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The Synthesis of Novel Crown Ethers. Part IV. Coumarin Derivatives of [18]crown-6 and Cation Binding from Fluorescence Spectra

ÇAKIL ERK,* AYTEN GÖÇMEN** and MUSTAFA BULUT ***
Technical University of Istanbul, Department of Chemistry, Maslak, 80626, Istanbul, Turkey.

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Abstract. 4-H, 4-methyl and 4-phenyl-1-benzopyran-2-one derivatives of [18]crown-6 derivatives were synthesised from 6,7- and 7,8-dihydroxy-1-benzopyran-2-one reacting with pentaethylene glycol ditosylate in K_2CO_3/DMF/water. The products were identified by elemental analysis, EI-GC-mass spectra and ^{1}H-NMR spectroscopy. The Na^+ association constants of some coumarin derivatives were determined with an ion selective electrode in water. The Na^+ , K^+, Ba^{2+} and Sr^{2+} binding role of such compounds were particularly observed as remarkable alterations in acetonitrile. The 1 : 1 associations constants of K^+ and Na^+ with some coumarin-[18]crown-6 derivatives estimated by this way in acetonitrile exhibited the utility of complexing enhanced quenching fluorescence spectra for the ion binding power of the such macrocycles.

Key words: macrocyclic ethers, coumarins, cation binding, fluorescence spectroscopy.

1. Introduction

Since the discovery of crown ethers possessing oxygen dipoles on a macrocyclic structure many molecules have been synthesised and investigated for ion binding and transport of alkali or alkaline-earth cations through membranes by means of optical spectroscopy, potentiometry, [1, 2], as well as NMR spectroscopic methods [3]. Accordingly, macrocyclics bearing suitable light sensitive moieties may undergo intermolecular changes at the electronic level upon cation-dipole interactions of the oxygen donors. Therefore the alterations in the fluorescence spectra of fluorogenic macrocyclics in the presence of the ions would be a good measure of ion-dipole interactions [4–7]. Recently, such types of molecules have attracted interest for molecular recognition making ion sensitive chemosensors [8].

We recently synthesised some fluorogenic coumarin[12]crown-4 and [15]crown-5 derivatives and examined their alkali ion binding effects [9]. Our studies on the same bis-coumarin ended podands and anthraquinone derivatives of the macrocyclic ethers have displayed the role of cation on the fluorescence spectra of the macrocyclic ionophores [10].

* Author for correspondence.
** Present address, Balikesir University, Chemistry Department, Balikesir, 10100, Turkey.
*** Present address, Marmara University, Chemistry Department, Kadiköy, Istanbul, 81040, Turkey.

Following a preliminary communication we now report the detailed synthesis with full experimental results and spectral data as well as the molecular recognition using fluorescence spectroscopy and potentiometry of 4-substituted-([18]crown-6)-1-benzopyran-2-one derivatives [9].

In the present work, dihydroxycoumarins were primarily obtained from 1,2,3- or 1,2,4-trihydroxy benzenes condensing with some β-ketoesters or d,l-malic acid in the presence of H_2SO_4, $HClO_4$ or CF_3COOH [10]. The coumarin crowns were prepared from the cyclic condensation of dihydroxycoumarins with pentaethylene glycol ditosylate in the presence of DMF/water/alkali carbonates (see Scheme 1).

In order to characterise the coumarin crowns we primarily estimated the potentiometric Na^+ ion association constants of the water soluble compounds of **3a**, **3b**, **3d** and **3e** in water using our earlier reported methods [4, 11].

The fluorescence emission and excitation spectra of 4-substituted-([18]crown-6)-1-benzopyran-2-one derivatives were investigated in the presence of alkali and alkaline earth cations in dry acetonitrile and the cation binding effects were observed using fluorescence spectroscopy [9–11]. Assuming that the spectral alterations are due to strong host–guest interaction between the fluorophore and the cations, Na^+ and K^+ ion binding powers of compound **3d** were quantitatively estimated according to Equations (1, 2) [11]. However, the relative binding powers estimated using the fluorescence intensities of the free and complexed macrocyclic ionophores could be treated as the equilibrium constants, Table III. The results were interesting for the analytical procedures since the ionophores possessed quite reliable behaviour as the fluorescent probes against the alkali and alkaline earth cations in acetonitrile.

