A squaraine-based near-infrared absorbing sensor for the selective detection of transition and other metal ions in aqueous media†

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A near infrared absorbing cationic squaraine dye 1 is shown to be capable of detecting trace amounts of transition and lanthanide metal ions in aqueous media, even in the presence of alkali and alkaline earth metal ions.

Design of fluorescent or chromogenic chemosensors for the selective detection of low concentrations of ions is an active area of research.[1–6] With a few exceptions,[3,4] most of the studies have been concerned with non-aqueous solutions of ions. Moreover, most of the chromophores hitherto reported suffer from the requirement of short wavelength excitation. For detection of metal ions in naturally occurring systems, particularly for intracellular applications, near-infrared absorbing water soluble chemosensors would be highly desirable.[2] In the course of our studies on the design of squaraine-based fluoro- and chromo-ionophores,[6] we have observed that a newly reported[7] squaraine dye, **1**, is highly suited for such applications. This dye is water soluble, has a very strong absorption in the near-infrared region and is capable of quantitatively and selectively detecting trace amounts of metal ions.‡ Complexation of **1** by different metal ions gives rise to a new absorption band, which in most cases is characteristic of the metal ion involved. Using this simple procedure, trace amounts of metal ions such as Cu^{2+}, Hg^{2+}, Pb^{2+}, Mn^{2+}, La^{3+}, Eu^{3+}, Tb^{3+}, Gd^{3+} and Lu^{3+} can be detected selectively.

The cationic dye **1** possesses two absorption maxima centred around 790 and 640 nm in a mixture (4 : 1) of water and acetonitrile at pH 6.7. Lowering the pH of the solution leads to a decrease in the intensities of these bands which is accompanied with the formation of a new band centred around 690 nm. The pK_a of **1** has been evaluated as 4.9, based on these pH dependent spectral changes and the probable structures of the acid/base species in equilibrium with each other are shown in Scheme 1.

Addition of low concentrations of copper ions to a solution of **1** in a mixture (4 : 1) of water and acetonitrile at pH 6.7, where the dye is predominantly in its deprotonated form, led to a decrease in the intensities of the absorption maxima at 790 and 640 nm, which was accompanied by the formation of a sharp new band around 670 nm (Fig. 1). It has been observed that even addition of 50 nm (4 ppb) of Cu^{2+} leads to a notable change in the absorption spectrum. Benesi–Hildebrand analysis of the complex formation, studied by following the changes in absorption spectra on addition of copper ions, indicated a 1 : 1 dye to metal stoichiometry with a stability constant of 1.5×10^5 dm^3 mol^{-1}. Similarly, complexation of **1** with other metal ions leads to the formation of a new absorption band characteristic of the metal ion involved. It may be noted that the pH of the solution remains unchanged on addition of metal ions. The absorption maxima and equilibrium constants measured for different metal ions are shown in Table 1. With the exception of the complexes of Hg^{2+} and Cu^{2+} which have a maximum at 670 nm, the other complexes have their own characteristic absorption maxima. This is specially important with reference to the lanthanides investigated, since it is known that lanthanides when complexed with most chromogenic agents have similar absorption spectra and are therefore difficult to distinguish.[8] In the present study, however, there is a marked difference in the absorption maxima of the complexes of the dye with the various lanthanides studied (Table 1). The minimum concentration detectable for Cu^{2+}, La^{3+}, Eu^{3+}, Tb^{3+}, Gd^{3+} and Lu^{3+} is > 50–80 nm, for Hg^{2+} is > 2 μm, for Pb^{2+} is > 20 μm and for Mn^{2+} is > 50 μm.

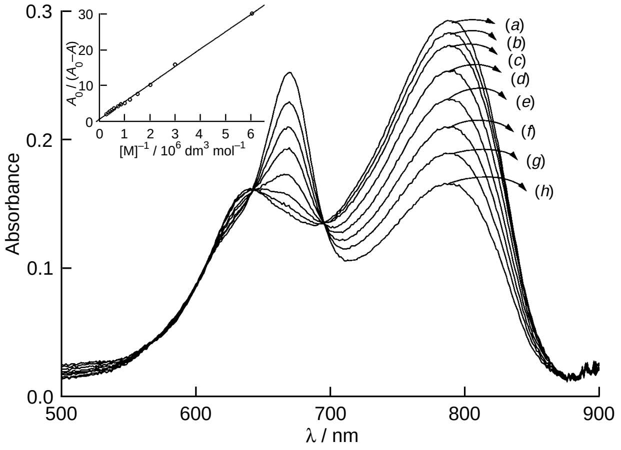
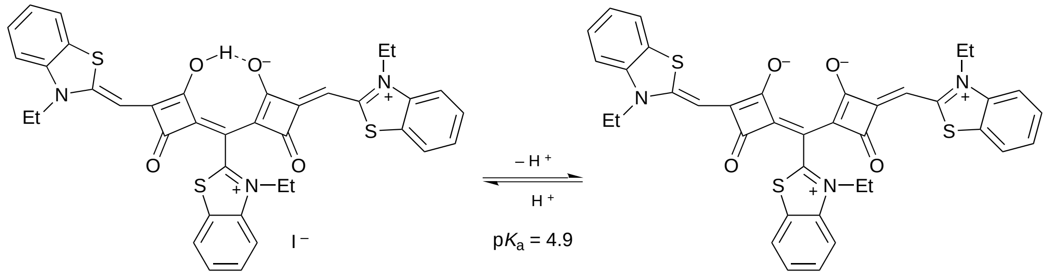


