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# Use of squarylium dyes as a sensing molecule in optical sensors for the detection of metal ions

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**Abstract**

The complex formation of squarylium (SQ) and dithiosquarylium (DTSQ) dyes with $Cu^{2+}$ and $Ag^{+}$ was investigated spectrophotometrically. Their absorption spectra showed cation selective spectral intensity changes in the presence of specific metal ions in $CH_2Cl_2$–$CH_3CN$ due to cation complexing. Highly selective ion sensing film optodes for the determination of two kinds of ions, $Cu^{2+}$and $Ag^{+}$, were prepared with plasticized PVC–PVAc–PVA membranes containing the SQ or DTSQ dye. © 1999 Elsevier Science Ltd. All rights reserved.

*Keywords:* Squarylium dye (SQ); Dithiosquarylium (DTSQ) dyes; Chromoionophore; Ion sensor; Film optode

## 1. Introduction

Squarylium dyes and derivatives are 1,3-disubstituted compounds synthesized from squaric acid and two equivalent of various types of electron donating carbocycles or heterocycles such as azulene [1], pyrroles [2], or heterocyclic methylene bases [3].

Although squarylium dyes exhibit a sharp visible absorption in solvents, their absorption in the solid state is panchromatic and very intense [4].

This class of dyes has attracted much attention because of their potential application in xerographic organic photoreceptors [5,6], optical recording media [7] and organic solar cells [8], on account of their advantageous properties such as photoconductivity and their sharp and intense absorption in the visible or near infrared regions [9].

We have previously reported the synthesis [10], electrochromic properties [11] and electroluminescence properties [12] of squarylium dyes (SQ) containing an indoline moiety. We have also reported that some novel dithiosquarylium (DTSQ) dyes absorbed near-infrared light at 700–750 nm in the solid state, and had good electrophotographic properties as charge generation materials (CGM) [13].

Sensitive and selective detection of metal ions is an ongoing research topic in biochemistry and analytical chemistry. Selective chromogenic reagents, alone or in combination with a masking agent, have satisfactorily been used for the colorimetric determination of most of the commonly

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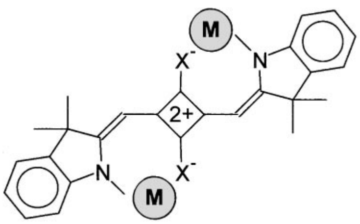
encountered metal ions. On account of high sensitivity, absorption spectroscopy is becoming of increasing importance for chemical trace detection. Sutherland et al. [14] have reported the use of a chromoionophore in an optical sensor.

We are currently working on the synthesis and study of newer derivatives of squarylium dyes, which can potentially yield a new class of chromogens for the selective and quantitative detection of metal ions, both for biological and environmental applications.

The ion selectivity of SQ and DTSQ was examined in $CH_2Cl_2$–$CH_3CN$. In addition, selectivity and application of the film optodes based on SQ and DTSQ were investigated. As a result, SQ and DTSQ show a striking selectivity for $Cu^{2+}$ or $Ag^{+}$ complexation and has a potential in optical sensors.




SQ, X= O
DTSQ, X= S
M = metal ion

## 2. Experimental

### 2.1. Reagents

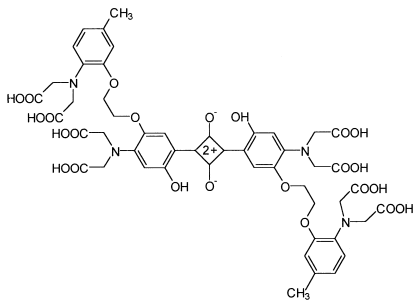
All chemicals used were of analytical grade; $Cu(NO_3)_2$, $AgNO_3$, $LiClO_4$, $KClO_4$, $Ca(NO_3)_2$, $Pb(NO_3)_2$, $Zn(NO_3)_2$, $Co(NO_3)_2$, $Mg(ClO_4)_2$ and $NaClO_4$ were obtained from Aldrich. For membrane preparation, dioctylphthalate (DOP), poly(vinyl chloride–vinyl acetate–vinyl alcohol, 91:3:6) (PVC–PVAc–PVA) and tetrakis- [3,5-bis(trifluoromethyl) phenyl]borate sodium salt ($NaTm(CF_3)_2PB$) were obtained from Fluka. The SQ and DTSQ dyes were synthesized as previously described.