2. Experimental

2.1. POTENTIOMETRIC MEASUREMENTS

The determinations of 1 : 1 (n : m) ratio binding associations constants, K_a, were carried out using Equations (1, 2). The Na^+/macrocyclic stock solutions prepared with identical concentrations, $[L_0] = [Na_0^+]$ in deionised water were inserted using an electronically controlled pump into a thermostated cell with a certain amount of deionised water equipped with a pre calibrated sodium selective electrode (ORION, model 86-11 Ross electrode). The millivolt readings of the ion meter (SCHOTT, model-CG804) after each addition of the agents were transferred to a PC via an interface (SCHOTT, model-TL145). The measured mV values ($\pm$ 0.01 mV) versus log concentration of the free and complex solutions gave the mole fractions of the complexed cation, P' where $P = P'$ for the 1 : 1 ($n = m = 1$) complex, Equations (1, 2) [11]. However, the results displayed in Table II were larger than those reported earlier for unsubstituted benzocrowns [1,2].

$$K_a = [Na_m^+ L_n]/[Na^+]^m[L]^n \tag{1}$$

$$1/(K_a[L_0]) = (1 - mP')(1 - nP')/P'. \tag{2}$$

Table I. The quantitative data for the 1:1 association of KSCN complex of compound **3d** in acetonitrile 25 °C.[a]

L_0 [b]	L[c]	P[d]	$1/L_0 \cdot 10^{-3}$	$(1-P)^2/P$[e]	$(1-P)^2/P$[f]
13.20	12.46	0.056	757.57	15.87	15.86
19.80	18.20	0.081	505.81	10.43	10.58
26.30	23.60	0.103	380.23	7.84	7.98
32.80	28.95	0.117	304.68	6.64	6.60
39.20	34.10	0.130	255.10	5.82	5.36
45.60	38.71	0.151	219.29	4.77	4.62
51.94	42.73	0.177	192.33	3.82	4.06
58.00	46.65	0.196	172.41	3.31	3.64

[a] log K_a value is 4.68 ($\Delta G = -13.43$ kJ/mol) estimated from fluorescence data.
[b] Initial ligand concentrations $\times 10^7$ mol/l.
[c] Uncomplexed ligand concentration found $\times 10^7$ mol/l.
[d] Mole fraction of complexed ligand found as explained in the appendix.
[e] Experimental ion mole fractions ratio.
[f] Least squares ion mole fractions ratio.

2.2. FLUORESCENCE MEASUREMENTS

The fluorescence spectra were measured with a Perkin Elmer Luminescence spectrometer model LS-50 in dry acetonitrile within a fluorophore concentration of 10^{-6}–10^{-7} mol/l in 10 mm quartz cells. Alkali salts were also dried under vacuum and used immediately. The cation concentrations were 3–4 times larger than those of the ligand for the qualitative spectra as represented in Figures 2, 3. Quantitative K_a measurements were made with the various identical cation-ligand concentrations with a micro syringe which inserted the aliquot into the acetonitrile containing stirred fluorescence cell to run the spectra. The standard spectrometer software was used for the measurements and the electronic noise was removed prior to peak maxima being measured and plotted. The slit width was arranged according to concentrations which were optimised to give no quenching for the higher values. The peak intensities relative to isoemissive points were taken as unity instead of peak areas. The estimated mole fraction of the complexed macrocycle, P' (=P), is assumed to be governed by the relative quantum yields, proportional to the ratio of fluorescence intensities of distinct species, Equations (1, 2) (see appendix), Table I, Figures 4, 5.

