Cation binding and photophysical properties of a monoaza-15-crown-5-ether linked cyanine dye[+]

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Abstract. A cyanine chromoionophore 1 has been synthesised and its photophysical properties have been investigated. Complexation with alkali metal cations (Li^+ and Na^+) brings about a significant shift in the absorption and emission spectra to shorter wavelengths, which is accompanied by an enhancement in the fluorescence quantum yield. These effects can be attributed to the suppression of intramolecular charge transfer processes of the cyanine dye, brought about by complexation with the metal cations.

Keywords. Cation binding; monoaza-15-crown-5-ether linked cyanine dye; cyanine chromoionophore; photophysical properties.

1. Introduction

There is considerable interest in the design and study of new molecules consisting of chromophores covalently linked to an ionophore, such as crown ethers, cryptands and calixeranes, since selective complexation of ions by the ionophore component can bring about significant changes in absorption and emission properties of the chromophores (Lehn 1991; Bourson et al 1993). Such ion-sensors have potential applications in trace-metal detection in biological systems as well as for molecular data processing (Bissel et al 1992; de Silva et al 1993). We have been interested in the study of dyes possessing intramolecular charge-transfer transitions (Das et al 1992, 1993; Kamat et al 1992; Patrick et al 1992). Crown ethers linked to such dyes can be designed such that cation binding can affect the intramolecular charge transfer processes depending on the size and charge-density of the cation (Bourson and Valeur 1989; Jonker et al 1990; Richardt and Asharin-Farid 1991; Letard et al 1993).

Aminostilbazolium dyes are used most frequently as fluorescence probes to follow the fast change of electrical membrane potential during an action potential in neurons since their emission properties are quite sensitive to the nature of the environment (Ephardt and Fromherz 1989). These dyes would therefore be ideally suited for the design of fluoroionophores. Here we report on the synthesis, photophysical properties as well as metal ion sensing ability of an aminostilbazolium dye linked to a crown ether moiety (1).

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[+] Dedicated to Professor C N R Rao on his sixtieth birthday
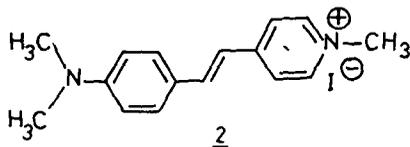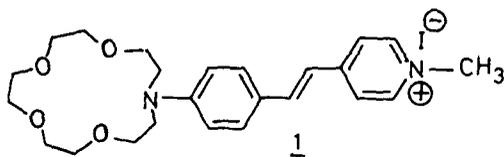
2. Experimental

The crown bearing cyanine dye 1 has been synthesized by condensing *p*-formyl-N-phenylaza-15-crown-5-ether (Dix and Vogtle 1980) and 4-picoline methiodide (Phillips 1947) adopting a method similar to the reported procedure for the synthesis of 4[4-(dimethyl)styryl]-1-methylpyridinium iodide 2 (Phillips 1947; Hassner *et al* 1984). The crude product was chromatographed over silica gel (100–200 mesh). Elution with a mixture (1:4) of methanol and chloroform gave a 46% yield of 4-[4-(N-aza-15-crown-5-ether) styryl]-1-methylpyridinium iodide 1, m.p. 202°C. Purity of the dye was confirmed through HPLC analysis and was characterized by comparing the IR and NMR spectral data with those of the model compound, 2. Absorption spectra were recorded on a Shimadzu-2100 spectrophotometer and the emission spectra were recorded using a Spex-Fluorolog F-112X spectrofluorimeter. Quantum yields of fluorescence were measured by the relative method using optically dilute solutions. Rhodamine 6G ($\phi_f = 0.9$) in ethanol was used as the standard.

3. Results and discussion

3.1 *Absorption and emission spectra*

The absorption spectrum of 1 in acetonitrile is shown in figure 1. The broad structureless band can be attributed to an intramolecular charge-transfer (CT) transition, where charge-transfer occurs from the electron-rich N-phenylaza-crown-ether to the electron-poor pyridinium moiety. Protonation of the amino moiety leads to the disappearance of the CT absorption band, which is accompanied by the appearance of a new band centred around 336 nm (figure 1). This new band could be attributed to transitions of the styrylpyridinium chromophore, which is known to absorb in this region (Shanmugasundaram *et al* 1986).

