solvent decreased, the complexation ability increased. **ACIA 9** exhibits higher Li^+ selectivity than Na^+ ion in CH_2Cl_2–CH_3CN. The specific spectral response to Li^+ ion by **ACIA 9** indicates potential suitability for optical sensor applications. © 2000 Published by Elsevier Science Ltd. All rights reserved.

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1. Introduction

Selective ion carriers have been of considerable interest as tools for the analysis and separation of metal ions as well as for many biological applications. Expanding applications in science, medicine, and technology have led to increased interest in lithium and its compound [1].

Lithium salts have been used in the treatment of manic depression and other neurological and psychiatric disorders [2]. In light of such applications, methodology for the separation and determination of Li^+ is receiving considerable attention. Ionophores for divalent cations and some alkali metal ions are well known [3,4] but so far few carriers specific for Li^+ have been described. The design of ionophores for Li^+ is a difficult problem owing to the fact that lithium ions are smaller than both sodium and potassium ions but are strongly hydrated in aqueous solution [5], and hence few lithium ionophores have been synthesized. Examples of selective ligands for lithium ions relative to sodium ion are the macrocyclic crown ethers [6], cryptands [7], spherands [8] and acyclic diamides [9], which have achieved remarkable binding selectivity. Some tetraaza macrocycles related to porphyrins and phthalocyanines [10], acyclic polyethers [11], and jasplakinolide [12], the only known lithium ionophores, have also been synthesized or isolated. Selective chromogenic reagents, alone or in combination with a masking agent, have satisfactorily been used for the colorimetric determination of

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most of the commonly encountered metal ions. On account of its high sensitivity, absorption spectroscopy is becoming increasingly important for chemical trace detection. Sutherland et al. have reported the use of a chromoionophore in an optical sensor [13]. We are currently working on the synthesis and study of newer derivatives of indoaniline dyes, which can potentially yield a new class of chromophores for the selective and quantitative detection of metal ions, both for biological and environmental applications. Such indoaniline dyes can be used as fat-soluble dyes. Dyes of this class are not now used for textile coloration, but they are applied in colour photography and also serve as intermediates for sulfur dyes. We have previously reported the synthesis and X-ray structural characterization of **ACIA 9** carrying a monoazacrown moiety [14]. Here we report the metal complexation properties of this new **ACIA** dye **9**.

2. Experimental

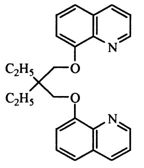
All chemicals used were of analytical grade; $LiClO_4$ and $NaClO_4$ were obtained from Aldrich. The monoazacrown indoaniline dye **9** was synthesized as previously described [14]. Acetonitrile was dried by boiling with CaH_2 and distilling before use. The absorption spectra were recorded on a Shimadazu UV-2100 spectrophotometer.

The absorption spectra were recorded immediately after preparation of the solutions. To the dye solutions were added different amounts of stock solutions of the metal salt.

Geometry optimization for the binding structure of dye **9** · M^+ was carried out by using MM2 (molecular dynamics) by the Chem 3D system (Cambridge Soft Corp.).

3. Results and discussion

If an ionophore bearing a chromophore or fluorophore in the vicinity of the metal ion binding site complexes a metal ion, the chromophore may be perturbed resulting in significant changes in the absorption or emission spectra [15].



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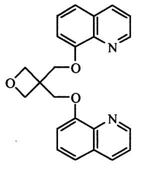

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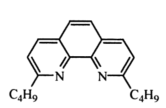

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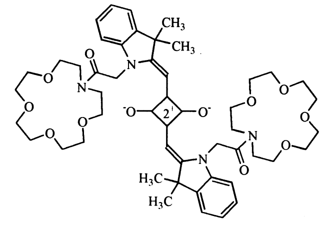