2.3. ORGANIC SYNTHESIS

The experimental procedures on synthesis and IR, mass and NMR data with first order coupling constants of compounds **3a-3d** are given. However, the nomencla-

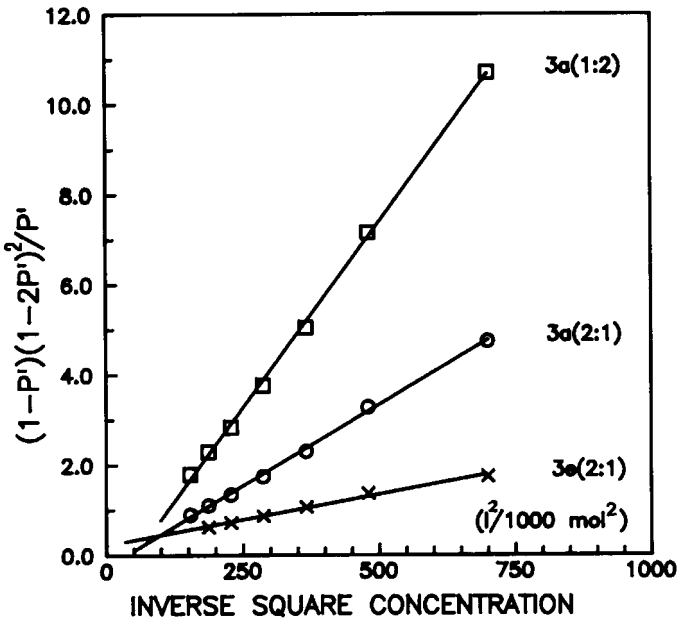
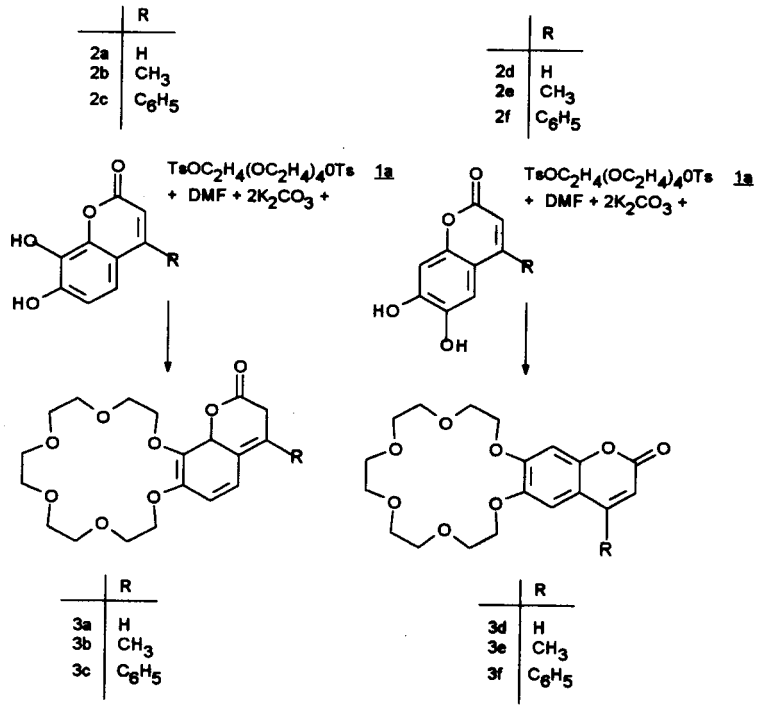


Figure 1. The dependence of the inverse square of the sodium concentration, $[1/L_0]^2$ vs $(1-P')(1-2P')^2/P'$ of complexed compounds of **3a** and **3e** for 1 : 2 and 2 : 1 (n : m) ratio of complexes in water.



Scheme 1.