Table 1 shows the change in the absorption maximum of 1 with increasing solvent polarity. The hypsochromic shift observed with increasing solvent polarity arises from the difference in solvation of the electronic ground and excited states of 1, suggesting that the molecule has a highly dipolar ground state and a relatively less dipolar excited state. The emission spectra show large Stoke's shift which is again indicative
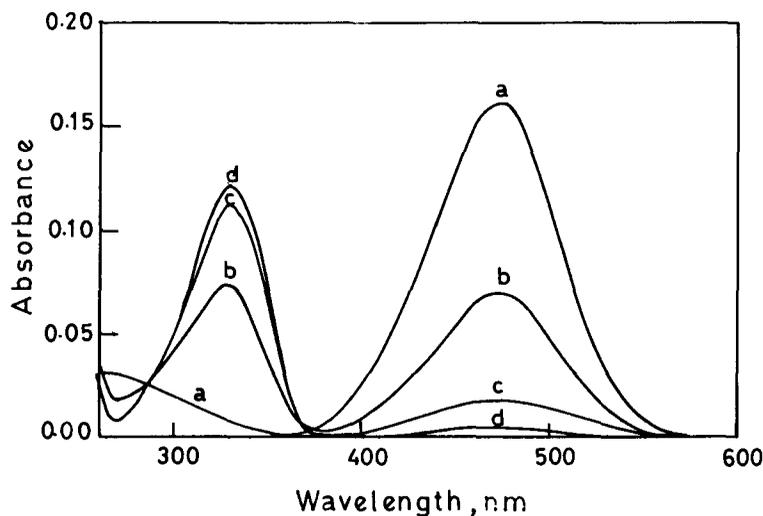
Figure 1. Effect of perchloric acid [$HClO_4$] concentration on the absorption spectrum of $\underline{1}$ (4 μM): [$HClO_4$] (a) 0; (b) 85; (c) 100 and (d) 140 μM.

of large dipole moment changes between the ground and excited states of $\underline{1}$. The quantum yield of emission decreases with increasing solvent polarity (table 1). This can be explained on the basis of the model for excited state twisting of double bonds (Rettig 1986). For ethylene derivatives there is an energetic maximum for the ground state (non-polar open shell) and a minimum for the excited state (polar closed shell)

Table 1. Absorption and emission data for the chromoionophore $\underline{1}$ in different solvents.

Solvent	λ_{max}(nm)		ϕ_f
	Abs	Em	
n-Butanol	490	606	0·114
Methanol	477	608	0·026
Acetone	478	615	0·020
Acetonitrile	474	615	0·014
Water	455	604	0·006

Table 2. Effect of lithium perchlorate and sodium perchlorate on the photophysical properties of cyanine chromoionophore $\underline{1}$.

[M](mM)	$LiClO_4$			$NaClO_4$		
	λ_{max}(nm)			λ_{max}(nm)		
	Abs	Em	ϕ_f	Abs	Em	ϕ_f
0	516	614	0·12	516	614	0·12
0·125	480	602	0·27	503	603	0·18

resulting from perpendicular geometry. The energy difference, ΔE, at the twisted geometry is given by the relative energies of these two states. Substitution of donor-acceptor groups can bring the two potential energy surfaces very close at the 90° twist. For $\underline{1}$, the increase in solvent polarity could also contribute to bringing the energies of these two states closer, thus further minimising the energy difference $(\Delta E \sim O)$. In such cases, ultrafast non-radiative decay can occur leading to a reduction in fluorescence quantum yield (Cremers and Windsor 1980; Rettig *et al* 1992; Rettig 1992).

3·2   *Cation-induced photophysical changes*

3.2a   *Absorption spectra*:   The ability of $\underline{1}$ to recognise alkali metal ions (Li^+ and Na^+) has been investigated by following the changes in its absorption and emission spectra. The absorption spectrum of $\underline{1}$ (figure 1, curve a) in acetonitrile–dichloromethane (5/95, v/v), showed a broad band centred around 576 nm. The changes in the absorption spectra on addition of lithium perchlorate are shown in figure 2. There is a decrease in absorption at the longer wavelength and a concomittant increase in absorption at the shorter wavelengths, and the changes are marked by the presence of a clear isosbestic point at 473 nm. These changes can be attributed to the formation of the metal ion complexed dye which absorbs at shorter wavelengths ($\lambda_{max} = 480$ nm) with lower oscillator strength. The equilibrium constant for the formation of a 1:1 chromoionophore–metal ion complex was analysed using the Benesi–Hildebrand equation,

