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Novel fluorescent chemosensor for Li^+ based on a squarylium dye carrying a monoazacrown moiety

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Abstract

A squarylium dye carrying a monoazacrown moiety has been synthesized and characterized. The new azacrown-squarylium (ACSQ) dye **7** demonstrates sensitivity to Li^+ complexation with spectroscopic changes in fluorescence. Complex formation of ACSQ with Cu^{2+} was also investigated by UV–Vis spectrometry. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Fluorescent chemosensor; Squarylium dye; Monoazacrown; Fluoroionophore; Cation complexation

1. Introduction

Molecular recognition is a subject of considerable interest because of its implications in many fields: biology, medicine (clinical biochemistry), the environment, etc. In particular, the detection of metal cations involved in biological processes (e.g. sodium, potassium, calcium, magnesium), clinical diagnostics (e.g. lithium, potassium, aluminum) or in pollution (e.g. lead, mercury, cadmium) has received considerable attention. Among the numerous methods employed, fluorescent sensors offer distinct advantages in term of sensitivity and selectivity. Recently, there have been several reports on the design and study of such fluoroionophores, some of which contain crown ether moieties as the ionophore unit [1–4]. Fluoroionophores consist of a fluorophore (fluorescent molecule) covalently linked to an ionophore (e.g. crown ether) (Scheme 1).

Squarylium dyes are known to have strong absorption and emission properties in the near-infrared region. Symmetrical squarylium dyes are 1,3-disubstituted products synthesized by condensing one equivalent of squaric acid with two equivalents of various types of electron donating carbocycles and heterocycles such as azulene [5], pyrroles [6], or heterocyclic methylene bases [7] in an azeotropic solvent. This class of cyanine dyes has attracted much attention because of their potential application in xerographic photoreceptors [8,9], optical recording media [10], and organic solar cells [11], on account of their special properties such as photoconductivity and sharp and

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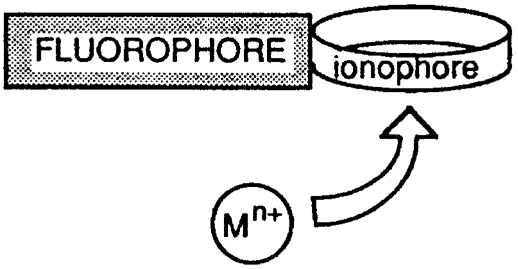


Scheme 1.

intense absorption in the visible or near-infrared region [12]. In our earlier study, we have reported the metal ion recognition of squarylium (SQ) and dithiosquarylium (DTSQ) dyes by film optode [13]. Here we report on the synthesis metal complexation properties of a newly synthesized fluorescent squarylium dye containing a mono-azacrown moiety (Scheme 2).

2. Experimental

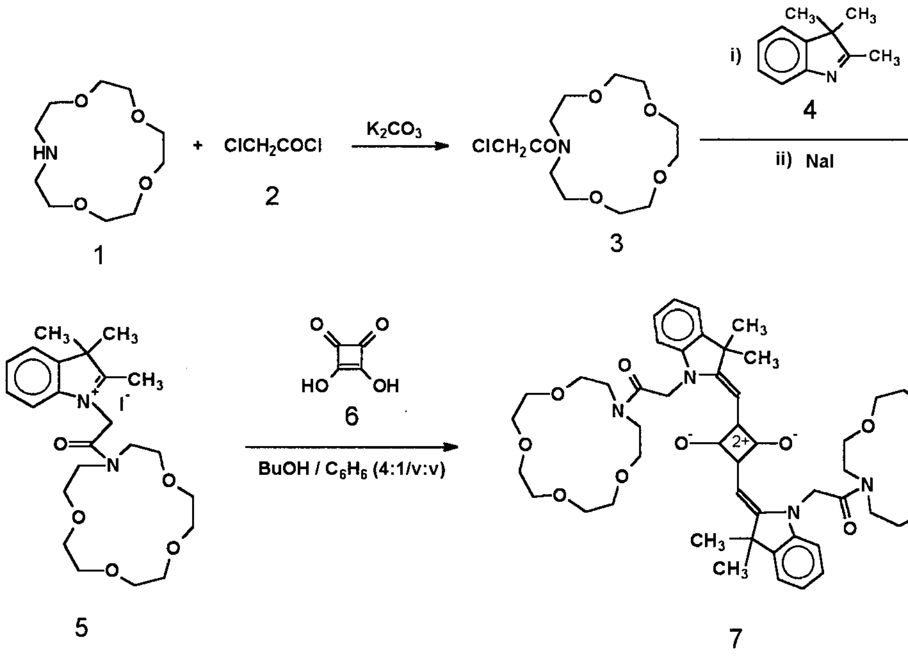
Melting points were determined using an Electrothermal IA 900, and are uncorrected. Visible spectra were recorded on a Shimadzu UV-2100 spectrophotometer and CHN analyses were carried out with a Carlo Elba model 1106 analyzer. Fluorescent measurements were performed on a Hitachi F-4500 spectrofluorometer.

