Journal of Inclusion Phenomena and Molecular Recognition in Chemistry **17:** 81–91, 1994.

Synthesis and Spectral Properties of a New Benzothiazolic Chromofluoroionophore Containing the Aza-15-Crown-5 Macrocyclic Moiety

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(Received: 7 September 1993; in final form: 30 December 1993)

Abstract. The synthesis of 1-[(4-benzothiazolyl)phenyl]-4,7,10,13-tetraoxa-1-aza-cyclopentadecane, a new chromofluoroionophore is described. Its interaction with alkali and alkaline-earth metal salts in acetonitrile is investigated both spectrophotometrically and spectrofluorimetrically.

Key words: Aza-15-crown-5, benzothiazole, chromoionophore, fluoroionophore.

1. Introduction

During the last several years considerable interest has been shown in the synthesis of monoprotonic, diprotonic and neutral chromoionophores containing macrocycles, which combine their colour characteristics with the ability to bind selectively certain metal ions [1,2]. Crown ether incorporating dyes have been reported to be appropriate photometric reagents for alkali and alkaline earth metal ions [2–4]. Crown ether-based fluorimetric reagents, which undergo drastic changes in their photophysical properties upon complexation, allow metal ion recognition at very low concentrations. They have been widely used in molecular and cellular biology [5,6].

Cation binding with a fluoroionophore leads to an enhancement of the fluorescence quantum yield [5,7–9] or to fluorescence quenching [10,11], as well as to various photophysical effects, depending on the ligand structure and the type of the ions in question [12–14]. When concentration dependence has been observed, stability constants of the complexes formed have been determined using both photometric and fluorimetric techniques [8–10,15–17].

In previous papers we have reported synthetic procedures for obtaining styryl dyes containing aza-15-crown-5 and an appropriate chromophore (**1**) and its analyt-

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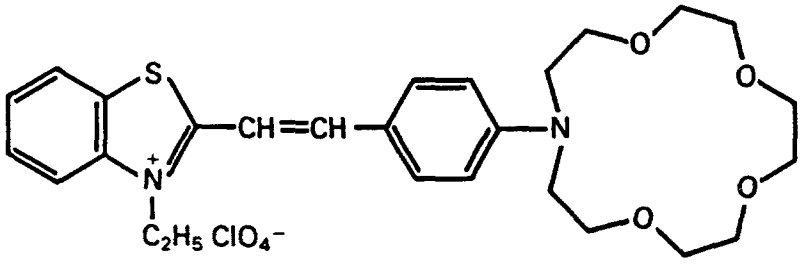
ical application as an extraction and spectrophotometric reagent [18,19]. Following our design logic we have synthesized a new chromofluoroionophore **2** and studied its interaction with alkali and alkaline earth metal salts.



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2. Experimental

The melting points were determined on a Koffler apparatus and are uncorrected. ^{1}H NMR and ^{13}C NMR spectra were recorded on Bruker WM 250 MHz instrument in $CDCl_3$ and DMSO-d_6 with TMS as internal reference. IR-spectra were recorded on a Specord IR71 spectrophotometer in chloroform and nujol. The absorption and fluorescence spectra were taken on a Perkin Elmer Lambda 17 UV/VIS spectrophotometer and on a Perkin Elmer MPF44 spectrofluorimeter respectively.

2.1. Preparation of 2

2.1.1. *N,N-(2-Benzoyloxyethyl)-aniline,* 4

Benzoylchloride (14 mL, 17.06 g, 0.121 mol) was added dropwise to a stirring solution of *N,N*-(2-hydroxyethyl)aniline **3** (10 g, 0.052 mol) in THF containing triethylamine (16.77 mL, 12.25 g, 0.121 mol). A thick white precipitate was formed and the temperature raised to 40–50°C. The reaction was followed by TLC (silicagel, petroleum ether:ethylacetate 5:1). The solution was poured into water, extracted with $CHCl_3$ and the extracts were washed with 1M HCl, $NaHCO_3$, sat.NaCl and H_2O, dried over $MgSO_4$ and distilled under reduced pressure. The residue solidified under petroleum ether. It was recrystallized from methanol. M.p. 72–73°C. Yield 75%.

Anal. Calcd. for $C_{24}H_{23}NO_4$: C 74.02; H 5.95; N 3.60. *Found*: C 73.98; H 5.96; N 3.50. IR (cm^{-1},$CHCl_3$): 1110,1280 (–C–O str.); 1500,1600 (Ar. –C=C– str.); 1720 (–C=0 str.).

