Journal of Inclusion Phenomena and Macrocyclic Chemistry **37:** 441–450, 2000.

The Synthesis of Novel Crown Ethers, Part VII [1]. Coumarin Derivatives of Benzocrowns and Cation Binding from Fluorescence Spectra

ÇAKIL ERK[1,⋆], MUSTAFA BULUT[2] and AYTEN GÖÇMEN[3]
[1]*Chemistry Department, Ístanbul Technical University, Maslak 80626, Ístanbul, Turkey;*
[2]*Chemistry Department, Marmara University, Istanbul 81040, Turkey;* [3]*Chemistry Department, Balıkesir University, Balıkesir 10100, Turkey*

(Received: 20 May 1999; in final form: 5 November 1999)

Abstract. 4-[3-(1-benzopyran-2-one)] derivatives of benzo[12]crown-4, benzo[15]crown-5 and benzo-[18]crown-6 were synthesized from 4-[3-(1-benzopyran-2-one)]-1,2-dihydroxy-benzene reacting with bis-ethyleneglycol dihalides or pentaethylene glycol ditosylate in alkali carbonate/DMF/water. The original products were identified by high resolution EI-mass spectra as well as IR, ^{1}H-NMR and ^{13}C-NMR spectroscopy. The 1 : 1 binding constants of Mg^{2+}, Li^{+}, Na^{+} and K^{+} with the coumarin-benzocrowns were estimated using fluorescence emission spectroscopy in acetonitrile. The complexing enhanced quenching fluorescence spectra (CEQFS) and complexing enhanced fluorescence spectra (CEFS) exhibited the ion binding powers due to cationic recognition rules of the macrocycles.

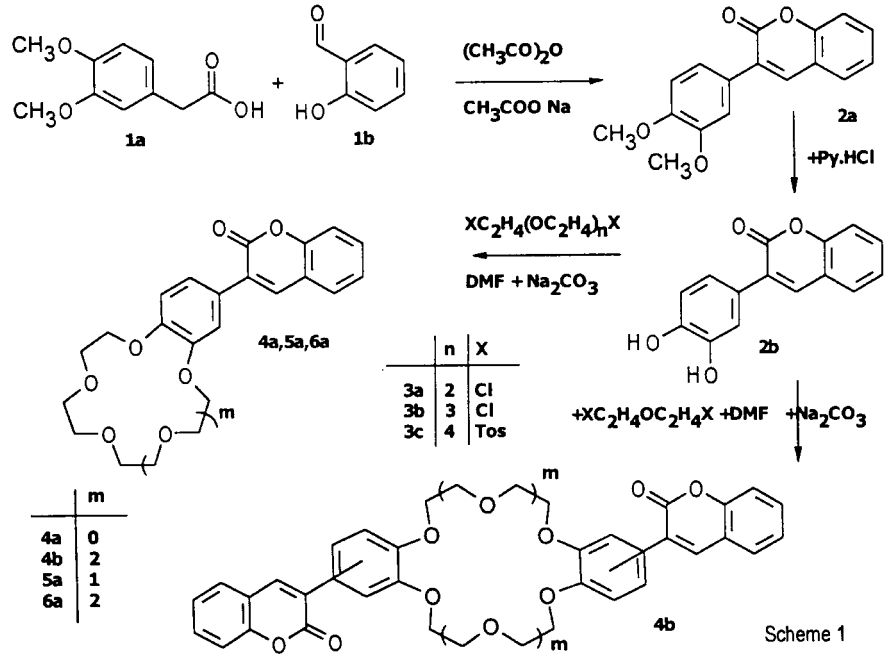
Key words: macrocycles, coumarins, cation binding, Mg^{2+}, Li^{+}, Na^{+}, K^{+}, fluorescence spectroscopy.

1. Introduction

Several macrocyclic ethers possessing oxygen dipoles have been synthesized to investigate their alkali and alkaline-earth cation membrane transport and binding properties by means of potentiometry [2, 3], optical spectroscopy [4], as well as NMR spectroscopy methods [5]. The ionophores bearing suitable light sensitive moieties may undergo intermolecular changes at the electronic level upon cationic interactions of donor oxygen atoms. Essentially, the fluorescence spectra of fluorogenic macrocycles is a reliable method to study cationic recognitions [6–9].