2.1. Materials

The monoaza-15-crown-5 **1** can be readily prepared on a large scale by a one-step procedure [14]. α-Chloroamide **3** [15] and exo-methylene indolenium iodide **5** [16] were prepared according to literature procedures. All chemicals were of the highest grade available and were used without further purification.

2.2. Azacrown-squarylium dye (ACSQ) 7

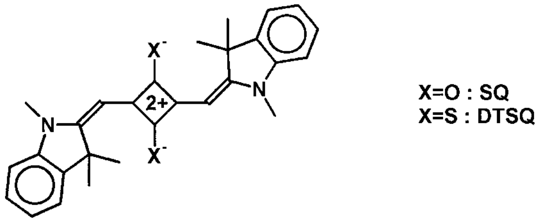
Squaric acid **6** 0.114 g (1 mmol) and 0.837 g (2 mmol) of exo-methylene indolenium iodide **5** were heated under reflux for 6 h in a mixture of 20 ml of *n*-butanol/benzene (4:1/v:v). Water was removed azeotropically using a Dean-Stark trap. The reaction mixture was cooled to room temperature, and the precipitated product were then filtered off.



Scheme 2. Synthesis of azacrown-squarylium (ACSQ) dye **7**.

Yield: 25% (0.23 g): m.p.: 255–256°C: calculated for $C_{50}H_{86}N_4O_{12}$; C, 65.66; H, 7.22; N, 6.13: found; C, 65.33; H, 7.28; N, 5.98: u.v.; λ_{max} (nm) ($CHCl_3$),($\varepsilon \times 10^{-5}$); 635, (2.19).

3. Results and discussion



Recently, the development of various types of optical chemical sensors has been actively investigated [17,18]. Highly selective ion sensing film optodes for the determination of metal ions were prepared with plasticized PVC–PVAc–PVA membranes containing an SQ or DTSQ dye [13]. As a result, SQ and DTSQ showed a striking selectivity for Cu^{2+} or Ag^{+} complexation. We have developed a new class of squarylium dye possessing a monoazacrown ring as a recognition site, conceptually new artificial receptors for metal ions. Addition of chloroacetyl chloride **2** to a mixture of **1** and potassium carbonate in toluene gave α-chloro amide **3**, which was isolated as an impure oil and characterized spectroscopically. The reaction of **3** with 2,3,3-trimethylindolenine **4** in acetonitrile gave the azacrown-linked indolenium iodide **5**. A mixture of **5** and squaric acid **6** in butanol/benzene (4:1/v:v) was refluxed 7 h to give the ACSQ **7** dye. Water formed was removed azeotropically using a Dean-Stark trap. Solvent was removed under reduced pressure and the residue was chromatographed on silica gel to give the target ACSQ **7** dye in the form of a dark blue solid, which showed λ max at 635 nm in chloroform. The overall yield in this three-step synthesis was 25%.

The absorption properties of ACSQ with Cu^{2+} were studied in CH_2Cl_2-CH_3CN and compared with those of other metal ions in order to investigate the effect of the ACSQ. Fig. 1 shows the spectral change induced by added Cu^{2+}; as the Cu^{2+} concentration increases, the absorbance of ACSQ decreases.

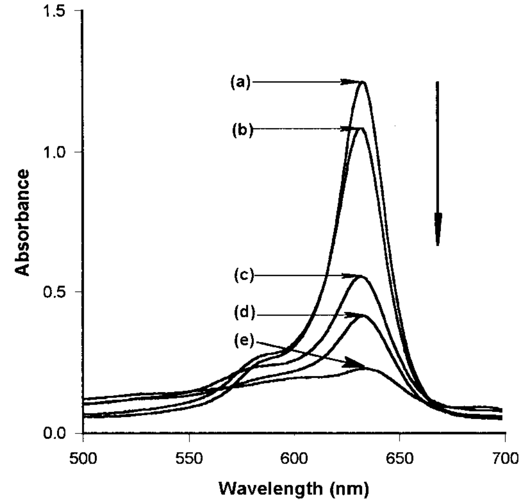


Fig. 1. Effect of Cu^{2+} concentration on the absorption spectra of ACSQ (5×10^{-6} M) in CH_2Cl_2–CH_3CN (1:4/v:v): [Cu^{2+}] (a) free, (b) 5×10^{-6} M, (c) 1×10^{-5} M, (d) 1.5×10^{-5} M, (e) 2×10^{-5} M.