^{1}H NMR($CDCl_3$, δ (ppm), J(Hz)): 7.95 (d,4H,J=7.8,H–2″); 7.73 (t,2H,J=8.5,H–3′); 7.52 (t,2H,J=7.2,H–4‴); 7.5 (t,1H,J=8.4,H–4′); 7.40 (t,4H,J=7.7,H–3‴); 6.82 (d,2H,J=8.3,H–2′); 4.58 (t,4H,J=6.0,H–2″); 3.87 (t,4H,J=6.0,H–1′).

^{13}C NMR: 166.26 (C–3″); 147.06 (C–1′); 132.83 (C–4‴); 129.63 (C–1‴); 129.41 (C–2‴); 129.30 (C–3′); 128.19 (C–3‴); 116.89 (C–4′); 112.08 (C–2′); 61.88 (C–2″); 49.53 (C–1″).

2.1.2. *4-Formyl-N,N-(2-benzoyloxyethyl)aniline,* **5**

A mixture of 2 mL $POCl_3$ and 18 mL DMF was stirred for 5 min at room temperature. It was then warmed to 50°C for 15 min. After cooling, a solution of **4** (0.021 mol) in 15 mL DMF was added dropwise during 30 min. The dark green solution was stirred for 30 min at room temperature and for 2h at 100°C. After cooling it was poured into ice and neutrallized to pH 7 with 40% NaOH. The product was extracted with $CHCl_3$, washed with H_2O, sat. NaCl, H_2O and dried over $MgSO_4$. The solvent was removed under reduced pressure. The remaining dark blue oil becomes solid under petroleum ether. It was purified by dissolving in $CHCl_3$ and precipitating with petroleum ether. The pure compound is a white solid. M.p. 70–71°C. Yield 82%.

Anal. Calcd. for $C_{25}H_{23}NO_5$: C 71.93; H 5.55; N 3.36. *Found*: C 71.70; H 5.72; N 3.43. IR (cm^{-1},$CHCl_3$): 1110,1280 (–C–O str.); 1600 (Ar.–C=C– str.); 1680 (–C=0 aldehyde str.); 1720 (–C=0 carboxyl str.).

^1H NMR($CDCl_3$, δ (ppm)): 9.76 (s,1H,H–5′); 7.98 (d,4H,J=7.95,H–2‴); 7.76 (d,2H,J=8.5,H–3′); 7.56 (t,2H,J=7.0,H–4‴); 7.42 (t,4H,J=7.95,H–3‴); 6.93 (d,2H, J=8.5,H–2′); 4.56 (t,4H,J=6.0,H–2″); 3.93 (t,4H,J=6.0,H–1″).

^{13}C NMR: 190.05 (C–5′); 166.28 (C–3″); 152.11 (C–1′); 133.14 (C–4‴); 132.07 (C–3′); 129.45 (C–1‴,C–2‴); 128.34 (C–3‴); 126.10 (C–4′); 111.37 (C–3′); 61.43 (C–2″); 49.43 (C–1″).

2.1.3. *4-Benzothiazolyl-N,N-(2-Benzoyloxyethyl)-aniline,* **6**

Four g (9.6 mmol) **5** and 1.2 g (1.02 mL, 9.6 mmol) 2-aminothiophenol were dissolved in 20 mL DMSO. The reaction mixture was heated till the temperature reached 160°C with simultaneous removal of the volatile products. About 10 mL DMSO were distilled under reduced pressure. The reaction mixture was cooled and diluted with water. The separated oil solidified. It was filtered and recrystallized from methanol. M.p. 113–115°C. Yield 78%.

Anal. Calcd. for $C_{31}H_{26}N_2O_4S$: C 71.25; H 5.01; N 5.36. *Found*: C 71.35; H 5.12; N 5.45. IR (cm^{-1},$CHCl_3$): 1110,1280(–C–O str.); 1490,1610 (Ar.–C=C– str.); 1720 (–C=0 str.).

