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Synthesis, Cation-Binding and Optical Spectral Studies of Photoemmitive Benzothiazole Crown Ethers

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Abstract

Crown ethers **1–4**, encompassing a photoemittive benzothiazole chromophore have been synthesised using standard protocols. Alkali metal picrate extraction profiles reveal that compared to the known crown ethers, benzothiazole benzo-15-crown-5 **1** and benzothiazole dibenzo-18-crown-6 **3** exhibit relatively higher % extraction for K^+ than Na^+ ions. The UV-visible and fluorescence spectra of **1–4**, in comparison to their neutral forms were found to be red shifted on protonation due to enhanced intramolecular charge transfer transition. The *ortho*-substituted benzothiazole crowns **2–4** showed higher Stokes shifts compared to the *para* analog **1** in the presence of CF_3CO_2H, presumably due to H-bond-assisted conformational restriction. No changes were noticeable in the absorption spectra in the presence of alkali metal ions. Even, fluorescence properties of **1–4** were not found to be drastically perturbed by these ions. While **1** exhibited slight quenching at alkali metal ion concentration over 10-fold with respect to that of **1**, interestingly, **2–4** showed a slight enhancement of fluorescent intensity at least up to 10-fold concentration of metal ions over those of **2–4**. Further increase of metal ion concentrations produces quenching effects. This behavior has been tentatively explained by invoking electrostatic interaction between these cations and the benzothiazole nitrogen ligand.

Introduction

Lately, there has been a great deal of interest to develop crown ethers and macrocyclic systems as molecular sensors for specific identification and quantification of metal ions [1–3]. The fluorescence chemosensor is one of the most sensitive detection techniques for the recognition in trace amounts of environmentally and biologically relevant cations. The design concept is based on the perturbation of optical properties of the crown-bound fluorophore in response to metal ion complexation [4–6]. During the past fifteen years or so a wide range of fluoroionophores derived from a combination of fluorophore such as coumarins, naphathalene, anthracenes and pyrene systems with receptors such as crown ethers, cryptands, calixarenes and macrocyclic systems have been investigated as potential optical sensors for metal ions. In addition, a few examples of crown ethers encompassing benzothiazole fluorophore have been reported for their potential applications as fluorescence-based metal ion sensors [7–12]. However, most of these crown ethers are characterized by the linkage of benzothiazole to the aza-crown ether via the nitrogen ligand. In these fluoroionophores, photoinduced electron transfer (PET) mechanism is the principle mode of fluorescent detection wherein the metal ion binding switches-on the emission by preventing the electron transfer quenching [13–14]. However, fluoroionophores in which the benzothiazole moiety is directly placed on the aromatic ring of the crown ether are quite scarce; synthesis of 4′-(2-benzothiazolyl)benzo-15-crown-5 **(1)** and the corresponding benzo-12-crown-4 analog being the only examples of this type reported so far in the literature [15].

The present paper deals with convenient synthesis of known **1** (Scheme 1) together with unknown benzothiazole crown ethers **2–4** (Scheme 2) and their metal ion complexation and spectral investigations under different conditions. The crown ethers **2–4**, in which the benzothiazole moiety has been placed at the *ortho* positions with respect to the crown domain are of interest in terms of providing extra binding mode via the nitrogen of the benzothiazole component. Unlike the aza-benzothiazole crown systems, where the PET mechanism operates, in the case of **1–4** which consist of donor and acceptor chromophores (crown and benzothiazole rings, respectively), the emission behavior is expected to be governed by the intramolecular charge transfer (ITC) mechanism [16–17].

Experimental

$LiClO_4$, $NaClO_4$ and $KClO_4$ were prepared by reacting metal carbonates with perchloric acid and dried under vacuum for 24 h. The chemicals and solvents for synthesis and column chromatography were purchased from SD Fine