We have recently synthesized fluorogenic coumarin[12]crown-4, [15]crown-5 and [18]crown-6 derivatives and examined cation binding effects using steady state fluorescence spectroscopy [10–13]. 9,10-Anthraquinone crowns showed cationic recognition with UV-VIS spectra but no fluorescence spectra were reported [14].

⋆ Author for correspondence.



Scheme 1.

We now present the synthesis, spectral data and cationic recognition using fluorescence spectroscopy of 4-(3-coumarin)-benzocrowns [15], (Scheme 1). The double chromophoric benzo and benzopyranone moieties in a macrocycle molecule have displayed interesting cation binding results.

In our earlier works we prepared the macrocyclic ether on the coumarin body showing good fluorescence response upon cation binding [10, 12]. The coumarin benzocrowns were prepared in the presence of DMF, water and alkali carbonates by the cyclic condensation of polyethylene glycol dihalides or ditosylates with 4-(3-coumarin)-substituted-1,2-dihydroxybenzene that was obtained from 3,4-dimethoxyphenyl acetic acid and salicylaldehyde via Perkin synthesis [15], (Scheme 1).

Introduction of fluorescence spectroscopy into the examination of host-guest interactions of ionophore macrocycles has opened an interesting field, although, different photophysical effects are involved. The developments in this field for detection and recognition of ions offered several analytical techniques dependent on the changes in fluorescence intensity or maximum of the wavelength to estimate the extent of host-guest interactions.

The fluorescence emission and excitation spectra of the new coumarin-hosts were observed in the presence of alkali cations in dry acetonitrile and the cation binding effects were quantitatively estimated. The relative Li^+, Na^+ and K^+ ion binding powers as well as the role of the counter ions SCN^- and ClO_4^- were

quantitatively estimated assuming that the spectral alterations are due to strong host-guest interactions between the fluorophore and the cations in acetonitrile [10, 14]. However, the coumarin-crowns were not soluble enough in water for quantitative metal-macrocycle studies.

2. Experimental

2.1. ORGANIC SYNTHESIS

The starting chemicals were from Merck or Fluka unless otherwise cited. The bis-polyethylene glycol dichlorides were available to us from the earlier work. IR spectra were recorded with KBr pellets on a Jasco FT-IR spectrometer, model 5300. Electron impact, EI, high resolution mass spectra were obtained with a Fisons instrument, model VG-ZapSpec. The melting points are not corrected. ^{1}H-NMR and ^{13}C spectra were recorded on a Bruker spectrometer, Model Avance 400-CPX in $CDCl_3$ or in DMSO-$d_6$and TMS was used as the internal standard.

3-(2,3-dimethoxyphenyl)-1-benzopyran-2-one **(2a)**; 3,4-dimethoxyphenylacetic acid, **1a**, (1.96 g, 10 mmol), *o*-hydroxybenzaldehyde, **1b**, (1.22 g, 10 mmol), acetic anhydride (2.45 g, 24 mmol), Na (4.10 g, 50 mmol) and acetic acid (40 mL) were refluxed for 24 h. The product was washed with water after the removal of acetic acid and crystallized from acetic acid, **2a**, m.p. 138 °C, 1.40 g, yield 49%, IR (KBr); ν = 3040, 2940, 1710, 1625, 1470 cm^{-1} – ^{1}H-NMR (400 MHz, DMSOd_6/TMS); δ = 3.81 (s, 6H, MeO), 7.01 (d, J = 8.0 Hz, 1H, arH), 7.36 (m, 4H, arH), 7.58 (t, J = 7.6 Hz, 1H, arH), 7.74 (d,J = 7.6 Hz, 1H, arH), 8.19 (s, 1H, cumH). –^{13}C-NMR 100 MHz (DMSOd_6/TMS) δ = 56.8, 113.0, 113.7, 117.3, 121.2, 122.9, 126.1, 128.0, 130.0, 132.9, 140.9 , 150.1, 151.2, 154.5, 161.6. – MW $C_{18}H_{16}O_3$, for HRMS required: 282.0892, found: 282.09184, MS (*m/z*) 282(M^+), 265(M^+ – 17), 196(M^+ – 86), 137(M^+ – 145).