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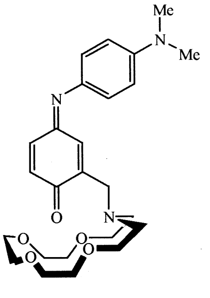
Acyclic Li^+ ionophores **1**–**3**, which are good neutral carriers in Li^+-selective electrodes, may also be applied to Li^+ fluorometry [16,17]. We reported that the fluorescence emission intensity of the azacrown squarylium dye **4** in CH_2Cl_2–CH_3CN (1:4/v:v) was significantly enhanced by the addition of lithium perchlorate. The presence of calcium ion increased the fluorescence slightly, but potassium and sodium had no effect. Chromoionophores are based on the idea that the selective complexation of a cation by a crown compound can be made visible by a colour effect initiated within the same molecule. This requires a chromophore adjacent to the ligand moiety and an electronic coupling between the two parts of the molecule (Fig. 1).

Complexation can induce either a red (bathochromic) and blue (hypsochromic) wavelength shift, as illustrated the pair of quinonimine ligands, a type of phenol blue, **5** and **6** [18].



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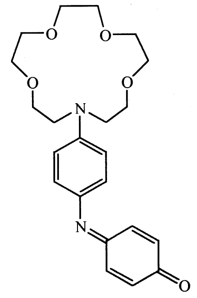

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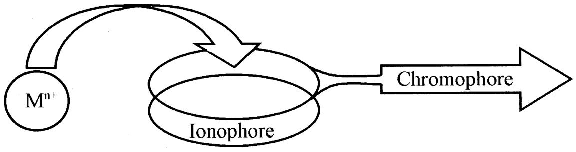
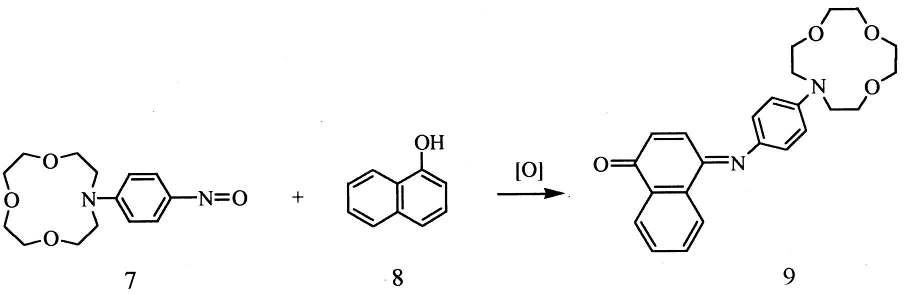


Fig. 1. Molecular construction of a chromoionophore.

Dye **5** displays strong bathochromic effects and at the same time strong hyperchromicity with ions of high charge density (Li^+ and divalent alkaline earth metal ions), which can be used spectrophotometrically. On the other hand, dye **6** gives the reverse case which involves destabilization of the excited state due to electrostatic repulsion between a guest cation and the positively charged sensor atom of the amino-nitrogen. The absorption properties of **ACIA 9** with Li^+ is here studied in CH_2Cl_2–CH_3CN. **ACIA** dye **9** was synthesized by condensing 10-(4′-nitrosophenyl)-1,4,7-trioxa-10-azacyclododecane **7** with α-naphthol **8** in alkaline solution by air oxidation (Scheme 1).

Fig. 2 shows the spectral changes induced by adding Li^+ to **ACIA** dye **9** in CH_2Cl_2–CH_3CN (4:1/v:v); as the Li^+ concentration increases, the absorbance decreases and the colour changes from blue to pale purple (hypsochromic shift).