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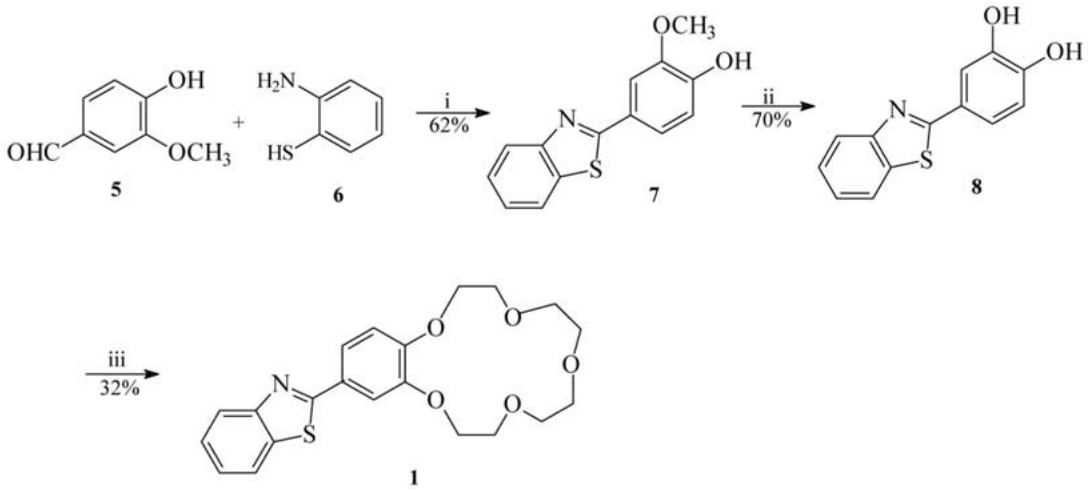
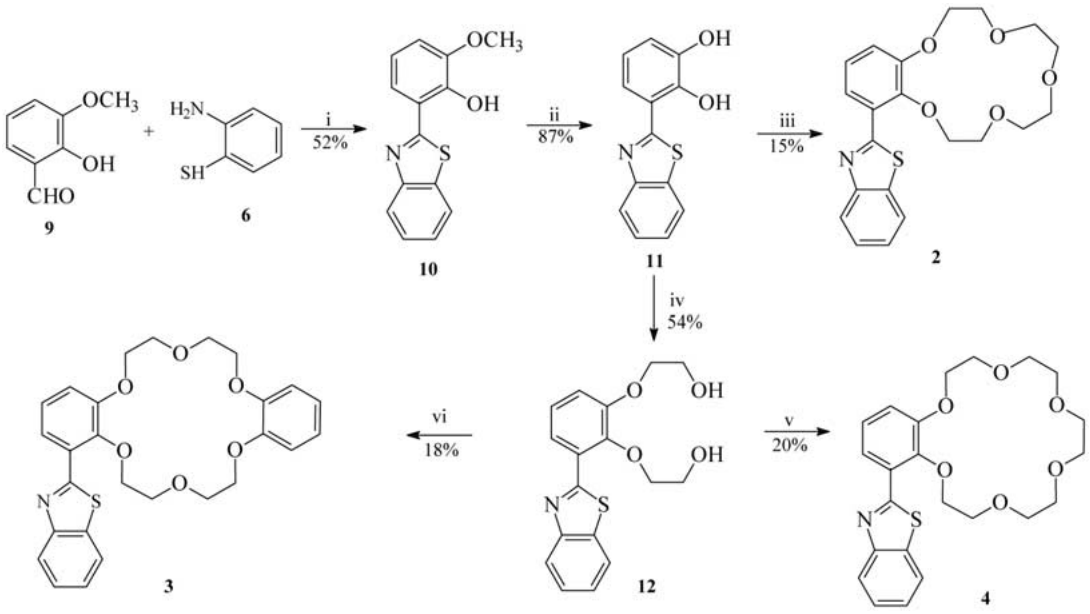


Scheme 1. Reagents and condition: (i) Ethanol, Δ, 24 h; (ii) 49% aq HBr, reflux, 10 h; (iii) $TsOCH_2$ $(CH_2OCH_2)_3CH_2OTs$, Bu^tOK, Dry THF, 18-crown-6, 50–56 °C, 40 h, N_2.



Scheme 2. Reagents and condition: (i) Ethanol, Δ, 24 h; (ii) 49% aq HBr, reflux, 10 h; (iii) $TsOCH_2$ $(CH_2OCH_2)_3CH_2OTs$, Bu^tOK, Dry THF, 18-crown-6, N_2, Reflux, 40 h; (iv) $ClCH_2CH_2OH$, 10% NaOH, R.T, 45 h; (v) $(TsOCH_2CH_2OCH_2)_2$, Bu^tOK, Dry THF, 18-crown-6, N_2, 50–56 °C, 40 h, N_2; (vi) 1,2-C_6H_4-$(OCH_2CH_2Ts)_2$, Bu^tOK, Dry THF, 18-crown-6, N_2, 50-56 °C, 40 h, N_2.