3-(2,3-dihydroxyphenyl)-1-benzopyran-2-one **(2b)**: 3-(2,3-dimethoxyphenyl)-1-benzopyran-2-one, **2a**, (1.41 g, 5 mmol) and pyridine hydrochloride, (2.30 g, 20 mmol) were heated at 150–160 °C for 5–6 h and cooled, mixed with water. The crude product filtered and dried was boiled with $CHCl_3$ in a Soxhlet extractor. **2b**, m.p. 189 °C, 0.88 g, yield 69%, IR (KBr) ν = 3050, 2940, 1740, 1625, 1520, 1490 cm^{-1} – ^{1}H-NMR 400 MHz(DMSOd_6/TMS) δ = 6.65 (d, J = 8.5 Hz, 1H, arH), 6.87 (d, J = 8.0 Hz, 1H, arH), 7.29 (m, 3H, arH), 7.52 (t, J = 7.6 Hz, 1H, arH), 7.71 (d, J = 7.6 Hz, 1H, arH), 8.05 (s, 1H, cumH). – ^{13}C-NMR (100 MHz, DMSOd_6/TMS) δ = 117.0, 117.2, 121.3, 121.5, 126.0, 127.3, 128.5, 129.9, 132.6, 140.0, 146.6, 148.0, 154.3, 161.6. – MW $C_{15}H_{10}O_4$, for HRMS required: 254.0579, found: 254.0497, MS (*m/z*) 254(M^+),152(M^+ – 102), 139(M^+ – 115), 126(M^+ – 128).

4-[3-(benzopyran-2-one)]benzo[12]crown-4 **(4a)**: **2b** (1.25 g, 5 mmol), **3a** (0.94 g, 5 mmol), Na_2CO_3 (1.06 g, 10 mmol) and DMF (40 mL Fluka) were heated at 90–95 °C during stirring for 50–55 h in a flask (100 mL) and acidified with HCl (50 mL 0.1 N). The crude product dried at 80 °C was dissolved in CH_2Cl_2 (20 mL) and chromatographed on alumina (basic) with CH_2Cl_2 (50 mL). **4a**, m.p. 86 °C, 0.51

g, yield 28%; IR (KBr) ν = 2940, 1730, 1630, 1370, 1170 cm^{-1} –^{1}H-MR (400 MHz, $CDCl_3$/TMS) δ = 3.81 (s, 4H, C_2H_4O), 3.88 (t, *J* = 6.5 Hz, 4H, $2CH_2O$), 4.25 (t, *J* = 6.5 Hz, 4H, $2CH_2O$), 6.99 (d, *J* = 8.5 Hz, H, arH), 7.24 (m, 1H, arH), 7.32 (m, 2H, arH), 7.40 (s, 1H, arH), 7.49 (m, 2H, arH), 7.74 (s, 1H, cumH). – ^{13}C-NMR(100 MHz, $CDCl_3$/TMS) δ = 70.7, 70.6, 71.8, 72.0, 72.3, 73.0, 117.4, 118.5, 120.1, 120.8, 124.3, 125, 6, 128.6, 128.9, 130.2, 132.4, 140.2, 151.5, 152.7, 154.6, 161.9. –MW $C_{21}H_{20}O_6$, for HRMS required: 368.1259 found: 368.1264, MS (*m/z*) 368(M^+), 280($M^+ - C_4H_8O$), 196(M^+ – 172), 149(M^+ – 219).

Bis(4,4′-[3-(benzopyran-2-one)])dibenzo[24]crown-8 **4b**): The mixture of **2b** (1.25 g, 5 mmol), **3a** (0.94 g, 5 mmol), Na_2CO_3 (1.06 g, 10 mmol) and DMF (40 mL Fluka) were studied as given at **4a** (Scheme 1). Further elutions with $CHCl_3$ (45 mL) gave another colorless product. **4b**, m.p. 77 °C, 0.25 g, yield 7%; IR (KBr) ν = 2940, 1730, 1630, 1270, 1180 cm^{-1} –^{1}H NMR (400 MHz, $CDCl_3$/TMS) δ = 3.81 (s, 8H, $2C_2H_4O$), 3.88 (t, *J* = 6.5 Hz, 8H, $4CH_2O$), 4.25 (t, *J* = 6.5 Hz, 8H, $4CH_2O$), 6.99 (d, *J*=8.5, 2H, arH), 7.24 (m, 2H, arH), 7.32 (m,4H, arH)7.40 (s, 2H, arH), 7.49 (m, 4H, arH), 7.74 (s, 2H,cumH). –^{13}C NMR (100 MHz, $CDCl_3$/TMS) δ = 70.4, 70.7, 71.7, 72.0, 72.2, 73.1, 117.4, 118.5, 120.1, 120.8, 124.3, 125, 6, 28.6, 28.9, 130.2, 132.4, 140.2, 151.5, 152.7, 154.6, 161.9. –MW $C_{42}H_{40}O_{12}$, for HRMS required: 736.2519, found: 736.2564, MS (*m/z*) 736(M^+), 280(M^+–280-4x44), 196(M^+–540).