^1H NMR ($CDCl_3$, δ (ppm), J(Hz)): 8.00 (d,4H,J=7.7,H–2‴); 7.98 (d,2H,J=8.6, H–3′); 7.95 (d,1H,J=8.0,H–4); 7.83 (d,1H,J=7.7,H–7); 7.54 (t,2H,J=7.4,H–4‴); 7.45 (t,1H,J=7.8,H–5); 7.40 (t,4H,J=7.4,h–3‴); 7.30 (t,1H,J=7.7,H–6); 6.93 (d,2H, J=8.6,H–2′); 4.54 (t,4H,J=6.0,H–2″); 3.88 (t,4H,J=6.0,H–1″).

^{13}C NMR: 168.6(C–2); 166.25(C–3″); 153.95(C–3a); 148.7(C–1′); 133.95(C–7a); 133.2(C–4″); 129.7(C–3′); 129.5,129.4,128.20(C–1‴,C–2‴,C–3‴); 125.92 (C–5); 124.045(C–4); 122.07,121.98(C–6,C–7); 111.5(C–2′); 59.6(C–2″); 52.7(C–1″).

2.1.4. *4-Benzothiazolyl-N,N-(2-hydroxyethyl)-aniline,* **7**

Four g (7.6 mmol) **6** were dissolved in 30 mL acetone. 2 g KOH in water was added and the mixture was boiled for several minutes. It was then stirred at room temperature. The reaction was continued till the complete disappearance of the starting product (TLC on silicagel, pet.ether:ethyl acetate 5:1). The acetone was removed and more water was added. The precipitate was filtered and washed with water. Yellow solid. M.p. 164–165°C. Yield 70%.

Anal. Calcd. for $C_{17}H_{18}N_2O_2S$: C 64.94; H 5.74; N 8.91. *Found*: C 64.80; H 5.90; N 9.20. IR (cm^{-1},nujol): 1500,1600 (Ar.–C=C– str.).

^1H NMR(DMSO–d_6, δ (ppm), J(Hz)): 7.96 (d,1H,J=8.0,H–4); 7.92 (d,1H,J=8.0, H–7); 7.83 (d,2H,J=8.0,H–3′); 7.44 (t,1H,J=7.7,H–5); 7.32 (t,1H,J=7.4,H–6); 6.80 (d,2H,J=8.0,H–2′); 3.62 (s,4H,H–2″); 3.53 (s,4H,H–1″).

^{13}C NMR: 167.87 (C–2); 154.04 (C–3a); 150.48 (C–1′); 133.83 (C–7a); 128.64 (C–3′); 126.26 (C–5); 124.34 (C–4); 121.86 (C–6,C–7); 119.66 (C–4′), 111.36 (C–2′); 58.12 (C–2″); 53.23 (C–1″).

2.1.5. *1-[(4-Benzothiazolyl)phenyl]-4,7,10,13-tetraoxa-1-aza-cyclopentadecane,* **2**

(a) A suspension of NaH (0.040 g) in 20 mL THF was placed in a three-necked flask. The mixture was boiled under reflux and solutions of **7** (0.300 g, 1 mmol) and triethylenglycolditosylate (0.300 g, 1 mmol) in 10 mL THF were added simultaneously from two dropping funnels over a period of 2h. The solvent was distilled, the residue was dissolved in $CHCl_3$ and the insoluble impurities ware filtered. The pure product was obtained by column chromatography(silicagel, ethyl acetate:heptane 1:1) in 60% yield. M.p. 113–114°C.

Anal. Calcd. for $C_{25}H_{28}N_2O_4S$: C 64.46; H 6.59; N 6.54. *Found*: C 64.20; H 6.40; N 6.50.

(b) 0.330 g (1 mmol) 4-formylbenzo-aza-15-crown-5 **8** and 0.130 g (1 mmol) 2-aminothiophenol were mixed in 7 mL DMSO, the volatile products were distilled and after cooling the mixture was poured into water. The solidified product was separated and recrystallized from methanol. M.p. 108–110°C. Yield 78%.

Anal. Calcd. for $C_{23}H_{28}N_2O_4S$: C 64.46; H 6.59; N 6.54. *Found*: C 64.32; H 6.35; N 6.70. IR (cm^{-1},$CHCl_3$) 1110 (–C–O str.); 1480,1600 (Ar –C=C– str.).

^1H NMR($CDCl_3$, δ (ppm), J(Hz)): 7.96 (d,1H,J=8.1,H–4); 7.91 (d,2H,J=8.9,H–3′); 7.82 (d,1H,J=7.6,H–7); 7.42 (t,1H,J=7.4,H–6); 7.29 (t,1H,J=7.6,H–5); 6.70 (d,2H,J=8.9,H–2′); 3.78 (t,4H,J=6.5,H–1″); 3.62–3.67 (m,16H,H–2″,H–3″,H–4″, H–5″).