Chemicals (India) and used as received. Spectral grade solvents were procured from Merck, India. Melting points (uncorrected) were determined on a Gallenkamp melting point apparatus. IR spectra were recorded on a Shimadzu FTIR-420 spectrophotometer. ^1H NMR spectra were recorded on a Bruker-AMX-500 spectrometer with TMS as an internal standard. Microanalyses were performed by the microanalytical section of the Department. Mass Spectra were recorded on GCMS-QP 5050A Shimadzu spectrophotometer. UV-visible spectra were taken on Shimadzu UV-visible spectrophotometer UV-2100 and Fluorescence spectra were recorded on a Shimadzu Spectrofluorometer RF-5301 PC.

2-(3,4-Dihydroxy phenyl)benzothiazole **(8)**: A solution of 2-aminothiophenol **6** (12.5 g, 10.68 mL, 100 mmol) and vanillin **5** (15.2 g, 100 mmol) in ethanol (100 mL) was refluxed for 24 h. The precipitated solid obtained upon dilution with water was crystallised from methanol to give yellow crystals of **7** in 62% yield (16 g), mp 154–156 °C (lit. [17] mp 156–157°). A solution of **7** (15 g, 58.4 mmol) in 49% aqueous HBr (150 mL) was heated at reflux for 10 h. The reaction mixture was cooled, diluted with water and extracted with ethyl acetate. The organic extract was washed with water, dried over anhyd. Na_2SO_4 and concentrated to give a crude solid, which was crystallized from ethyl acetate to give white crystals of 8 in 70% yield (9.86 g), mp 192–195 °C (lit. [18] mp 194–196 °C).

4′-(2-Benzothiazolyl)benzo-15-crown-5 (**1**): 2-(3,4-dihydroxyphenyl)benzothiazole **(8)** (1.22 g, 5.0 mmol), t-BuOK (1.68 g, 15.0 mmol) and a catalytic amount of 18-crown-6 were dissolved in dry THF (150 mL) under N_2 atmosphere. To this solution at 50–60 °C, a solution

of tetraethylene glycol ditosylate [19] (2.51 g, 5 mmol) in dry THF (200 mL) was added dropwise during 10 h. The reaction was heated at reflux for another 30h, cooled to room temperature and filtered through a pad of Celite. The crude product obtained on solvent removal was purified by chromatography on silica gel($CHCl_3$-ethyl acetate, 75:25 as eluent) to give a colorless solid. Crystallization from cyclohexane provided colorless crystals of **1** in 30% yield (0.65 g), mp 112–115 °C ^{1}H NMR ($CDCl_3$): δ 3.75–4.35 (m, 16 H), 6.94 (1 H, d), 7.32–7.40 (1 H, m), 7.44–7.50 (1 H, m), 7.56–7.62 (1 H, dd), 7.7 (1 H, d), 7.86–7.90 (1 H, dd), 8.0–8.06 (1 H, dd); IR (KBr, ν/cm^{-1}): 3000, 1600, 1580, 1530, 1490, 1280, 1140, 940, 760; (Found: C, 62.66; H, 5.98; N, 3.38; S, 7.87. $C_{21}H_{23}NO_5S$ requires C, 62.84; H, 5.74; N, 3.49, S, 7.98%); m/z (CI) 401 (M^+), 294, 282, 268, 256, 240, 226, 192, 138,124, 109.

2-(2,3-Dihdroxyphenyl)benzothiazole **(11)**: 2-(2-hydroxy-3-methoxyphenyl)benzothiazole **(10)** was prepared following the same procedure as described for **8**. Thus, *o*-vanillin **9** (15.2 g, 100 mmol) was reacted with 2-aminothiophenol (12.5 g, 10.68 mL, 100 mmol) in ethanol to give yellow crystals of **10** in 52% yield (13.4 g), mp 155–158 °C. Demethylation of **10** was carried out as described for **6** by heating with 49% aqueous HBr. Work-up followed by crystallization from 1:1 ethyl actate-petroleum ether gave colorless crystal of **11** in 87% yield (6.2 g) mp 200–204 °C (lit. [20] mp 205–206 °C).