4-[3-(benzopyran-2-one)]benzo[15]crown-5 **(5a)**: **2b** (1.25 g, 5 mmol), **3b** (1.15 g, 5 mmol), Na_2CO_3 (1.06 g, 10 mmol) and DMF (40 mL Fluka) were heated at 90–95 °C during stirring for 50–55 h and acidified with HCl (50 mL 0.1 N). The crude product dried at 80 °C was crystallized from methanol, **5a**, m.p. 144 °C, 0.80 g, yield 39%; IR (KBr) ν = 2939, 1725, 1645, 1260, 1045 cm^{-1} –^{1}H-NMR (400 MHz, $CDCl_3$/TMS) δ = 3.78 (s, 8H, $2C_2H_4O$), 3.95 (2m, *J* = 6.5 Hz, 4H, $2CH_2O$), 4.20 (t, *J* = 6.5 Hz, 2H, CH_2O), 4.24 (t, *J* = 6.5 Hz, 2H, CH_2O), 6.89 (d, *J* = 8.5 Hz,1H, arH), 7.32 (m,5H, arH), 7.54 (m, 2H, arH), 7.78 (s,1H,mH). -^{13}C-NMR (100 MHz, $CDCl_3$/TMS) δ = 68.8,69.1, 69.4, 70.3, 70.4, 70.4, 70.8, 70.9, 114.6, 115, 8, 117.4, 120.9, 122.9, 125.6, 128.9, 128.9, 128.9, 132.3, 139.9, 150.0, 151.2, 154.6, 162.0; MW $C_{23}H_{24}O_7$, for HRMS required: 412.1522, found: 412.1554 MS (*m/z*) 412(M^+), 280(M^+–3x44), 196(M^+–216).

4-[3-(benzopyran-2-one)]benzo[18]crown-6**(6a)**: **2b** (1.25 g, 5 mmol), **3c** (1.37 g, 5 mmol), Na_2CO_3 (1.06 g, 10 mmol) and DMF (40 mL) were heated at 90–95 °C during stirring for 50–55 h and acidified with HCl (50 mL, 0.1 N). The dried product was dissolved in CH_2Cl_2 (10 mL) then chromatographed on alumina (basic) with CH_2Cl_2 (4 × 25 mL). **6a**, m.p. 89 °C, 0.41 g, yield 18%; IR (KBr) ν = 2928, 1727, 1651, 1280, 1190 cm^{-1} – ^{1}H NMR (400 MHz, $CDCl_3$/TMS) δ = 3.75 (m, 4H, C_2H_4O), 3.79 (m, 4H, $2CH_2O$), 3.83 (m, 4H, $2CH_2O$), 4.01 (m,4H,$2CH_2O$), 4.29 (2t, *J* = 4.5 Hz, 4H, $2CH_2O$), 6.98 (d, *J* = 8.5 Hz, 1H, arH), 7.36 (m, 4H, arH), 7.58 (m, 2H, arH), 8.03 (s, 1H, CumH). –^{13}C-NMR (100 MHz, $CDCl_3$/TMS) δ = 68.6, 68.9, 69.3, 70.4, 70.5, 70.6, 70.7, 70.7, 70.8, 113.3, 114.4, 116.3, 120.0, 121.9, 124.7, 128.0, 128.4, 128.9, 131.2, 139.0, 148.7, 150.0, 153.5,

161.0. –MW $C_{25}H_{28}O_8$, for HRMS required: 456.1784, found: 456.1773 MS (*m/z*) 456(M^+), 280(M^+–4x44), 196(M^+–216).