$$\frac{1}{A - A_0} = \frac{\varepsilon_L}{\varepsilon_L - \varepsilon_{mL}}\left[\frac{1}{K_s[M]} + 1\right], \tag{1}$$
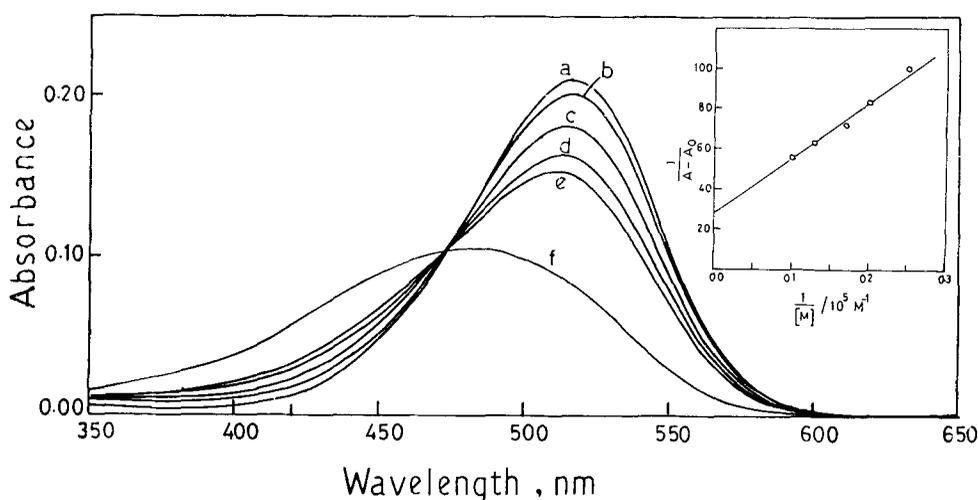

Figure 2.   Effect of lithium perchlorate [$LiClO_4$] concentrations on the absorption spectrum of $\underline{1}$ (5 μM) in dichloromethane–acetonitrile (95/5, v/v) mixture. [$LiClO_4$] (a) 0; (b) 12·5; (c) 18·7; (d) 25·0; (e) 31·25; and (f) 125·0 μM. Inset shows the plot of $1/(A - A_0)$ versus the reciprocal of lithium perchlorate concentration (changes in absorbance were monitored at 400 nm).
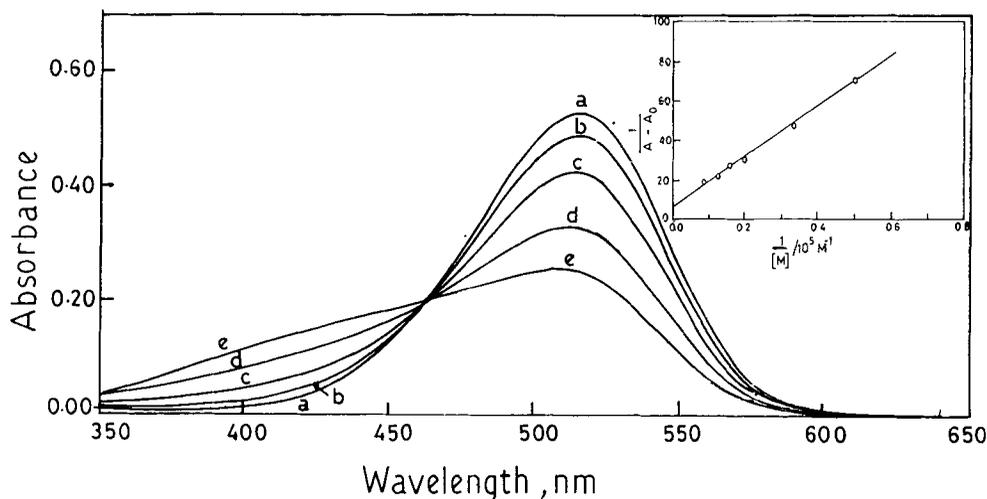
Figure 3. Effect of sodium perchlorate [$NaClO_4$] concentrations on the absorption spectrum of $\underline{1}$ (12 μM) in dichloromethane–acetonitrile (95/5, v/v) mixture. [$NaClO_4$] (a) 0; (b) 6·25; (c) 18·75; (d) 31·25; and (e) 187·5 μM. Inset shows the plot of $1/(A - A_0)$ versus the reciprocal of sodium perchlorate concentration (changes in absorbance were monitored at 400 nm).

where K_s is the stability constant, A_0 is the absorbance of the free ligand, A is the absorbance of the solution containing different concentrations of metal ions [M], ε_L and ε_{mL} are the molar extinction coefficients of the free ligand and the complex, respectively. The linear dependence of $1/(A - A_0)$ on the reciprocal concentration of lithium ions indicates the formation of a 1:1 complex between the dye and the metal ion (figure 2, inset) having a stability constant $K_s(Li^+) = 1·1 \times 10^4 \, M^{-1}$. Similar spectral changes were observed on addition of sodium perchlorate to solutions of $\underline{1}$ (figure 3). The equilibrium constant for a 1:1 ligand to Na^+ complex formation was estimated using the Benesi–Hildebrand equation as $K_s(Na^+) = 0·56 \times 10^4 \, M^{-1}$.