### 2.2. Membrane preparation

The optode membranes were prepared from 1.58 mg of dye, 1.2 mg of $NaTm(CF_3)_2PB$, 1 g of DOP and 675 mg of PVC–PVAc–PVA copolymer. The membrane components were dissolved in 5 ml freshly distilled THF, dropped onto dust free Corning 7059 glass, and prepared as a thin membrane using a spin-coating device (spinning rate: 2500 rpm, Kokaliken K-359SD). After a spinning time of about 20 s, the glass support plate with sensing membrane was removed and heated at 90°C for 1 h. Components of the film optode are shown in Fig. 1.

## 3. Results and discussion

The design of fluorescent or chromogenic chemosensors for the selective detection of low concentrations of ions is an active area of research. The strong fluorescence emission and photosensitivity in the red-IR region, which makes squarylium dyes potentially useful as fluoroionophores [15] and as fluorophores in the biological applications [16], have also been explored. In 1997, Akkaya [17] reported the squarylium-based near IR fluorescent chemosensor **1** for metal ion. A red to NIR emitting, highly $Ca^{2+}$-specific fluorescent chemosensor has been synthesized. In pH 7.2 aqueous buffers, the chemosensor signals $Ca^{2+}$ by a decrease in emission intensity, whereas a large excess of $Mg^{2+}$ ions has no effect on either the absorption or the emission spectrum.




1

Das et al. [15] have observed that a near infrared absorbing cationic squarylium dye **2** is 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 [18].

Complexation of dye **2** by different metal ions gives rise to a new absorption band, which in most cases is characteristic of the metal ion involved.

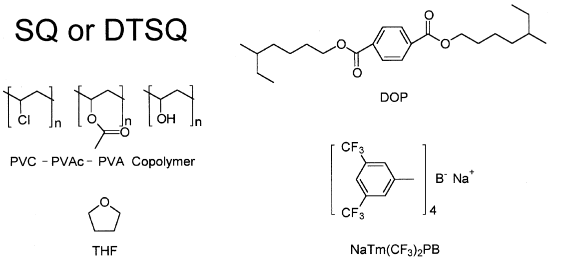
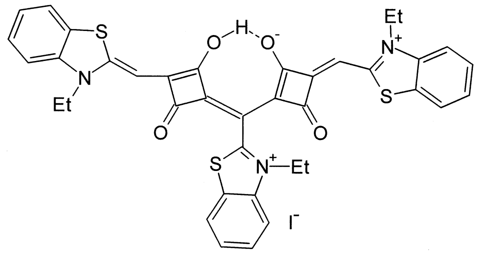



Fig. 1. Components of film optode.



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Our aim is to develop a different type of squarylium dye as a chromoionophore able to form complexes with metal ions which may have interesting analytical applications.

### 3.1. In-solution ion sensor

Chromoionophores showing the required high extinction coefficient, a narrow absorption band and absorption at high wavelength can be found in the cases of the SQ and DTSQ dyes. The absorption properties of SQ with $Cu^{2+}$ is here studied in $CH_2Cl_2$–$CH_3CN$, and compared to those of other metal ions in order to investigate the effect of the SQ as a chromoionophore. Fig. 2 shows the spectral change induced by added $Cu^{2+}$; as the $Cu^{2+}$ concentration increases, the absorbance of SQ decreases.

Fig. 3 shows that addition of other metal ions such as $Li^+$, $Na^+$, $Ca^{2+}$, $Mg^{2+}$ and $K^+$ up to $5\times10^{-3}$ M does not have any significant effect on the absorption spectrum of SQ. However, addition of even $5\times10^{-6}$ M quantities of $Cu^{2+}$ causes a decrease in the intensities of absorption of SQ. Similar results were obtained for DTSQ (Figs. 4 and 5).

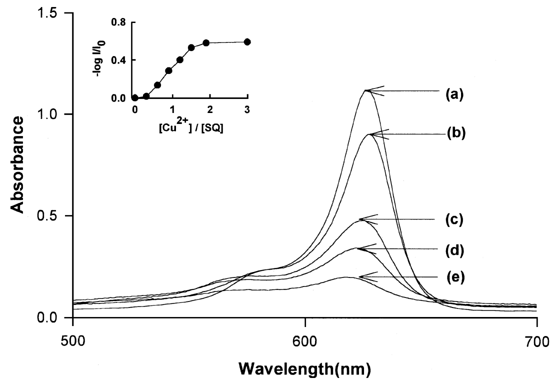


Fig. 2. Effect of $Cu^{2+}$ concentration on the absorption spectra of SQ ($5\times10^{-6}$ M) in $CH_2Cl_2$–$CH_3CN$ (1:4): [$Cu^{2+}$] (a) 0, (b) $2.5\times10^{-6}$, (c) $5.0\times10^{-6}$, (d) $7.5\times10^{-6}$, (e) $10\times10^{-6}$ M. Inset shows the plot of $-\log I/I_0$ vs [$Cu^{2+}$]/[SQ].