Synthesis of 3′-(2-benzothiazolyl)benzo-15-crown-5 **(2)**: 2-(2,3-dihydroxyphenyl)benzothiazole **(11)**: (1.22 g, 5.0 mmol) was reacted with tetraethylene glycol ditosylate (2.51 g, 5.0 mmol) under the conditions described for **1**. Purification of the crude product by column chromatography on silica gel using chloroform-ethyl acetate (75:25) as eluent, followed by crystallisation from cyclohexane gave white crystals of **2** in 15% yield (0.3 g, mp 115–118 °C). ^{1}H NMR ($CDCl_3$): δ 3.74–4.40 (16 H, m), 6.98–7.04 (1 H, dd), 7.14–7.24 (1 H, m), 7.34–7.42 (1 H, m), 7.46–7.52 (1 H, m), 7.90–7.96 (1 H, dd), 8.02–8.12 (2 H, m); IR (KBr, ν/cm^{-1}): 3000, 1582, 1503, 1430, 1367, 1351, 1270, 1180, 1070, 981, 880; (Found: C, 62.66; H, 5.59; N, 3.76; S, 8.13. $C_{21}H_{23}NO_5S$ requires C, 62.84; H, 5.74; N, 3.49; S, 7.98%); m/z (EI) 401 (M^+), 342, 327, 296, 282, 269, 253, 243, 214, 186, 173, 164, 107.

Preparation of diol **(12)**: To solution of 2-(2,3-dihydroxy phenyl)benzothiazole **(11)** (3.0 g, 12.35 mmol) in 10% NaOH (100 mL) was added 2-chloroethanol (6.68 mL, 100 mmol) at 0–5 °C and the reaction flask was sealed with a rubber septum. The reaction mixture was stirred at this temperature for 5 h and further at room temperature for 40 h. The mixture was diluted with water and extractively worked-up in ethyl acetate. The organic extract after water washing was dried over anhyd Na_2SO_4. Removal of solvent followed by column chromatography of the crude product on silica gel using chloroform-ethyl acetate (75:25) as eluent furnished a colorless solid, which on recrystallization from ethyl acetate gave an analytical sample of **12**, mp 98–100 °C (yield: 2.2 g, 54%). ^{1}H NMR ($CDCl_3$ + DMSO-d_6): δ 3.7**2–4**.64 (m, 10 H, –CH_2–CH_2–OH); δ 6.93–8.24 (m, for Ar-H). IR (KBr, ν/cm^{-1}): 3410, 2911, 1580, 1504, 1463, 1380, 1278, 1166,1082, 930, 880, 860; (Found: C, 61.42; H, 5.33; N, 4.35; S, 9.56. $C_{17}H_{17}NO_4S$ requires C, 61.63; H, 5.14; N, 4.23; S, 9.67%).

3′-(2-Benzothiazolyl) dibenzo-18-crown-6 **(3)**: Compound **3** was prepared by cyclizing diol **12** (1.32 g, 4.0 mmol) with ditosylate of 1,2-bis(2-hydroxyethoxy) benzene (2.53 g, 5.0 mmol) under the conditions described for **1**. Purification of the crude product was effected by column chromatography on silica gel using chloroform-ethyl acetate (75:25) as eluent to give **3** as a colorless, crystalline solid, mp 170–175 °C in 18% yield (0.35 g). ^{1}H NMR ($CDCl_3$): δ 3.92–4.46 (m, 16 H), 6.86–6.96 (4 H,m), 6.98–7.04 (1 H, dd), 7.12–7.20 (1 H, m), 7.34–7.42 (1 H, m), 7.44–7.52 (1 H, m), 7.92–7.98 (1 H, dd), 8.04–8.12 (2 H, dd); IR (KBr, ν/cm^{-1}): 3003, 1603, 1582, 1505, 1471, 1362, 1289, 1180, 1078, 950, 784; (Found: C, 65.56, H, 5.65; N, 2.96; S, 6.22. $C_{27}H_{27}NO_6S$ requires C, 65.72; H, 5.48; N, 2.84; S, 6.49%). MS: m/z (EI) 493 (M^+), 463, 448, 430, 404, 314, 296, 282, 243, 214, 136, 121, 109, 91.