Complexation of cations like Li^+ and Na^+ by the crown ether moiety reduces the donor character of the amino group by decreasing the electron density. Thus, the cation-induced enhancement of the ionization potential of the amino group would lead to the observed shift to shorter wavelengths in the absorption maximum of the CT band. Similar hypsochromic and hyperchromic effects on the absorption band of other chromoionophores on complexation with metal ions have been reported (Bourson and Valeur 1989).

3·2b *Emission spectra*: As discussed earlier, $\underline{1}$ has a broad emission around 600 nm region. In the acetonitrile–dichloromethane (5/95, v/v) solvent mixture in which the complexation studies were carried out, $\underline{1}$ has an emission maximum centred around 615 nm with a quantum yield of fluorescence of 0·12. Figure 4 shows the effect of addition of lithium ions to a solution of $\underline{1}$. Addition of lithium or sodium ion results in a gradual shift in the emission maximum to shorter wavelengths, which is accompanied by an increase in the quantum yield of fluorescence. This effect is much more striking with lithium than with sodium ions (figure 5).

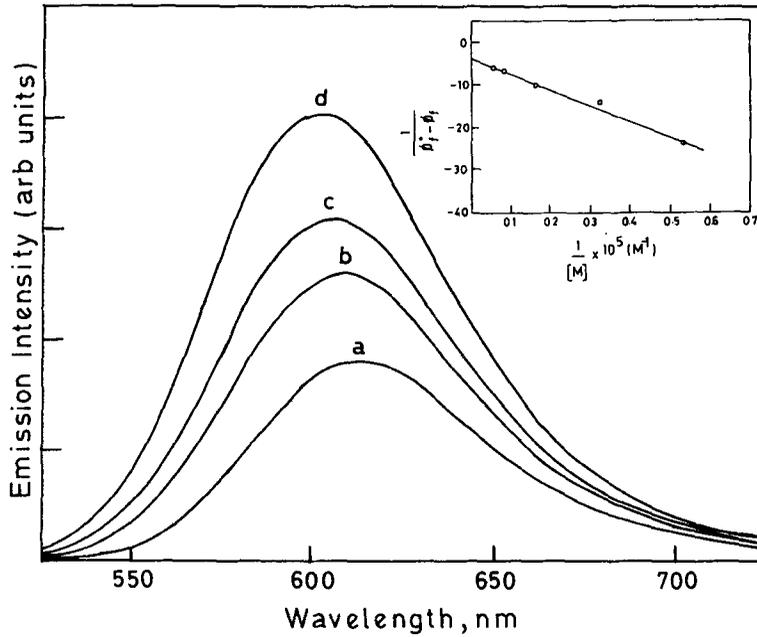Blank experiments carried out in similar solvents with the model compound $\underline{2}$