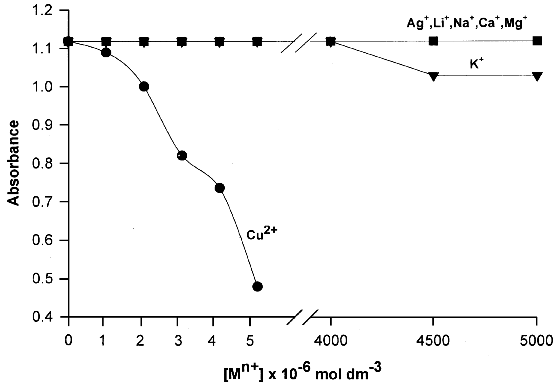


Fig. 3. Absorption intensity change in SQ ($5\times10^{-6}$ M) upon addition of metal salt in $CH_2Cl_2$–$CH_3CN$ (1:4) following the $\lambda_{max}$ (629 nm) of SQ.

We then tried to determine the associations constant ($K_{ass}$) for the $Cu^{2+}$-dye complex. In Figs. 2 and 4, the $-\log I/I_0$ was plotted against [$Cu^{2+}$]/[SQ], where $I_0$ and I are the absorption intensities of dyes before and after addition of $Cu^{2+}$ ion. Analysis of the complex formation, studied by the changes in absorption spectra on addition of $Cu^{2+}$ ion, indicated a 1:2 dye to $Cu^{2+}$ stoichiometry, with $K_{ass}=7.7\times10^5\,M^{-1}$ in SQ and $K_{ass}=1.5\times10^6\,M^{-1}$ in DTSQ.

The $K_{ass}$ of DTSQ in greater by 2-fold than that of SQ. These results show that these dyes is potentially usable for $Cu^{2+}$ sensing.

### 3.2. Ion sensing film optode

The growing need to have analytical results available in ever shorter periods of time for an efficient evaluation requires the development of analytical techniques which allow results be obtained without great expense of time and labour.

Ion selective optodes have been developed in the last decade [19,20]. Optodes are for disposable use, and can detect ions by simply immersing them into a glass cell filled with the sample solution, and determining the ion by measuring the absorbance change at the respective maximum absorption wavelength of the chromoionophore in the visible region. The major characteristic points of optodes are (i) small instrumentation, (ii) easy operation, (iii) low cost. From a practical viewpoint, these points are necessary in order to use optodes in a wide variety of fields and measure many samples.

Here, we report the development of ion sensing film optodes which can easily determine the metal ions such as $Cu^{2+}$ and $Ag^{+}$. The absorbance measuring system for the film optodes is shown in Fig. 6.

The ion sensing film optodes prepared were a polymer matrix membrane containing a SQ or DTSQ, DOP, and $NaTm(CF_3)_2PB$. The life-time of an ion-selective optode membrane can be defined as the period of time over which all the requirements with respect to selectivity, sensitivity, response time and stability are fulfilled.

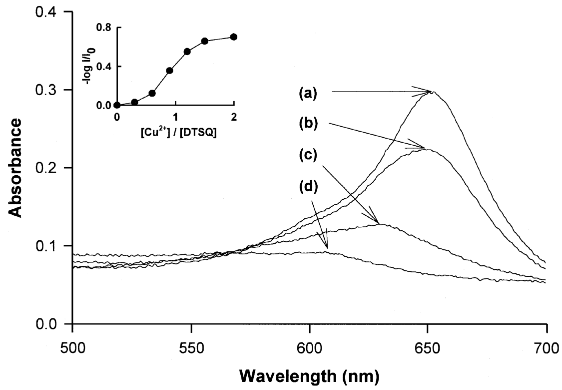


Fig. 4. Effect of $Cu^{2+}$ concentration on the absorption spectra of DTSQ ($5\times10^{-6}$ M) in $CH_2Cl_2$–$CH_3CN$ (1:4): [$Cu^{2+}$] (a) 0, (b) $2.5\times10^{-6}$, (c) $5.0\times10^{-6}$, (d) $7.5\times10^{-6}$ M. Inset shows the plot of $-\log I/I_0$ vs [$Cu^{2+}$]/[DTSQ].