2.2. FLUORESCENCE MEASUREMENTS

The fluorescence spectra of non-degassed samples were measured with a Perkin Elmer Luminescence spectrometer model LS-50 in dry acetonitrile in 10 mm quartz cells at room temperature. Salts and fluorophores dried under vacuum were used immediately. The free fluorophore [L_0] and cation-fluorophore concentrations [L_0] = [M_0] were prepared with a microsyringe which inserted the aliquot into the dry acetonitrile contained in a stirred fluorescence cell placed in the spectrometer compartment. The standard spectrometer software was used for the emission maxima measurements. The spectral bandwidth at the excitation maxima of 336 nm was arranged optimizing the concentrations to give no peak quenching. The peak intensities at 482 nm of the uncorrected emission spectra, I_i of free and complexed substances were taken as unity instead of Guassian peak areas. The mole fraction of the complexed macrocycle, P_{ML}, were found for equilibrium constants, log K_e ($\pm$0.20) estimations of a 1/1 ratio of cation, M, and ionophore, L, as given by Equations (1)–(3) [12, 13].

$$L + M \leftrightarrow ML, \tag{1}$$

if K_e = [ML]/{([M_0] – [ML])([C_0] - [ML])} is simply expressed,

$$K_e = C_{ML}/C_L\ C_M. \tag{2}$$

However, Equation (3) is used since [M_0] = [C_0], the initial cation, C_0, and macrocycle, C_M, concentrations are experimentally equivalent.

$$1/(C_0K_e) = (1 - P_{ML})^2/P_{ML}. \tag{3}$$

The fluorescence emission spectra of the cation-fluorophore macrocycle gave the intensities, $I_0 = \xi_L\varphi_L\ d\ C_0$ of free and $I = \xi_L\varphi_L\ d\ C_L + \xi_{ML}\varphi_{ML}\ d\ C_{ML}$ of complexed macrocycle and $I_{lim} = \xi_L\varphi_{ML}\ \varphi_{ML}\ d\ C_0$ for a fully complexed cation, where ξ_i are the molar extinction coefficients and φ_i are the quantum yields of the thermodynamically distinct species [7, 8]. The mole fraction of the 1/1 complex, $P_{ML} = C_{ML}/(C_{ML} + C_L) = C_{ML}/C_0$ is used for the estimation of the equilibrium constant, K_e using Equation (3).

Equations (4) and (5) should be obtained for explanations, namely, $I_0 - I = \xi_L\varphi_L\ d\ C_0 - \xi_L\varphi_L\ d\ C_L - \xi_{ML}\varphi_{ML}\ d\ C_{ML}$. This gives, $I_0 - I = \xi_L\varphi_L\ d\ (C_L + C_{ML}) - \xi_L\varphi_L\ d\ C_L - \xi_{ML}\varphi_{ML}\ d\ C_{ML}$, so that $I_0 - I/I_{lim} = d\ C_{ML}\varphi_L\ (\xi_L - \xi_{ML})/\xi_{ML}\varphi_{ML}\ d\ C_0 = \varphi_L(\xi_L - \xi_{ML})\ P_{ML}/\xi_{ML}\varphi_{ML}$. Therefore, the mole fraction of the cationic complex is described as, $P_{ML} = (I_0 - I)/I_{lim} \cdot \xi_{ML}\varphi_{ML}/(\xi_L - \xi_{ML})\varphi_L$. However, in the case of CEFS, Equation (4) is obtained, since $\xi_{ML}\varphi_L \gg \xi_L\varphi_L$.