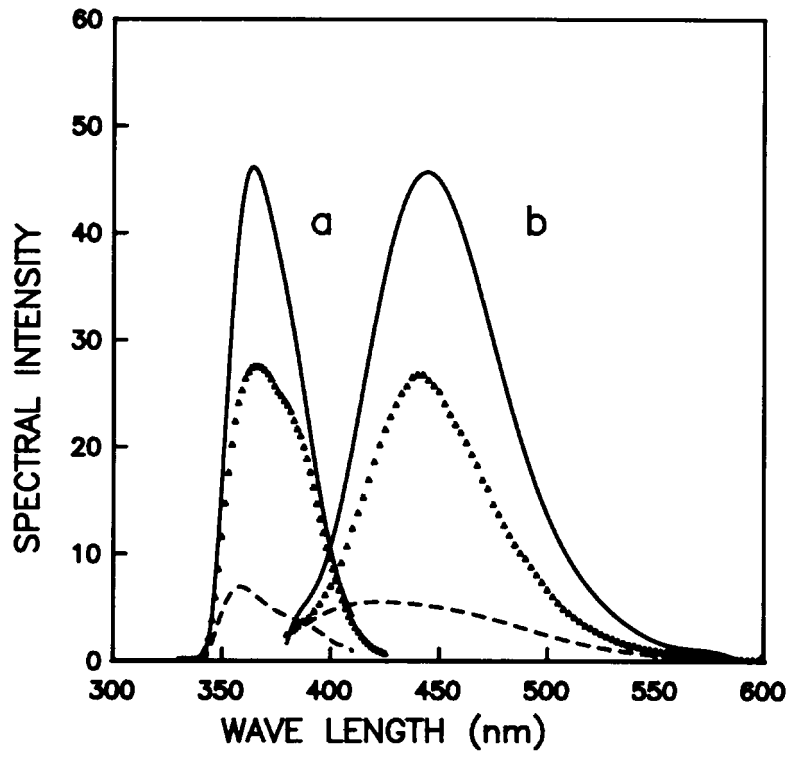


Figure 2. (a) The fluorescence excitation spectra of free **3b** (- - - -) and in the presence of Li^+ (▲▲▲▲) and Ba^{2+} (——) in acetonitrile, the emission λ_{max} = 460 nm. (b) The fluorescence emission spectra of free **3b** (- - - -) and in the presence of Li^+ (▲▲▲▲) and Ba^{2+} (——) in acetonitrile, the excitation λ_{max} = 379 nm.

ture given for coumarin[18]crown-6 derivatives is the assemblies of sub units and multiplicative connecting groups according to the IUPAC, Scheme 1.

The starting chemicals were from MERCK or FLUKA unless otherwise cited. The dihydroxycoumarins, **2a-c** and **3a-c**, were available from an earlier work [10]. IR spectra were recorded with KBr pellets on a JASCO FT-IR spectrometer, model 5300. Electron impact GC/MS mass spectra were obtained with a Carlo-Erba instrument, model Trio-1000 equipped with a capillary column, DB 50. The melting points are uncorrected. ^{1}H-NMR spectra were recorded on a BRUKER spectrometer Model AVANCE 400 in $CDCl_3$ and TMS was used as the internal standard. Analytical carbon-hydrogen measurements were carried out with a LECO CHN analyser, model 932.

7,8-(1,4,7,10,13,16-hexaoxaoctadecylene)-2-(H)-1-benzopyran-2-one (**3a**): A solution of **2a** (324 mg, 1.82 mmol), **1a** (1000 mg, 1.82 mmol) and K_2CO_3 (0.56 g,