Fig. 2 shows that addition of other metal ions such as Li^{+}, Na^{+}, Ca^{2+}, Mg^{2+} and K^{+} up to 5×10^{-3} M does not have any significant effect on

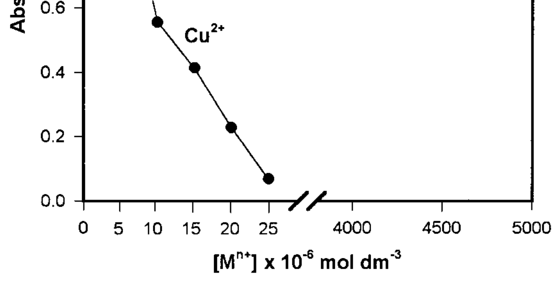


Fig. 2. Absorption intensity changes in ACSQ (5×10^{-6} M) upon addition of metal salt on CH_2Cl_2–CH_3CN (1:4) following the λ_{max}(635 nm) of ASCQ.

the absorption spectrum of ACSQ. However, addition of even 5×10^{-6} M quantities of Cu^{2+} causes a decrease in the intensifies of absorption of ACSQ.

The fluorescence intensity at 644 nm of a ACSQ increases markedly upon the Li^+-binding (Fig. 3).

As summarized in Fig. 4, the increase of the fluorescence intensities of ACSQ on addition with Li^+ was larger than that of other metal ions. ACSQ is more readily complexed with Li^+ ion. This can be explained by comparing the cavity size of the monoaza-15-crown-5 ether (1.2–1.5 Å) and the ionic diameter of the Li^+ ion (ionic diameter of $Li^+ = 1.36$ Å). The ionic diameter of Li^+ ion matches well with the cavity size of the monoaza-15-crown-5 ether moiety.

Several crown ether compounds designed to signal the presence of metal cation by showing enhanced fluorescence intensity have been synthesized and studied. Fluoroionophores consisting of a merocyanine, styryl derivative of benzoxazinone and Coumarin 153 linked to a macrocycle (azacrown ether) undergo drastic change in emission properties under cation complexation [19]. Complexation can be expected to alter the photophysical properties of the fluorophore, and these changes can then be used for the detection of ions. ACSQ dye consist of a fluorophore (squarylium moiety) covalently linked to an ionophore (azacrown ether moiety).

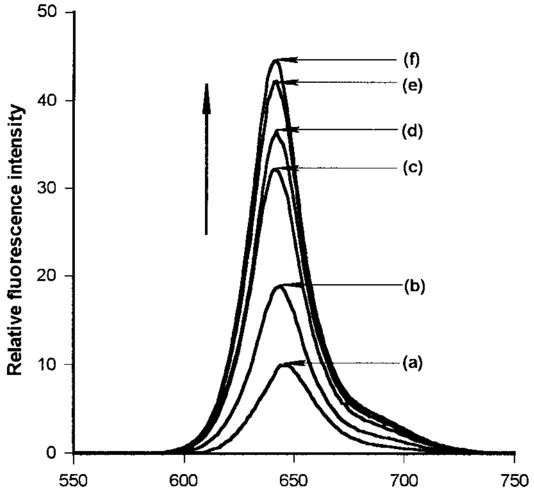


Fig. 3. Fluorescence spectral changes of ASCQ (5×10^{-6} M) with different concentrations of Li^+ in CH_2Cl_2 - CH_3CN (1:4/v:v): [Li^+] (a) free, (b) 5×10^{-4} M, (c) 1×10^{-3} M, (d) 1.5×10^{-3} M, (e) 2×10^{-3} M, (f) 2.5×10^{-3} M. Excitation at 632 nm.

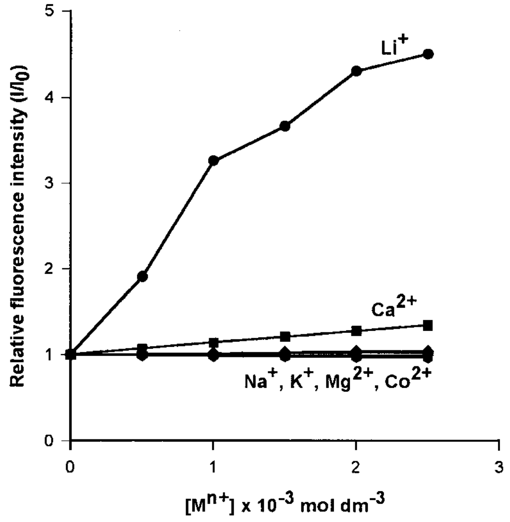


Fig. 4. Relative fluorescence intensity of ACSQ (5×10^{-6} M) in CH_2Cl_2–CH_3CN (1:4/v:v) versus the concentration of added metal ions.

Acknowledgements

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