$$P_{ML} = (I - I_0)/I_{lim}. \tag{4}$$

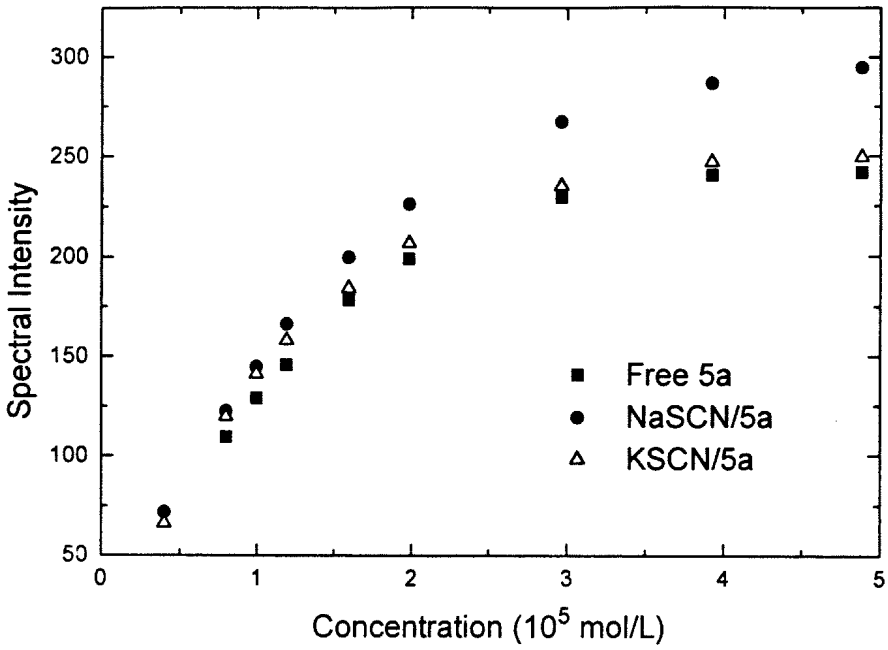


Figure 1. The spectral emission intensities of **5a**, **5a**/KSCN and **5a**/NaSCN at 482 nm (excitation $\lambda_{max} = 336$ nm) versus their concentrations.

In the case of CEQFS effect on complex formation, $\xi_L \varphi_L \gg \xi_{ML} \varphi_L$ is expected, then Equation (5) is obtained (see Figures 1, 2 and Tables I, II).

$$P_{ML} = (I_0 - I)/I_{lim}. \tag{5}$$

In both cases, Equations (4) or (5) would give P_{ML} to estimate K_e using Equation (3) (see Tables I, II). The dicotomus role of the fluorophores originating from the photophysical interactions could result in Equation (5) where the quantum yields are ruling out the equilibrium [8–13].

3. Results and Discussion

3.1. SYNTHESIS

We synthesized 3-(3,4-dimethoxyphenyl)coumarin, **2a** from **1a** and **1b** in a good yield. **2a** heated with py.HCl afforded **2b**. The cyclic condensations of **2b** with dihalide, **3a**, afforded **4a,** with **3b** afforded **5a**, and with **3c** afforded **6a** (Scheme 1). However, we have not tried to improve the yields of the compounds since they were well crystalline and pure substances for the spectral measurements after column chromatography and crystallization.

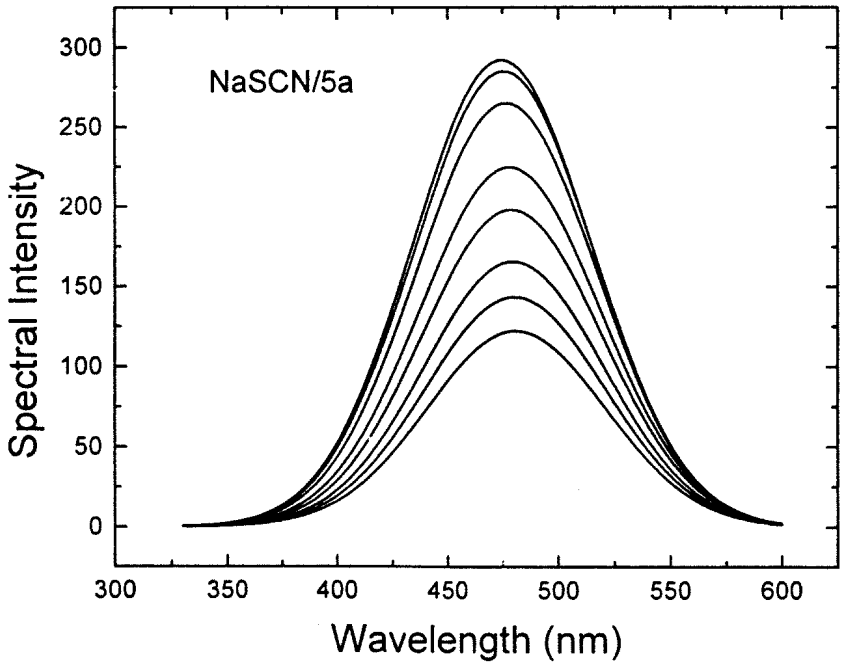


Figure 2. The fluorescence emission spectra of **5a**/NaSCN with increasing concentrations from the bottom line given in Table I, column 1.