3′-(2-Benzothiazolyl) benzo-18-crown-6 **(4)**: Intermediate diol **12** (1.32 g, 4.0 mmol) was cyclized with triethyleneglycol ditosylate (1.83 g, 4.0 mmol) under the conditions described for **1**. The crude product obtained upon work-up was purified by column chromatography on silica gel to provide **4** as a colorless solid, mp 112–115 °C in 20 % yield (0.36 g). ^{1}H NMR ($CDCl_3$): δ 3.69–4.43 (20 H, m), 7.00–7.05 (1 H, dd), 7.15–7.23 (1 H, m), 7.36–7.55 (2 H, m), 7.91–7.96 (1 H, dd), 8.12–8.20 (2 H, dd); IR (KBr, ν/cm^{-1}): 3000, 1583, 1452, 1370, 1325, 1256, 1130, 1031, 980, 781; (Found: C, 62.34; H, 5.91; N, 3.29; S, 6.92. $C_{23}H_{27}NO_6S$ requires C, 62.02; H, 6.07; N, 3.17; S, 7.19%); MS: m/z (EI): 445(M^+), 402, 384, 372, 282, 270, 257, 209, 139, 100, 89.

Extraction of alkali metal picrates: According to literature procedure [21], metal picrate solutions (conc. 7×10^{-5} M) were extracted with the solution of appropriate benzothiazole crown systems **1–4** dissolved in dry CH_2Cl_2 (conc. 7×10^{-4} M). Equal volumes (20 ml each) of crown ether solution and the given alkali metal picrate solution were vigorously shaken for ca. 10 min to achieve the equilibrium. The molar absorbance of the aqueous metal-picrate solution before extraction A_0 and after extraction A_C were recorded at the position of the absorption maxima at 354 nm (due to the picrate ion). The % of metal ion extracted into the organic phase was calculated by the expression A_0–$A_C/A_0 \times 100$. The experiments were replicated thrice and the average extraction data are shown in the Table 1.

Results and discussion

Synthesis

The synthesis of 4′-(2-benzothiazolyl) benzo-15-crown-5 **(1)** was accomplished by using the sequence shown in Scheme1. The condensation of readily available vanillin **5** with 2-aminothiophenol **(6)** in ethanol afforded yellow crystals of 2-(4-hydroxy-3-methoxy phenyl) benzothiazole **(7)** in

Table 1. Extraction of alkali metal ion picrates with **1–4**[a]

Crown ethers	Li^+ %	Na^+ %	K^+ %	Relative extraction	
				K^+/Li	K^+/ Na^+
Benzo-15-crown 5	4.3	24.4	43.1	10	1.8
1	0.7	10	41	58	4.1
2	0.3	4.3	28	100	6.5
Dibenzo-18-crown-6	0.0	1.8	24.8	–	13.7
3	0.4	0.6	25	60	42
Benzo-18-crown-6	1.8	6.8	70	39	10
4	0.2	4.5	22	105	4.9

[a]Extraction values for benzothiazole crown ethers **1–4** and the model crown ethers, benzo-15-crown-5, dibenzo-18-crown-6 and benzo-18-crown-6 are derived using the procedure reported in the literature [21–22].

62% yield. Demethylation of 7 with 49% aqueous HBr gave 2-(3,4-dihydroxy-phenyl) benzothiazole **(8)** in 69% yield. The cyclization of **8** with tetraethylene glycol ditosylate in t-BuOK/ THF system under high dilution conditions provided **1** in 32% yield as a colorless compound. For the synthesis of 3′-(2-benzothiazolyl)benzo-15-crown-5 **(2)**, a sequence similar to that described for **1** was employed except that *o*-vanillin **9** was used as the starting material (see Scheme 2). Condensation of bis-phenol **11** and tetraethylene glycol ditosylate afforded the desired crown ether **2** in 15% yield.

In order to prepare crown ether **3**, diol **12** was readily prepared in 54% yield by reacting diol 11 with 2-chloroethanol in 10% aqueous NaOH. The macrocyclisation of diol **12** with ditosylate of 1,2-bis(2-hydroxyethoxy)benzene and t-BuOK in THF afforded crown ether **3** as a colorless solid in 18% yield. Finally, synthesis of **4** was achieved in 20% yield by condensing diol **12** with triethylene glycol ditosylate (Scheme 2). The structures of **1–4** and their precursors are fully supported by combustion analysis and mass, IR and ^{1}H NMR spectra.