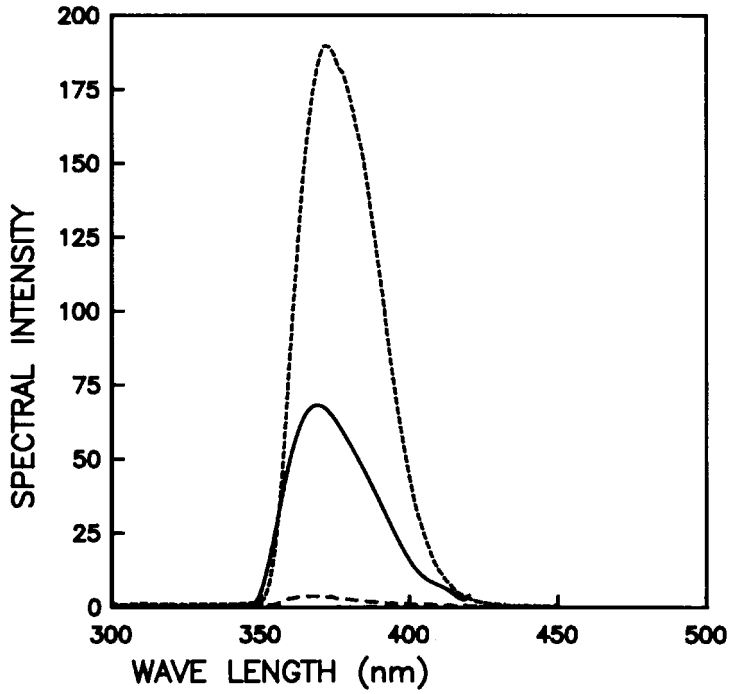


Figure 3. The fluorescence excitation spectra of free **3b** (- - - -) and in the presence of K^+ (——) and Pb^{2+} (. . . . .) in acetonitrile, the emission λ_{max} = 460 nm in acetonnitrile.

3.64 mmol) in DMF/water (60 ml, 75/25) was heated for 36 h while mixing at 85 °C. The raw product was extracted with $CHCl_3$. Chromatography on Al_2O_{31} CH_2Cl_2 yielded **3a** (325 mg, 47%), mp 90 °C, from heptane. ν_{max} (KBr)/cm^{-1} 2895 (CH_2), 1710 (C=O), 1605 (ArH), 1120 (C—O); δ_H ($CDCl_3$) 3.67 (12H, m, $3C_2H_4O$), 3.92 (2H, t, CH_2O, *j* 4.9), 4.04 (2H, t, CH_2O, *J* 5.0), 4.25 (2H, t, CH_2O, *J* 4.9), 4.32 (2H, t, CH_2O, *J* 5.0), 6.26 (1H, d, cum-H, *J* 9.5), 6.78 (1H, d, ArH, *J* 8.6), 6.86 (1H, d, ArH, *J* 8.6), 7.62 (1H, d, cum-H, *J* 9.5); m/z = 380(M^+), 204 (M^+-4 × C_2H_4O); $C_{19}H_{24}O_8$ MW = 380.39 requires, C, 59.99; H, 6.36 Found; C, 60.05, H, 6.32.

7,8-(1,4,7,10,13,16-hexaoxaoctadecylene)-4-methyl-2-(H)-1-benzopyran-2-one (**3b**): **3b** was obtained from **2b** (349 mg, 1.82 mmol) and **1a** (1000 mg, 1.82 mmol) at 90 °C and purified as explained above. Colourless large crystals (410 mg, 57%) mp 86 °C from THF. ν_{max} (KBr)/cm^{-1} 2890 (CH_2), 1705 (C=O), 1376 (ArH), 1100 (C—O); δ_H ($CDCl_3$) 2.64 (3H, s, Me), 3.88 (4H, s, C_2H_4O), 4.00 (4H, m, C_2H_4O), 4.02 (4H, m, C_2H_4O), 4.17 (2H, t, CH_2O, *J* 5.0), 4.46 (2H, t, CH_2O, *J* 4.9), 4.51 (2H, t, CH_2O, *J* 4.9), 4.57 (2H, t, CH_2O, *J* 5.0), 6.39 (1H, cum-H), 7.12