Fig. 1 Effect of Cu^{2+} concentrations on the absorption spectrum of **1** (4.7 μm) in H_2O–MeCN (4 : 1): [Cu^{2+}] (*a*) 0, (*b*) 0.15, (*c*) 0.3, (*d*) 0.6, (*e*) 1.2, (*f*) 1.8, (*g*) 2.4, (*h*) 3.0 μm. Inset shows the plot of $A_0/(A_0 - A)$ *vs.* 1/[Cu^{2+}]



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Scheme 1

Table 1 Complexation properties of **1** with various metal cations in H_2O–MeCN (4 : 1)

Cation	Cu^{2+}	Hg^{2+}	Pb^{2+}	Mn^{2+}	Zn^{2+}	La^{3+}	Eu^{3+}	Gd^{3+}	Tb^{3+}	Lu^{3+}
λ_{max}/nm	670	670	732	720	718	735	733	727	724	732
log K_s[a,b]	5.19	3.90	3.52	2.87	—	5.90	5.75	5.44	5.23	5.24
Charge density	2.778	1.818	1.667	2.500	2.703	2.953	3.158	3.198	3.250	3.529

[a] Benesi–Hildebrand equation for 1 : 1 complex formation between dye and metal ion, $A_0/(A_0 - A) = [E_L/(E_L - E_{mL})]\ \{1/(K_s[M]) + 1\}$, was used for determining the stability constant. K_s is the stability constant, A_0 and A are the absorbance of dye solution (790 nm band was followed) in the absence and presence of metal ions, $[M^{n+}]$. E_L and E_{mL} are the molar extinction coefficient of the free ligand and the complex respectively. All the K_s values reported are within the experimental error of ±5%. [b] Complexes of all the metal ions studied except with Cu^{2+} and Mn^{2+} are stable in H_2O–MeCN (4 : 1) and the solutions were kept for 15 min for equilibration before carrying out the measurements. In the case of Cu^{2+} and Mn^{2+}, the measurements were carried out immediately after the addition of the metal ions.

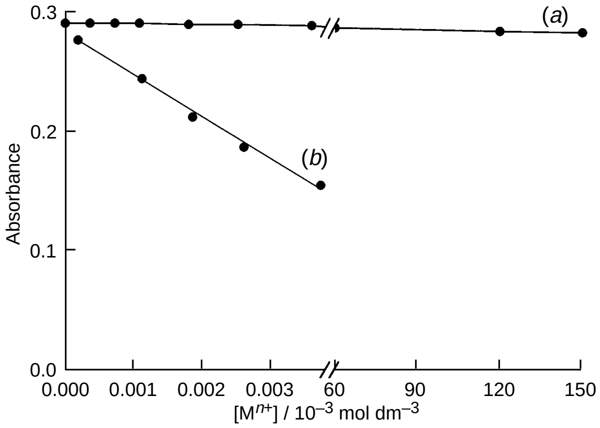

Fig. 2 Determination of Cu^{2+} in the presence of Na^+ using **1** (4.7 μm) in H_2O–MeCN (4 : 1) following the absorbance at 790 nm: (*a*) effect of addition of Na^+ (up to 150 mm); (*b*) effect of addition of Cu^{2+} containing 150 mm of Na^+

An interesting feature of this extremely simple method of detecting trace amounts of metal ions is that although Hg^{2+} and Cu^{2+} complexes absorb at the same wavelengths, the differences in equilibrium constants for complex formation permit the analysis of low concentrations of Cu^{2+} (> 50 nm) even in the presence of 1 μm of Hg^{2+}. The equilibrium constants listed in Table 1 indicate that the selectivity among the heavy metal ions is relatively high whereas within the lanthanide series it is not appreciable. The absorption spectrum of **1** was found to be unaffected by the addition of alkali and alkaline earth metal ions. For example, Fig. 2, curve (*a*) shows that addition of Na^+ ions up to 150 mm does not have any significant effect on the absorption spectrum of **1**. However, addition of even nm quantities of Cu^{2+} (> 50 nm) to the above solution containing 150 mm of Na^+ [curve (*b*)] causes a decrease in the intensities of absorption of the dye accompanied by the formation of the 670 nm band characteristic of Cu^{2+}–dye complex. Thus, trace amounts (*ca.* 50 nm) of metal ions like Cu^{2+} can be detected even in the presence of mm concentrations of Na^+, Li^+, K^+ and Ca^{2+} (Fig. 2).

In the anionic form of the dye **1**, the oxygen atoms of the two cyclobutane rings are ideally located to yield the suitable geometry for strong complexation with metal ions. The intense absorption band observed in the NIR region of squaraines is essentially due to the intramolecular charge transfer transition which is primarily confined to the C_2O_4 unit.[9] The hypsochromic shift in the absorption spectra, upon complexation, can therefore be attributed to a reduction in the electron-donating ability of the O^- atoms on complexation by the metal ions. Comparison of the shift in absorption maxima with charge density of the metal ions within the lanthanide series as well as between other metal ions (Table 1) indicate that, with the exception of Cu^{2+} and Hg^{2+}, the hypsochromic shift does indeed increase with increasing charge density of the metal ion.

In conclusion, we have observed that the cationic squaraine dye **1** can act as a near-infrared absorbing chromogen for detecting trace amounts of toxic and environmentally hazardous metal cations such as Cu^{2+}, Hg^{2+}, Pb^{2+} and Mn^{2+} as well as several lanthanide metal ions in aqueous media. We are currently working on the synthesis and study of newer derivatives of the cationic squaraine dye, which can potentially yield a new class of chromogens for the selective and quantititative detection of metal ions, both for biological and environmental applications.

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Footnotes

[†] This is contribution No. RRLT-PRU-70 from the Regional Research Laboratory, Trivandrum.

[‡] Since the dye and dye–metal ion complexes undergo a slow precipitation and loss in absorption in aerated aqueous media all experiments were carried out in argon-purged 4 : 1 water–acetonitrile mixtures.

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