Alkali metal ion complexation using fluoroionophores **1–4**

Since polyoxa-crown ethers are better known for the extraction of alkali metal ions, this initial report is confined to extraction studies of Li^+, Na^+, and K^+ ions by crown systems **1–4** using the well-known two-phase picrate extraction procedure [21]. It was of interest to see any possible effects of extra ligation provided via "nitrogen" of the benzothiazole moiety in the *ortho*-substituted crown ethers **2–4**. For comparison, the reported extraction values of the known model crown ethers, benzo-15-crown-5, dibenzo-18-crown-6 and benzo-18-crown-6 [21–22] are also shown in Table 1.

Our results show that p-benzothiazole crown **1** extracts alkali ions in the order $K^+ > Na^{+>} Li^+$ with 41% extraction for the K^+ which is in agreement with data reported with benzo-15-crown-5 (42%) [21–22]. However, extractions of Li^+ or Na^+ by **1** are lower compared to benzo-15-crown-5. Thus *para*-benzothiazole-crown **1** exhibits improved selectivity for K^+ over Li^+ and Na^+ compared to benzo-15-crown-5. This result is in agreement with that reported by Chang *et al.* [15].

For the case of *ortho*-benzothiazole crown **2**, extractions of Li^+, Na^+ and K^+ picrates were found to be inferior to that of benzo-15-crown-5 [22] but, the selectivity for K^+ over both Li + and Na^+ by crown **2** is superior (Table 1). The lower extraction of alkali metal ions by **2** is in contrast to our anticipation that extra binding by the benzothiazole nitrogen might reinforce the binding character of the crown ether to translate into higher extractability compared to 15-crown-5 as well as *para*-benzothiazole crown **1**. We can rationalize the relative lower extractability of **2** on the ground that (a) the twist between the bezothiazole group and the aryl ring might cause the benzothiazole ring to move appreciably away from the crown binding domain and (b) the benzothiazole substituent at the *ortho* position could deform the crown ether geometry by steric congestion to leading to weakening of the complexing ability. The benzothiazole crown ether **3** was found to extract K^+ ions in comparable amounts to that of the known, dibenzo-18-crown-6. Thus, as indicated in the Table 1, *ortho*-benzothiazole crown **3** exhibits relatively superior extraction selectivity for K^+ ions over that of the Na^+ ions in comparison to dibenzo-18-crown-6 as well as benzothiazole crowns **1** and **2**. On the other hand, **4** displayed lower extraction for all the three alkali metal ions studied, namely Li^+, Na^+ and K^+ compared to the model, benzo-18-crown-6. However, in the case of **4**, the % extractibility of K^+ was better than Li^+ compared to benzo-18-crown-6.

UV-visible and fluorescence spectroscopic studies on benzothiazole crown ethers **1–4**

The absorption spectra of **1–4** measured in $CHCl_3$ solvent displayed a main band in the region between 302–326 nm. The individual λ and ϵ values are collected in the Table 2. A low intensity band is also present at 240–245 nm for these crown compounds. Addition of CF_3CO_2H to the $CHCl_3$ solutions of **1–4** caused red shifts of the long wavelength absorption band by 21–40 nm. It is understandable that the protonation of the basic benzothiazole nitrogen with CF_3CO_2H would cause enhancement of the π-acceptor properties of this hetero-ring. The consequent increased intramolecular charge transfer (ITC) transition from the HOMO of the π-rich benzo-crown ring to the LUMO of the benzothiazolium ring in **1–4** is responsible for the observed red shifts upon protonation [23]. Such red shifts are reminiscent of donor-acceptor chromophores, including donor-acceptor crown ethers, cyanine dyes, etc. [24]. Interestingly, inspection of Table 2 indicates that the *para*-benzothiazole crown ether **1** displays greater red shifts (40 nm) compared to the *ortho* analogs **2–4** which are red shifted by lower λ of 21–34 nm. The relatively lower magnitude of red shifts in the latter crown systems may be attributed to weakening of the resonance π-conjugation due to torsion between the aryl and the benzothiazole ring. The absorption spectra of **1–4** in the presence of an excess of complexing metal ions, specifically Na^+ and K^+ in the form of soluble salts, $NaPF_6$ and KPF_6 did not show noticeable change, either in the absorbance or intensity with respect to their original values.