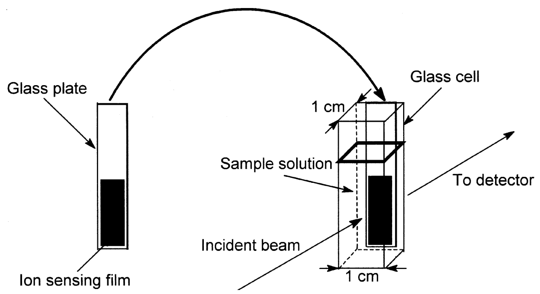


Fig. 6. Absorbance measuring system for the film optode.

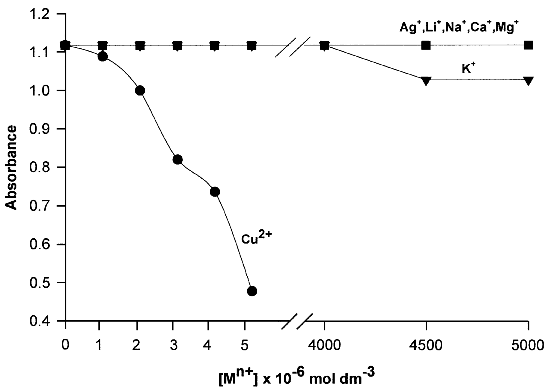


Fig. 5. Absorption intensity change in DTSQ ($5\times10^{-6}$ M) upon addition of metal salt in $CH_2Cl_2$–$CH_3CN$ (1:4), following the $\lambda_{max}$ (650 nm) of DTSQ.

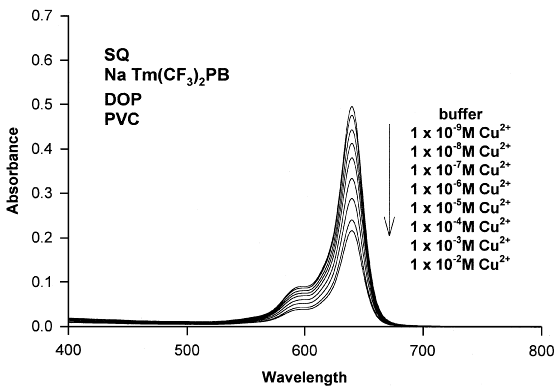


Fig. 7. Absorption spectra of $Cu^{2+}$ selective optode film (3.7 μm thick) with various $Cu^{2+}$ concentrations in pH buffered solutions (pH 7.0).

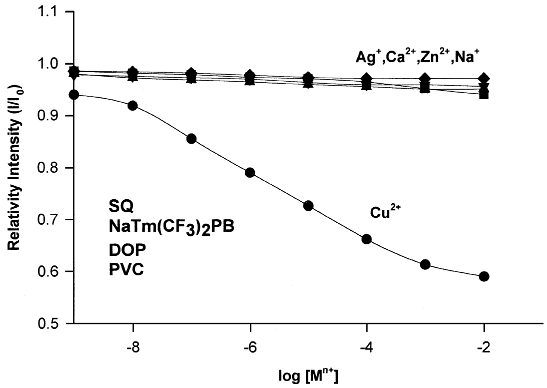


Fig. 8. Response curve obtained with the film optode based on SQ.

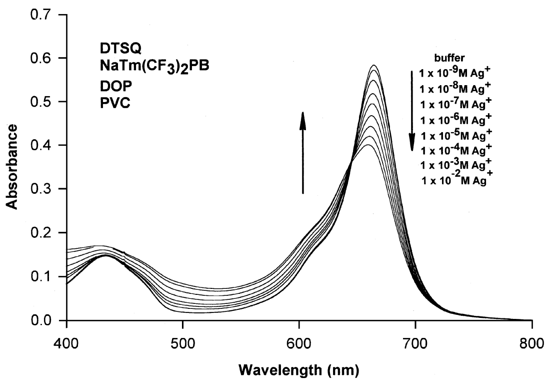


Fig. 9. Absorption spectra of $Ag^+$ selectivity optode film (4.5 μm thick) with various $Ag^+$ concentrations in pH buffered solutions (pH 7.0).