^{13}C NMR: 168.59 (C–2); 154.33 (C–3a); 149.67 (C–1′); 134.41 (C–7a); 128.95 (C–3′); 125.85 (C–5); 124.047,122.14,121,24 (C–4,C–6,C–7); 121.09 (C–4′); 111.23 (C–2′); 71.19,70.14,69.9,68.19 (C–2″,C–3″,C–4″,C–5″); 52.58 (C–1″).

2.2. PREPARATION OF 1-[4-(3-METHYLBENZOTHIAZOLYL)PHENYL]-4,7,10,13-TETRAOXA-1-AZA-CYCLOPENTADECANE **9**

A mixture of 0.300 g (0.7 mmol) **2** and 0.350 mL $(CH_3O)_2SO_2$ in 10 mL chlorbenzene were boiled for 4h. After cooling a yellow oil separated. Ethyl ether was added to obtain the residue of the product. The oil was dissolved in ethanol, $NaClO_4$ was added and the product was precipitated as perchlorate by adding ethyl ether. M.p. 138–140°C. Yield 70%.

Anal. Calcd. for $C_{24}H_{31}ClN_2O_8S$: C 53.08; H 5.75; N 5.16. *Found*: C 52.95; H 5.82; N 5.30. IR (cm^{-1},nujol): 1110 (–C–O str.); 1500,1600 (ar. –C=C–str.).

^1H NMR(DMSO–d_6, δ (ppm), J(Hz)): 8.39 (d,1H,J=7.5,H–7); 8.25(d,1H,J=8.1, H–4); 7.89 (t,1H,J=8.1,H–5); 7.78 (t,1H,J=7.5,H–6); 7.82 (d,2H,J=8.9,H–3′); 7.00 (d,2H,J=8.9,H–2′); 4.25 (s,3H,H–8); 3.72,3.58 (s,s,16H,H–2″,H–3″,H–4″,H–5″); 3.52 (s,4H,H–1″).

2.3. PREPARATION OF 4-BENZOTHIAZOLYL-*N*, *N*-(2-METHOXYETHYL)ANILINE **11**

0.400 g (1.3 mmol) **7** was dissolved with slight warming in 10 mL dioxane, 0.200 g NaOH in 2 mL H_2O and 30 mg Bu_4NI were added. The two-phased system was stirred at room temperature and 0.5 mL $(CH_3O)_2SO_2$ were added dropwise. The mixture was stirred for 48 h at room temperature. A further 2 mL $(CH_3O)_2SO_2$ were added and 50% aqueous NaOH was used to keep the reaction medium alkali and to prevent quaternisation. After the starting compound disappeared (TLC,silicagel,hexane:ethyl acetate 1:1) the dioxane was distilled, the alkali solution was extracted with CH_2Cl_2, the organic layers were washed with water and dried over $MgSO_4$. Both products **10** and **11** were separated by column chromatography (hexane:ethyl acetate 1:1).

10: M.p. 111-113°C, yield 65%.

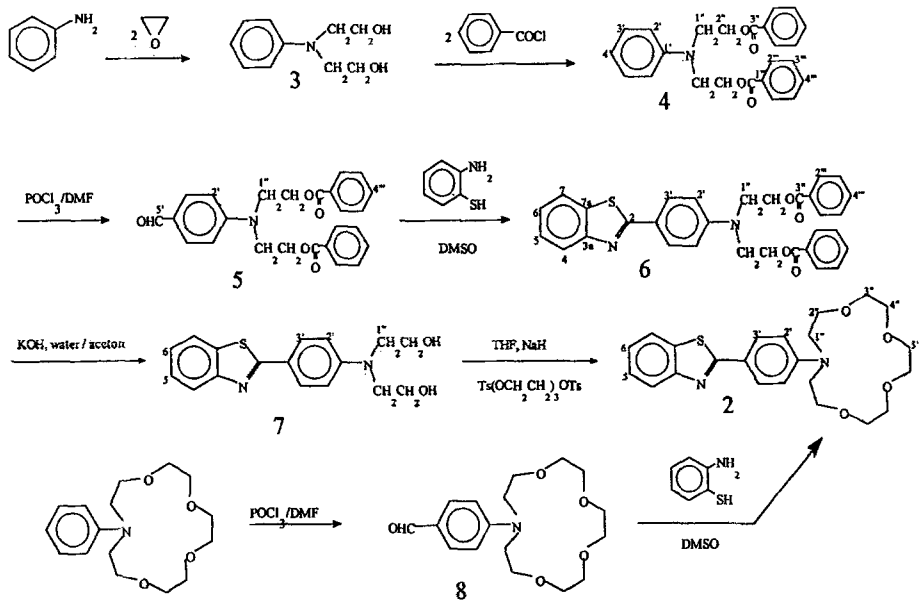
Anal. Calcd. for $C_{18}H_{20}N_2O_2S$: C 65.83; H 6.13; N 8.53. *Found*: C 65.92; H 6.02; N 8.80.