Table 2. UV-visible spectra of **1–4** in $CHCl_3$ and $CHCl_3$ + 1%CF_3CO_2H

Crown ethers	$CHCl_3$		$CHCl_3$ + 1%CF_3CO_2H		Stokes shift
	λmax (nm)	ϵmax ($mol^{-1}cm^{-1}$)	λmax (nm)	ϵmax ($mol^{-1}cm^{-1}$)	(nm)
1	326	20,020	366	20,400	40
2	303	18,950	331	19,900	28
3	302	21,340	336	23,320	34
4	312	20,290	333	20,650	21

Table 3. Emission spectra of **1–4** in $CHCl_3$ and $CHCl_3$ + 1%CF_3CO_2H

Crown ethers	$CHCl_3$			$CHCl_3$ + 1%CF_3CO_2H		
	λex (nm)	λf (nm)	Stokes shift (nm)	λex (nm)	λf (nm)	Stokes shift (nm)
1	326	381	55	366	453	87
2	303	382	79	331	463	132
3	302	382	80	336	457	121
4	312	380	68	333	443	110

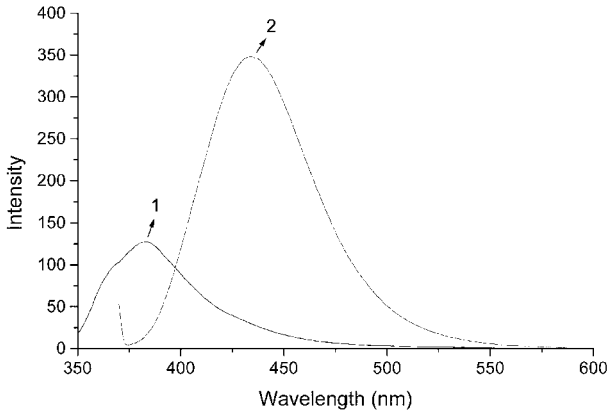


Figure 2. Emission spectra of **1** in (1) $CHCl_3$ and (2) $CHCl_3$ + CF_3COOH.

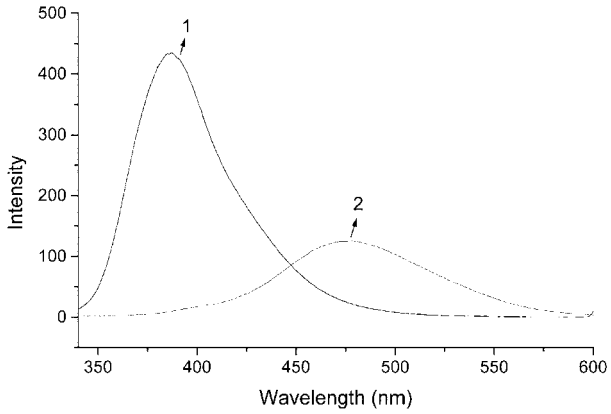


Figure 3. Emission spectra of **2** in (1) $CHCl_3$ and (2) $CHCl_3$ + CF_3COOH.

Fluorescence spectral data of benzothiazole crown ethers **1–4** recorded in $CHCl_3$ and $CHCl_3$ containing 1% CF_3CO_2H are collected in Table 3. As representative cases, the fluorescence spectra of *para*-benzothiazole crown **1** and *ortho*-benzothiazole crown **2** under neutral and acidic conditions are shown in Figures 1 and 2, respectively. It is noteworthy that the Stokes shifts (SS) of 78–80 nm observed for the *ortho*-benzothiazole crowns **2–4** are larger than for the *para*-analog **1** (55 nm). This suggests that the excited states in **2–4** are relatively more relaxed than in **1** [25]. Upon addition of CF_3CO_2H, the emission maxima for **1–4** are red shifted in accord with the red shifts also observed in their absorption spectra in acidic condition. However, the SS for *ortho*-benzothiazole crown ethers **2–4** (110–132 nm) are significantly higher than observed for **1** which is only 87 nm. We attribute the higher SS for **2–4** to increased rigidification of donor-acceptor chromophores. The N-protonation of benzothiazole moiety in these molecules could provide an oppurtunity for the H-bonding involving the neighbouring "crown-oxygen". The H-bonding could reduce the biaryl type torsion between the benzo-crown ring and the benzothiazole substituent so as to impose restriction on the degree of conformational freedom. In such an event, emission could occur from a highly relaxed, lower levels of the Frank Condon excited states to produce higher red shifts [24]. Further, higher value of SS in **2–4** is also indicative of major change in the excited state dipole moments relative to that of the ground states [26–28]. However, H-bonding is not structurally possible in case of 1 and hence the magnitude of SS is relatively less.