ACIA dye **9** has electron donor (aniline moiety) and acceptor (quinone imine moiety) sites within the molecule so that charge transfer from the donor to acceptor according to electronic excitation gives rise to their strong visible light absorption. The interaction of metal ions with the dye molecule inhibits this charge transfer and leads to a hypsochromic shift of the charge transfer band. The decrease in absorbance can be explained by a reduced overlap of *p*-orbitals between quinonimine and aniline moieties associated with a decrease in coplanarity. In order to determine the dihedral angle between quinonimine and aniline moiety, MM2 was performed. Geometry optimization was carried out both before and after the Li^+ interaction with azacrown ring of **ACIA** dye **9**. The optimization resulted in values of dihedral angle of 36.5° and 40° in the absence and presence of Li^+, respectively. X-ray results showed that the **ACIA** dye **9** is non-planar, with a dihedral angle of 36.53°. The addition of Li^+ induced an increase in the dihedral angle between quinonimine ring and aniline ring. From these results it was deduced that the hypochromic effect of added Li^+ may be due to the increased dihedral angle between quinone imine and aniline ring. Similar spectral changes were observed for **ACIA** dye **9** on the addition of Li^+ in CH_2Cl_2–CH_3CN (1:4/v:v) (Fig. 2b). It was found that complexation between **ACIA** dye **9** and Li^+ was influenced by the polarity of the solvent. The same complex with Li^+ is more stable in a non-polar solvent (CH_2Cl_2:CH_3CN/4:1/v:v) than in a polar solvent (CH_2Cl_2:CH_3CN/1:4/v:v) (Fig. 2). As is already known, the type of solvent used determines the conformation of the crown ether ring [19]. We considered that in a polar medium, the oxygen atoms of the azacrown will point outwards, thus creating a lipophilic hydrocarbon core (Fig. 3a). The interior of the crown ether can thus be compared with a droplet of oil in water. In a non-polar medium the polarities are inverted: conformationally, the oxygen atoms will be forced inwards, with the hydrophobic CH_2 groups being turned outward. The interior now behaves as a droplet of water in oil (Fig. 3b).



Scheme 1.

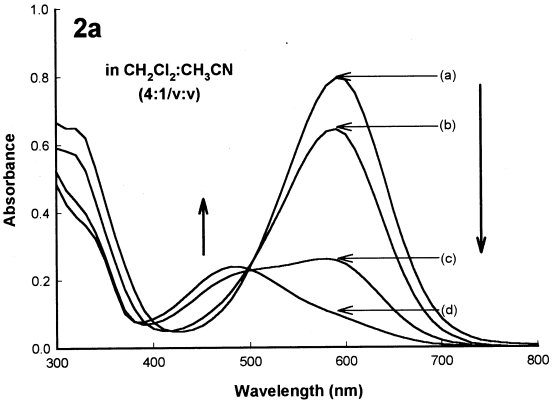
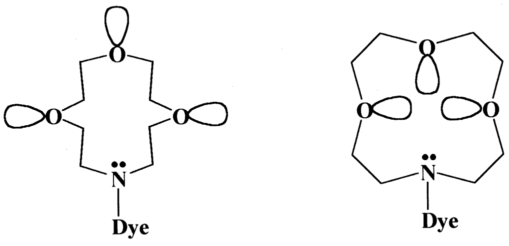


Fig. 2. Effect of Li^+ concentration on the absorption of spectra of **ACIA** dye **9** (5×10^{-5} M): [Li^+] (a) 0, (b) 5×10^{-4} M, (c) 5×10^{-3} M, (d) 5×10^{-2} M.



(a) (b)

Fig. 3. Conceivable conformation of azacrown ring: (a) in polar medium; (b) in non-polar medium.

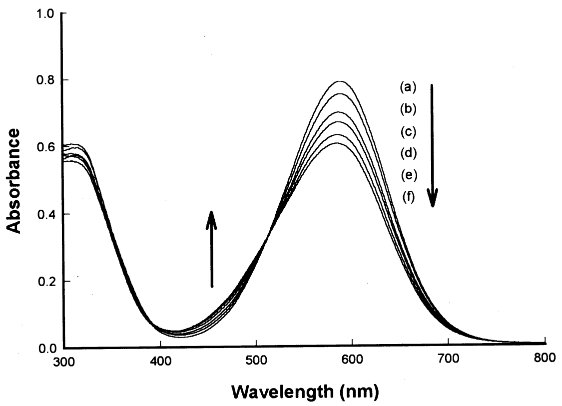


Fig. 4. Effect of Na^+ concentration on the absorption spectra of **ACIA** dye **9** (5×10^{-5} M) in CH_2Cl_2:CH_3CN (4:1/v:v): [Na^+] (a) 0, (b) 5×10^{-4} M, (c) 1.5×10^{-3} M, (d) 2.5×10^{-3} M, (e) 4×10^{-3} M, (f) 5×10^{-3} M.