^1H NMR($CDCl_3$, δ (ppm), J(Hz)): 7.99 (d,1H,J=8.2,H–4); 7.94 (d,2H,J=9.1,H–3′); 7.84 (d,1H,J=7.8,H–7); 7.44 (t,1H,J=7.7,H–6); 7.31 (t,1H,J=8.1,H–5); 6.73 (d,2H,J=9.1,H–2′); 3.85 (t,2H,J=4.8,H–1″); 3.72–3.65 (m,6H,H–1^{IV},H–2^{IV}); 3.63 (t,2H,J=4.8,H–2″); 3.37 (s,3H,H–3^{IV}).

11: 54–55°C, yield 30%.

Anal. Calcd. for $C_{19}H_{22}N_2O_2S$: C 66.64; H 6.48; N 8.30. *Found*: C 66.45; H 6.30; N 8.30.

^1H NMR($CDCl_3$, δ (ppm), J(Hz)): 7.97 (d,1H,J=8.3,H–4); 7.92 (d,2H,J=8.9,H–3′); 7.83 (d,1H,J=7.8,H–7); 7.43 (t,1H,J=7.5,H–6); 7.30 (t,1H,J=7.7,H–5); 6.76 (d,2H,J=8.9,H–2′); 3.64–3.58 (m,8H,H–1″,H–2″); 3.37 (s,3H,H–3″).



Scheme 1

3. Results and Discussions

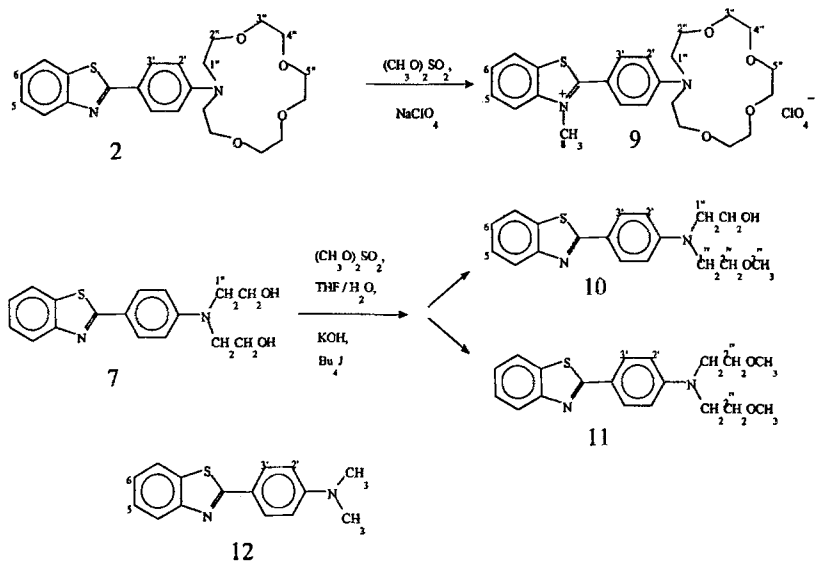
The desired compound **2** was obtained in two independent ways (Scheme 1). The 6-step synthetic procedure includes introduction of a benzoyl protecting group [20] which was easily removed from the benzothiazole containing compound **6** thus obtaining **7** in good yield. The preparation of **4** was performed according to the Vilsmeier procedure [20].

An improved method for the synthesis of benzothiazolic compounds [21] was applied to obtain both **6** and **2**. After deprotection a cyclisation reaction was performed and **2** was isolated as a main product [22].

Compound **11**, which does not posses a macrocycle, was synthesized by two-phase methylation together with the monomethylated product **10** [23] (Scheme 2).