Table I. The data for the 1 : 1 binding of the NaSCN/**5a** complex in acetonitrile at 25 °C

$L_0.10^{-6a}$	$1/L_0.10^{-3b}$	I_0^c	I^d	P^e	$(1-P)^2/P^f$	$(1-P)^2/P^g$
7.97	125.5	109.6	122.5	0.049	18.28	18.36
9.97	100.3	129.1	144.6	0.059	14.90	14.70
13.45	74.4	145.8	166.3	0.079	10.81	10.92
14.90	67.1	178.4	200.3	0.084	10.00	9.87
18.90	52.9	199.0	226.7	0.106	7.53	7.80
29.56	33.8	230.0	267.7	0.144	5.07	5.02
39.22	25.5	241.0	286.8	0.175	3.87	3.81
48.78	20.5	241.5	294.9	0.205	3.08	3.09

[a] Macrocycle concentrations (identical to salt concentrations).
[b] Inverse of concentrations.
[c] Intensity of free ligand.
[d] Intensity of complex mixture.
[e] Mole fraction of complexed ligand.
[f] Experimental mole fractions ratio.
[g] Least squares of mole fractions ratios.

Table II. Fluorescence maxima and 1 : 1 binding data of **4a**–**6a** at 298 K (ΔG in $kJmol^{-1}$)

Comp	$Ex\lambda_{max}$	$Em\lambda_{max}$	NaSCN		KSCN		$NaClO_4$		$Mg(ClO_4)_2$		$LiClO_4$	
	(nm)	(nm)	ln K	$-\Delta G$	ln K	$-\Delta G$	ln K	$-\Delta G$	ln K	$-\Delta G$	ln K	$-\Delta G$
4a	333	470	7.59	18.72	6.79	16.75	6.84	16.87	5.34	13.17	5.37	13.24
4b	337	482	12.27	30.26	8.57	21.13	–		–		–	
5a	336	480	8.84	21.80	6.78	16.73	(low)		(low)		(low)	
6a	337	482	8.41	20.74	9.10	22.45	–		–		–	

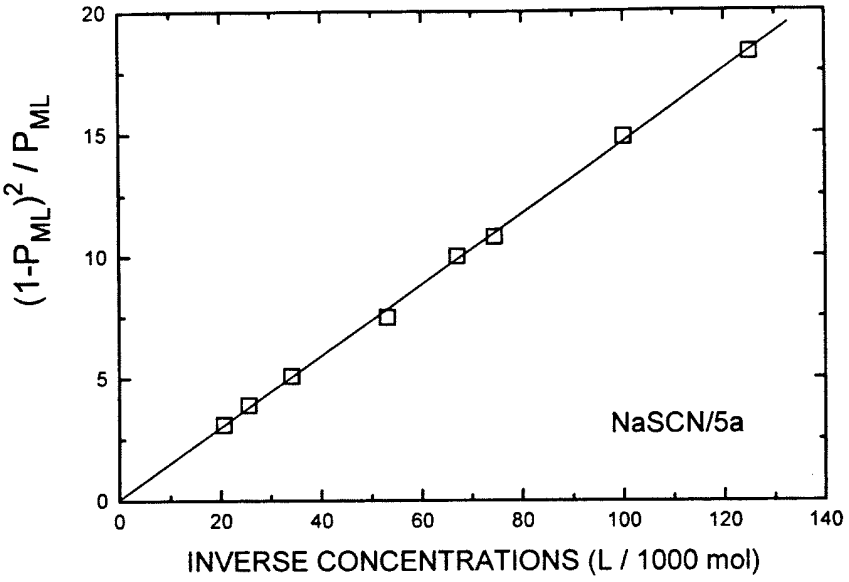


Figure 3. Dependence of mole fraction ratios, $(1\text{-}P)^2/P$ on the inverse cation/macrocycle concentrations of **5a**/NaSCN for 1/1 complexation constant.