In this case, polar electron rich cavity be corporated, i.e. coordinated. It becomes apparent why the type of solvent will influence the ability of the azacrown to complex with Li^+. Fig. 4 shows typical absorption spectra for the determination of Na^+ ion based on **ACIA** dye **9**, where the absorbance values decreased only slightly with increasing concentration of Na^+ in the sample solution (CH_2Cl_2:CH_3CN/4:1/v:v). The changes in the absorption spectrum induced by added Na^+ are not so significant as those by Li^+.

In Fig. 5, the absorbance at 589 nm (λ_{max} of **ACIA** dye **9**) was plotted against metal ion concentration. Of the two metal ion tested, Li^+ showed the largest spectral changes, with the spectrum of **ACIA** dye **9** scarcely changed by the addition of Na^+. From these results, we can conclude that selectivity for Li^+ ion is relatively high. Whereas dyes **5** and **6** are characterized by a response to many kinds of metal ions such as Mg^{2+}, Ca^{2+}, Ba^{2+}, Li^+, Na^+ and K^+, **ACIA** dye **9** responds more selectively to Li^+. The ionic diameter of Li^+ ion matches well with the cavity size of the azacrown moiety.

Fig. 6 shows the optimized geometry of complex of **ACIA** dye **9** with Li^+ and Na^+ using the MM2 method. On the basis of the comparison of the several dominant low-energy structures, a possible recognition mode is shown in Fig. 6. The complex of **ACIA** dye **9** with Li^+ shows the

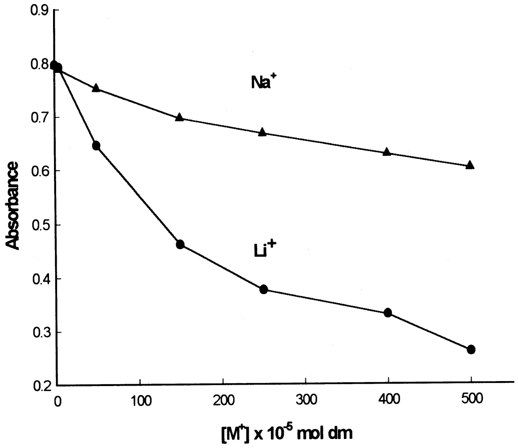


Fig. 5. Absorption intensity changes in **ACIA** dye **9** (5×10^{-5} M) upon addition of metal ion in CH_2Cl_2:CH_3CN (4:1/v:v) following the λ_{max} (589 nm) of **ACIA** dye **9**.

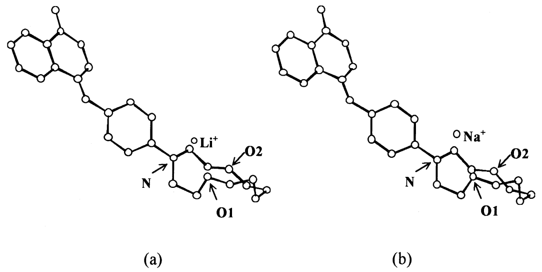


Fig. 6. Optimized geometry of complex with metal ions by MM2: (a) **ACIA**-Li^+; (b) **ACIA**-Na^+.

distance between N-Li^+ = 2.130 Å, O1-Li^+ = 2.125 and O2-Li^+ = 3.506, which are significantly shorter than those of complex with Na^+, where the N-Na^+ = 2.616 Å, O1-Na^+ = 2.457, and O2-Na^+ = 4.084. We are now planning to extend the present system to selective Li^+ recognition of the self-assembled monolayer (SAM) on gold by surface plasmon resonance technique.

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