All compounds were characterized by means of ^{1}H NMR (**2–7** by ^{13}C NMR also), UV, IR spectra, m.p. and elemental analysis. The methods used confirmed the proposed structures.

The influence of alkali and alkaline earth metal ions on the absorption and emission spectra of **2**, **9**, **11** and **12** was investigated in acetonitrile at large M^{n+} excess (Figs. 1–3). It is evident that addition of metal ions cause changes both in the absorption and emission spectra of **2**, as well as in the absorption spectrum of **9**. Since, in some cases, compounds without a macrocyclic cavity are also active towards metal ions [23] we have checked the complexation ability of **11** and **12** and established that they do not exhibit a tendency to metal binding. Obviously, the



Scheme 2

changes in the absorption and emission spectra of **2** and **9** are due to the complex formation with the crown cavity.

The long- wavelength absorption band in the spectrum of **2** is ascribed to charge transfer from the donor macrocyclic N- atom to the benzothiazolic acceptor N (λ_{max} 360 nm, $\varepsilon = 40000$). Upon complex formation the metal ion attracts the electron pair of the N atom, thus lowering its donor ability. As a result, a hypsochromic λ_{max} shift combined with a hypochromic effect has been observed. The larger the charge density of the ion and the better it fits into the crown cavity, the stronger the influence on the absorption spectrum [1]. The most significant changes on the absorption and emission spectra of **2** were caused by Ba^{2+} and Ca^{2+} cations. The CT peak of the complex appears at 326 nm ($\Delta\lambda = 34$ nm) and it is combined with a decrease in the ligand peak intensity at 360 nm (Figure 1).

Using a large excess of salt (10^{-2} M salt solutions and 10^{-6} M ligand solution in acetonitrile) fluorescence quenching of the ligand emission maximum at 420 nm was observed. (At lower salt concentrations we have established other effects, which will be published elsewhere.) At the same time no λ_{max} shift was caused by the investigated cations. Similar observations and reasons for this have been discussed in [10]. Evidently, the complexation is connected with a significant reorganization of the ligand structure and re-distribution of the electron density.

Among the alkali metals the strongest λ_{max} hypsochromic shift (16 nm) in the absorption spectrum of **2** was observed in the presence of Na^{+} as might be expected