3.2. FLUORESCENCE SPECTROSCOPY FOR ION BINDING

The fluorescence of the complexed ionophores, **4a**–**6a**, were observed almost without any isoemissive peaks with the dichotomous behavior depending on the macrocyclic ether, the cation as well as the counter ion in acetonitrile at room temperature. Complexation induced changes are involved at the triplet state relative to the ground, $T_1 \rightarrow S_0$ and excited states, $S_1 \rightarrow T_1$ of fluorogenic moieties in the presence of alkali cations [7–9]. The binding of **4a**,**4b**,**5a** and **6a** with Mg^{2+}, Li^+, Na^+ and K^+ were determined in acetonitrile observing peak intensities of steady state emission and excitation fluorescence spectra [11–13]. The 1 : 1 ratio of association constants were calculated from Equations (1)–(5) depended on the cationic radii and the size of the macrocycle host (see Tables I, II). The role of complete encapsulation of a guest in a host and the conformational ability of the host is quite clear since the best fitting macrocycle gave better binding (Table I) if the solvent has little interaction with the host. The small cations, showed almost no effect on the large macrocyclic hosts (Table II).

The results are interesting, namely, the binding order for SCN^- salts is $Na^+ > K^+$ for four, five and even six oxygen macrocycles with CEFS effects (Figures 1, 2 and Equation (5)) while perchlorate salts displayed rather common results with CEQFS, Equation (6), Table II [6]. However, the presented molecules exhibited interesting results showing the electronic communications among the benzo and benzopyranone rings since the coumarin crowns are almost 100 times more tightly bound compared to those of benzocrown ethers as reported in our earlier works [11,

12]. The solvent polarity of AN, in fact, stabilizes the polar structures, although, the solute-solvent interactions deactivate the nonradiative $T_1 \rightarrow S_0$ process. Note that **4a** exhibited good Na^+ selectivity among the cations. Compound **4b**, the largest host, displayed the best selectivity for Na^+, (Table II) [6, 7]. No such quantitative work was tried yet for the alkaline earth salts due to their limited solubility in acetonitrile. Similar studies on this topic have given good examples as reported by Cox et al. [16].

Acknowledgement

The support of TUBITAK for the TBAG-1681 project covering this work is gratefully acknowledged by the author.

References

1. Part VI: Ref [14].
2. J.-M. Lehn: *Supramolecular Chemistry, Concepts and Perpectives*, VCH, Weinheim (1995).
3. Y. Inoue and G.W. Gokel: *Cation Binding by Macrocycles*, Marcel Dekker, New York (1990).
4. F. Vögtle: *Supramolecular Chemistry*, John Wiley, Chichester (1991) references cited.
5. G.W. Buchanan: *Prog. in NMR Spectroscopy* **34**, 327 (1999).
6. L.R. Sousa and M. Larson: *J. Am. Chem. Soc.* **100**, 1943 (1978).
7. (a) S. Fery-Forgues, M.-T. Le Bris, J.-P. Guettě and B. Valeur, *J. Phys. Chem.* **97**, 6233 (1988); (b) J. Bourson, J. Pouget and B. Valeur,: *J. Phys. Chem.* **97**, 4552 (1993).
8. J.-P. Desvergne and A.W. Czarnik, eds.: *NATO ASI Series*, Series C, Kluwer Academic Press, Dordrecht, Vol. 492 (1997).
9. A.P. de Silva, H.Q.N. Gunaratne, T. Gunnlaugsson, A.J.M. Huxley, C.P. McCoy, J.T. Rademacher and T.E. Rice: *Chem. Rev.* **97**, 1515 (1993).
10. A. Göçmen, M. Bulut and Ç Erk: *Pure Appl. Chem.* **65**, 447 (1993).
11. (a) A.Göçmen and Ç Erk: *J. Incl. Phenom.* **26**, 67 (1996); (b) A. Göçmen and Ç Erk: in A.W. Coleman (ed.), *Molecular Recognition and Inclusion*, Kluwer Academic, Dordrecht, p. 337 (1998).
12. Ç Erk, A. Göçmen and M. Bulut: *J. Incl. Phenom.* **31**, 319 (1999).
13. Ç Erk, A. Göçmen and M. Bulut: *Supramol. Chem.* **11**, 49 (1999).
14. Ç Erk and E. Erbay: *J. Incl. Phenom.* **36**, 229 (2000).
15. M. Crawford and J.A M. Shaw: *J. Chem. Soc.* 3435 (1953).
16. B.G. Cox, T.V. Hurwood, L. Prodi, M. Monalti, F. Boletta and C. Ian F. Watt: *J. Chem. Soc., Perkin Trans. 2*, 289 (1999).