We have also probed the effects on fluorescence spectra of **1–4** (10^{-6} M) in acetonitrile solvent in the presence of different concentrations of alkali metal ions. The results are shown in Table 4. Although the λ of emission bands of **1–4** practically remained unaffected, the fluorescence intensities showed marked changes by added metal ions. The fluorescence spectra of **1** in the presence of Li^+, Na^+ and K^+ revealed little or practically no change in the intensity up to 1:10 concentration. Only a weak fluorescence quenching is noticed at metal ion concentrations 100 times that of the crown ether **1**. Surprisingly, even the better complexing K^+ showed hardly any effect of emission intensity suggesting that metal ion interaction with the crown cavity does not significantly perturb the excited state structures for the case of **1**. A rather weak fluorescence quenching by alkali metal ions observed at higher concentrations can be attributed to reduced ICT (metal ions bind with the benzo-crown ring where the HOMO is located) which can enhance nonradiative return of the excited states to the ground states [29].

In contrast to **1**, an unusual behavior is observed with *ortho*-benzothiazole crown ethers **2–4** in the presence of varying concentrations of alkali metal ions. Alkali metal ions, rather than the quenching produce slight enhancement in the fluorescence intensity of crown ethers **2–4** at least up to a 10 time concentration of metal ions, and thereafter further increase in the amounts of metal ions had a weak quenching effects (Table 4). In donor-acceptor type fluoroionophores, it is well known that metal ion binding with the donor component results in quenching of emission. However, the opposite seems to be happening with crown

Table 4. Relative fluorescence intensities of **1–4** in the presence of alkali metal perchlorates

Metal ions	Crown ether **1**			Crown ether **2**			Crown ether **3**			Crown ether **4**		
	0.1 μM	1.0 μM	10 μM	0.1 μM	1.0 μM	10 μM	0.1 μM	1.0 μM	10 μM	0.1 μM	1.0 μM	10 μM
Free	581			230			229			172		
Li^+	580	575	420	265	260	258	294	283	241	209	202	204
Na^+	572	543	424	245	241	198	250	253	191	208	211	199
K^+	580	589	567	257	244	211	237	230	232	202	204	192

ethers **2–4**. We propose that metal ion complexation with the crown moiety might increase the torsion between the crown-carrying aryl ring and the benzothiazole component, thereby delinking these two chromophores. If true, then electronic communication between the benzothiazole fluorophore and metal bound crown ether could be hampered. Furthermore, it is likely that alkali metal ions might also electrostatically interact the basic benzothiazole-nitrogen ligand in **2–4** via ion-dipole type interaction [30]. These factors in part could lead to initial enhancement in fluoroscent intensity, which at much higher salt concentrations begin to exhibit quenching effects. Unfortunately, the fluorescence intensity changes are either insignificant or lacked monotonous behavior with increase in the metal ion concentrations, so we are unable to adapt the fluorescence parameters to calculate the apparent stability constants.

Conclusion

In conclusion, we have synthesized benzothiazole substituted crown ethers **1–4** and investigated their alkali metal ion binding and optical properties. The UV-visible spectra were found to be red-shifted upon N-protonation on account of enhanced D–A charge transfer transition, but the addition of alkali metal perchlorates does not modify the absorption characteristics. However, interesting emission behaviors have been observed for these fluoroionophores. In contrast to the *para*-analog **1**, the *ortho*-benzothiazole crown ethers **2–4** exhibit larger Stokes shifts in the presence of CF_3CO_2H, which is presumed to arise from the H-bonding effect involving the basic benzothiazole nitrogen and the crown "oxygen". Unusual fluorescence properties of **2–4** observed in the presence of different concentrations of alkali metal ions have been explained on basis of possible electrostatic interaction of metal ions with the benzothiazole nitrogen ligand. Evidently, crown ethers **1–4** are of interest and further studies to evaluate thermodynamic parameters of metal ion complexation are under way.

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