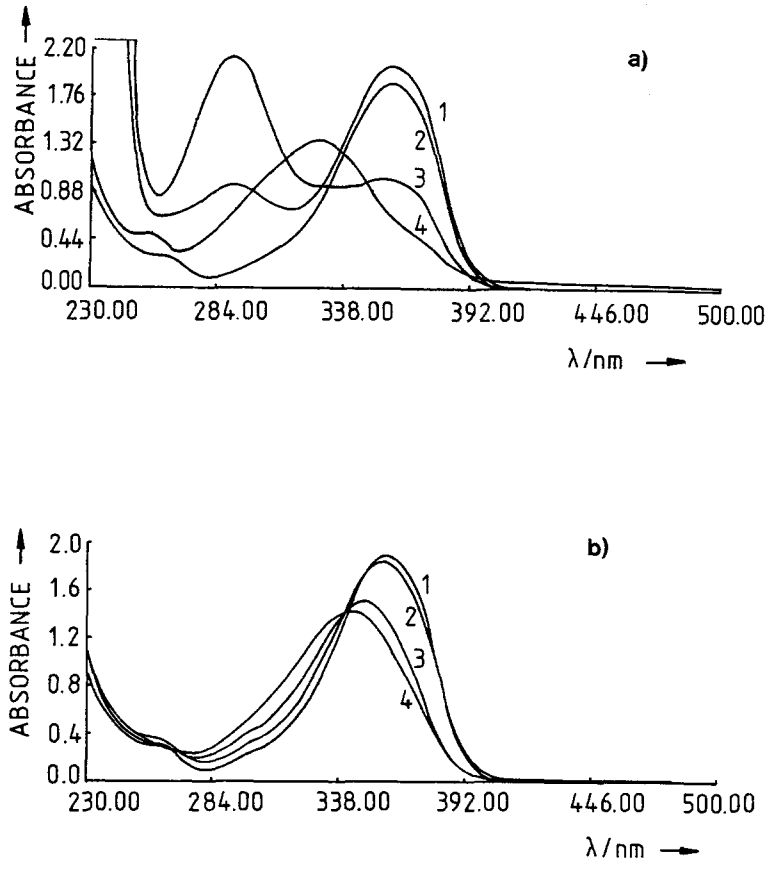


Fig. 1. (a) Absorption spectra in acetonitrile of compound **2** (4.5×10^{-5}M) (1) and in the presence of 0.1M $Mg(NO_3)_2.6H_2O$ (2), $Ca(NO_3)_2.4H_2O$ (3) and 0.01M $Ba(ClO_4)_2.3H_2O$ (4). (b) Absorption spectra in acetonitrile of compound **2** (4.5×10^{-5}M) (1) and in the presence of 0.07M $KClO_4$ (2), 0.1M $LiClO_4.3H_2O$ (3) and 0.1M $NaClO_4.H_2O$ (4).

due to the good fit of the Na^+ ionic radius and the cavity dimension [25]. The small Li^+ caused a shift of 10 nm and the much larger K^+ cation influenced the absorption only very slightly. The fluorescence spectrum of **2** was hardly influenced by alkali metals.

The absorption spectrum of the quaternized compound **9** ($\lambda_{max} = 416$ nm) was only slightly affected by the investigated ions. The free ion pair in the macrocyclic nitrogen is engaged in the conjugated system of the chromophore, so that its donating ability is considerably lower than in the non-quaternized compound. It shows an insignificant shift (6 nm) with $NaClO_4$, 2 nm with $LiClO_4$ and no changes were observed in the presence of $KClO_4$ as well as with all alkaline earth metal ions

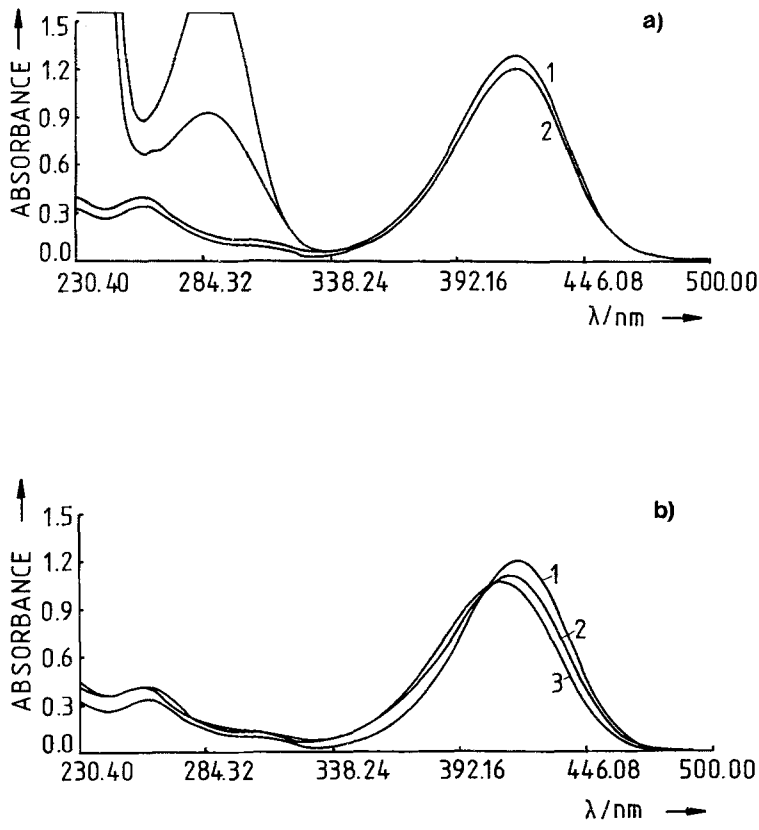


Fig. 2. (a) Absorption spectra in acetonitrile of compound **9** (2.82×10^{-5}) (1) and in the presence of 0.1M $Mg(NO_3)_2.6H_2O$, $Ca(NO_3)_2.4H_2O$ and 0.01M $Ba(ClO_4)_2.3H_2O$ (2). (b) Absorption spectra in acetonitrile of compound **9** (2.82×10^{-5}) (1) and in the presence of 0.1M $LiClO_4.3H_2O$ (2) and 0.1M $NaClO_4.H_2O$ (3).

investigated. Most probably the quaternization is connected with rearrangement of the electronic states in the system, leading to a non-emitting first excited state.