Figure 4. Influence of lithium perchlorate [LiClO$_4$] concentration on the emission spectrum of 1 (5 μM) in dichloromethane–acetonitrile (95/5, v/v) mixture [LiClO$_4$] (a) 0; (b) 18·75; (c) 31·25 and (d) 62·5 μM. Inset shows the plot of $1/(\phi_f^0-\phi_f)$ versus the reciprocal of lithium perchlorate concentration.
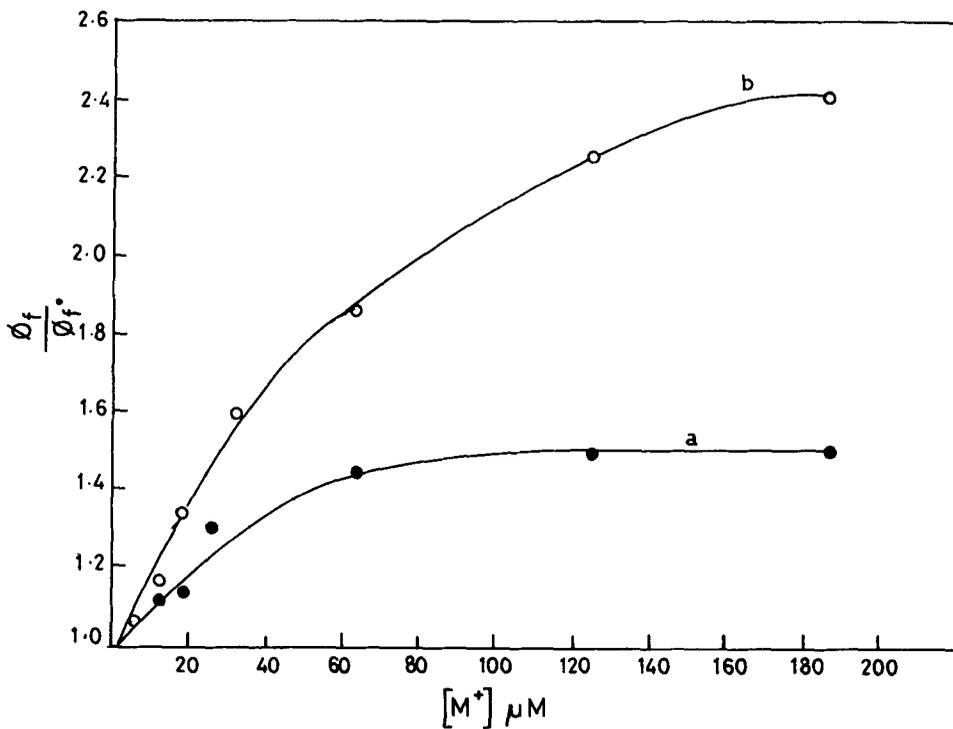

Figure 5. Dependence of the relative enhancement in the quantum yield of fluorescence on the concentration of alkali metal perchlorates; (a) NaClO$_4$ and (b) LiClO$_4$.

showed that its absorption and emission characteristics were unaffected by the addition of metal ions. These results clearly indicate that the complexation of metal ions is essentially by the crown ether moiety.

The ligand to metal stoichiometry and the stability constant for the complexation process can also be obtained by analysing the emission data using the Benesi–Hildebrand equation,

$$\frac{1}{\phi_f^0 - \phi_f} = \frac{1}{\phi_f^0 - \phi_f'}\left[\frac{1}{K_s[M]} + 1\right], \tag{2}$$

where K_s is the stability constant, ϕ_f^0, the quantum yield of fluorescence of free ligand, ϕ_f', the quantum yield of the complexed ligand, ϕ_f, the observed quantum yield of fluorescence and [M], the concentration of metal perchlorate. The plot of $1/(\phi_f^0 - \phi_f)$ against the reciprocal of lithium ion concentration showed a linear dependence. Stability constant K_s was calculated as $1.06 \times 10^4\,M^{-1}$.

The shift in the emission maximum to shorter wavelength can be interpreted in the same manner as the corresponding changes in the absorption spectra. Complexation with metal ions also brings about a significant enhancement in the quantum yield of fluorescence of the chromoionophores. Similar enhancement in the fluorescence quantum yield on complexation with metal ions was observed for a benzoxazinone derivative linked to monoaza-15-crown ether, where it was proposed that twisting out of the planar geometry of the azacrown moeity in the excited state was hindered due to complexation by metal ions, thus leading to an enhancement in the fluorescence quantum yield (Bourson *et al* 1993). A similar mechanism may be operative in the case of the cyanine fluoroionophore. Further studies on the excited state lifetimes of the free and complexed fluoroionophore are in progress to elucidate the exact mechanism involved in its metal ion induced fluorescence enhancement.

The size of the cavity of the N-aza-15-crown-5-ether moiety $(1.7 - 2.2\,\text{Å})$ is large enough to accommodate both Na^+ $(1.94\,\text{Å})$ and Li^+ $(1.36\,\text{Å})$. Although the size of Na^+ matches that of the crown-cavity more closely, the fluorescence properties of 1 are much more sensitive to Li^+ than to Na^+. This may be attributed to the higher charge density of Li^+ ion (Bourson *et al* 1993).

Conclusions

The long wavelength absorption band observed in the case of cyanine dye linked to the aza-crown-ether moiety (1) arises from a charge transfer transition. Complexation by alkali metal cations (Li^+ and Na^+) leads to changes in the absorption and emission spectra of the dye due to suppression of its intramolecular charge transfer transitions. The fluorescence enhancement of the dye, observed on metal ion complexation is much more with lithium than with sodium, which may be attributed to the higher charge density of lithium ions. This chromoionophore can be used for detecting micromolar concentrations of alkali metal cations.

Acknowledgement

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