If the composition of a membrane changes during a measurement, this can then lead to a corruption of the properties of the optode. Because of its higher stability and liphophilicity, the Kobayahi-reagent, $NaTm(CF_3)_2PB$, was therefore mainly used for the cation selective optode membrane. Ion sensing film optodes on SQ and DTSQ dyes as a chromoionophore for the determination of $Cu^{2+}$ and $Ag^+$ ion were developed.

Fig. 7 shows typical absorption spectra for the film optode for the determination of $Cu^{2+}$ ion based on SQ, where the absorbance values decreased with increasing concentration of $Cu^{2+}$ in the sample solution. The obtained relative ion sensitivity of $Pb^{2+}$, $Ca^{2+}$, $Zn^{2+}$ and $Na^+$ for major interfering ions are shown in Fig. 8. Fig. 8 indicates

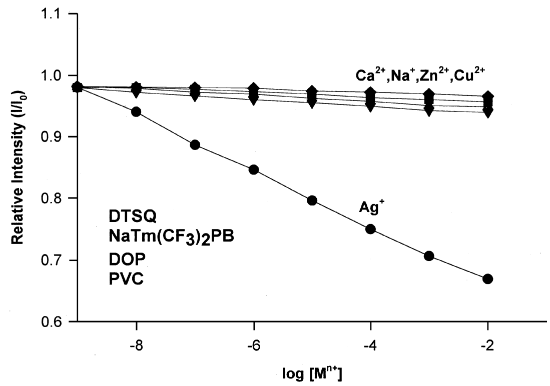


Fig. 10. Response curve obtained with the film optode based on DTSQ.

that the selectivity for $Cu^{2+}$ ion is relatively high, whereas with other metal ions, it is not applicable.

Using the thio-substituted dye, DTSQ, a high selective response for $Ag^+$ was observed (Figs. 9 and 10). By spectroscopic titration of the film optode based on DTSQ with $Ag^+$, a well defined isobestic point at 646 nm was observed. Owing to the trace detection and specific response to $Cu^{2+}$ and $Ag^+$ ion in the absorption spectra, SQ and DTSQ dyes appear to be potentially suitable for practical sensor application.

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## References

[1] Ziegenbein W, Sprenger HE. Angewandte Chemie 1966;78:937.
[2] Treibs A, Jacob K. Angewandte Chemie 1965;77:680.
[3] Sprenger HE, Ziegenbein W. Angewandte Chemie 1967;79:581–2.
[4] Loutfy RO, Hsiao CK, Kazmaier PM. Photographic Science and Engineering 1983;27:5–9.
[5] Tam AC. Applied Physics Letters 1980;37:978–81.
[6] Law KY, Bailey FC. Journal of Imaging Science 1987;31:172–7.
[7] Gravesteijin DJ, Steenbergen C, Vander Veen J. Proceeding SPIE International Society for Optical Engineering 1988;420:327.

[8] Merritt VY, Hovel HJ. Applied Physics Letters 1976;29:414.
[9] Fabian J, Nakazumi H, Matsuoka M. Chemical Review 1992;92:1197–225.
[10] Kim SH, Hwang SH. Dyes and Pigments 1997;35:111–21.
[11] Kim SH, Hwang SH. Dyes and Pigments 1998;36:139–48.
[12] Kim SH, Han SK, Park SH, Park LS. Dyes and Pigments 1998;38:49–56.
[13] Kim SH, Han SK, Kim JJ, Hwang SH, Yoon CM, Keum SR. Dyes and Pigments 1998;39:77–87.
[14] Alder JF, Ashworth DC, Narayanaswamy R, Moss RE, Southerland IO. Analyst (London) 1987;112:19.
[15] Das S, Thomas KG, Thomas J, George MV, Kamat PV. Journal of Physical Chemistry 1994;98:9291.
[16] Terpetschnig E, Szmacinski H, Ozinskas A, Lakowicz JR. Analytical Biochemistry 1994;217:197–204.
[17] Akkaya EU, Turkyilmaz S. Tetrahedtron Letters 1997;38:4513–16.
[18] Thomas KG, Thomas KJ, Das S, George MV. Journal of the Chemical Society Chemical Communications, 1997:597–8.
[19] Arnold MA. Analytical Chemistry 1992;64:1015A–1025A.
[20] Janata J. Analytical Chemistry 1992;64:196R–219R.