4. Conclusions

The absorption and emission spectra of compound **2** are selectively affected by Ba^{2+} and Ca^{2+} cations. The other alkali and alkaline earth metal ions do not cause significant changes. Quaternization leads to a lower complexation ability of the aza-15-crown-5 macrocycle. Because of the specific sensitivity towards Ba^{2+} and Ca^{2+} the newly synthesized chromofluoroionophore **2** could be used for the recognition and determination of these ions.

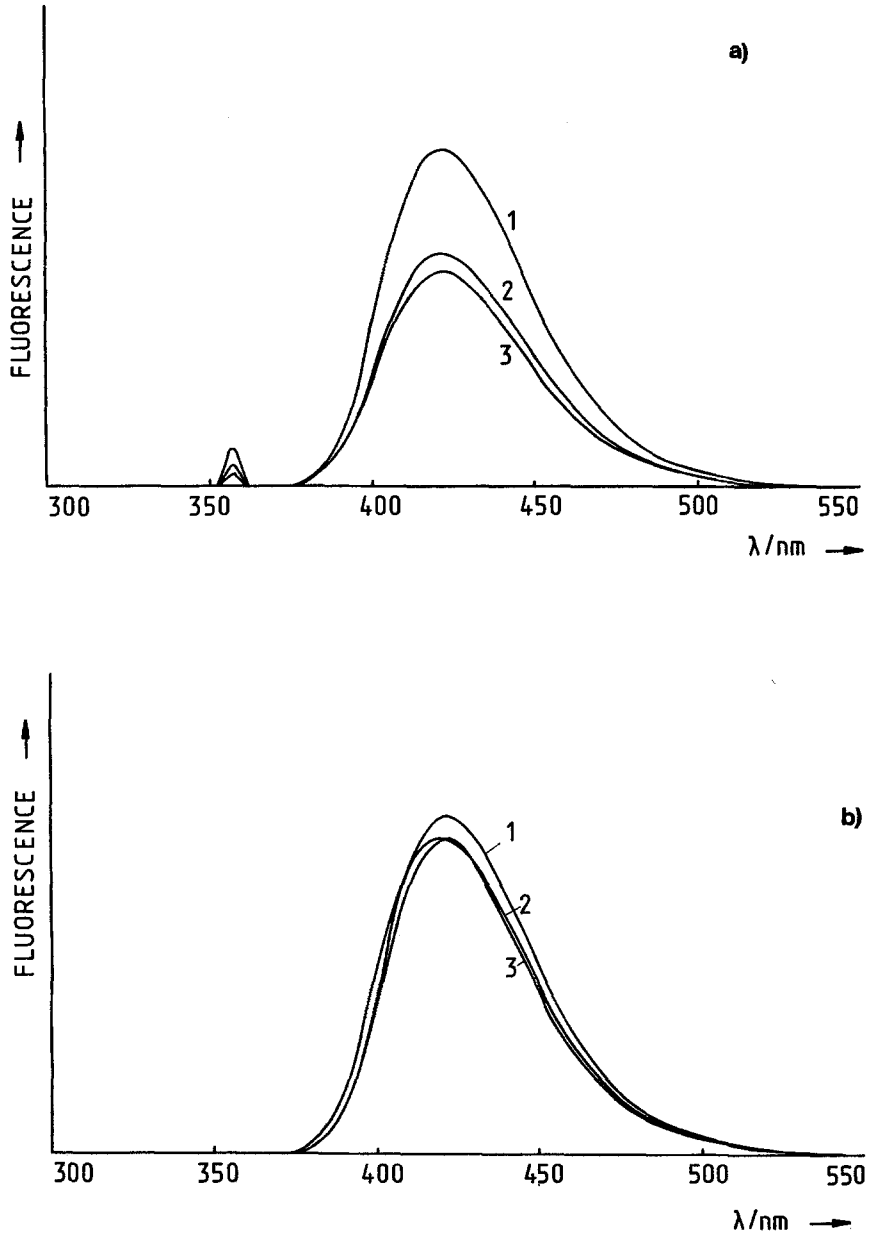


Fig. 3. (a) Emission spectra in acetonitrile of compound **2** (1×10^{-6}M) (1) and in the presence of 0.01M $Ba(ClO_4)_2.3H_2O$ (2) and 0.01M $Ca(NO_3)_2.4H_2O$ (3). (b) Emission spectra in acetonitrile of compound **2** (1×10^{-6}M) (1) and in the presence of 0.1M $LiClO_4.3H_2O$ (2) and 0.1M $NaClO_4.H_2O$ (3).

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