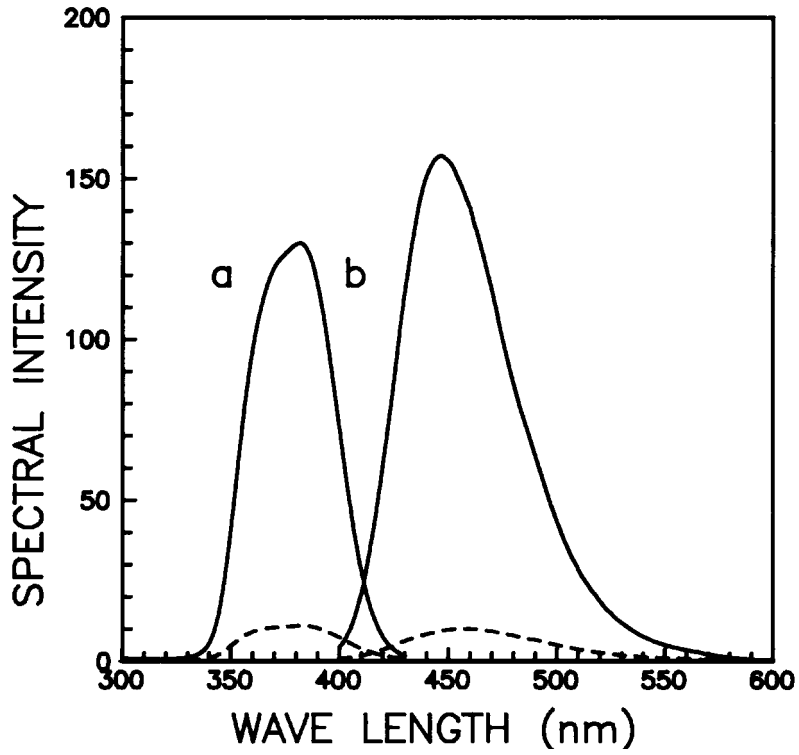


Figure 4. (a) The fluorescence excitation spectra of free **3b** (- - - -) and in the presence of Sr^{2+} (——), the emission λ_{max} = 460 nm in acetonitrile. (b) The fluorescence emission spectra of free **3b** (- - - -) and in the presence of Sr^{2+} (——) in acetonitrile, the excitation λ_{max} = 379 nm.

(1H, d, ArH, *J* 8.9), 7.52 (1H, d, ArH, *J* 8.9); m/z = 394 (M^+), 218 (M^+-4 × 44); $C_{20}H_{26}O_8$ MW = 394.41 requires, C, 60.95; H, 6.65 Found; C, 60.77, H, 6.58.

7,8-(1,4,7,10,13,16-hexaoxaoctadecylene)-4-phenyl-2-(H)-1-benzopyran-2-one (**3c**): The mixture of **2c** (460 mg, 1.82 mmol) and **1a** (1000 mg, 1.82 mmol) reacted as explained above yielded **3c** (126 mg, 16%) dec 180 °C; ν_{max} (KBr)/cm^{-1} 2890 (CH_2), 1720 (C=O), 1400 (ArH), 1110 (C—O); δ_H ($CDCl_3$); 3.71 (12H, m, $3C_2H_4O$), 3.93 (4H, m, OC_2H_4O), 4.15 (2H, t, CH_2O, *J* 4.9), 4.26 (2H, t, CH_2O, *J* 4.9), 6.20 (1H, s, cum-H), 6.44 (2H, d, ArH, *J* 8.5), 6.85 (2H, d, ArH, *J* 8.5), 7.27 (5H, m, Ph); m/z 456 (M^+) 280 (M-4 × 44); $C_{25}H_{28}O_8$ MW = 456.49 requires, C, 65.79; H, 6.18 Found; C, 65.59, H, 6.06.

6,7-(1,4,7,10,13,16-hexaoxaoctadecylene)-2-(H)-1-benzopyran-2-one (**3d**): The mixture of **2d** (162 mg, 0.91 mmol) **1a** (500 mg, 0.91 mmol) and K_2CO_3 (280 mg,

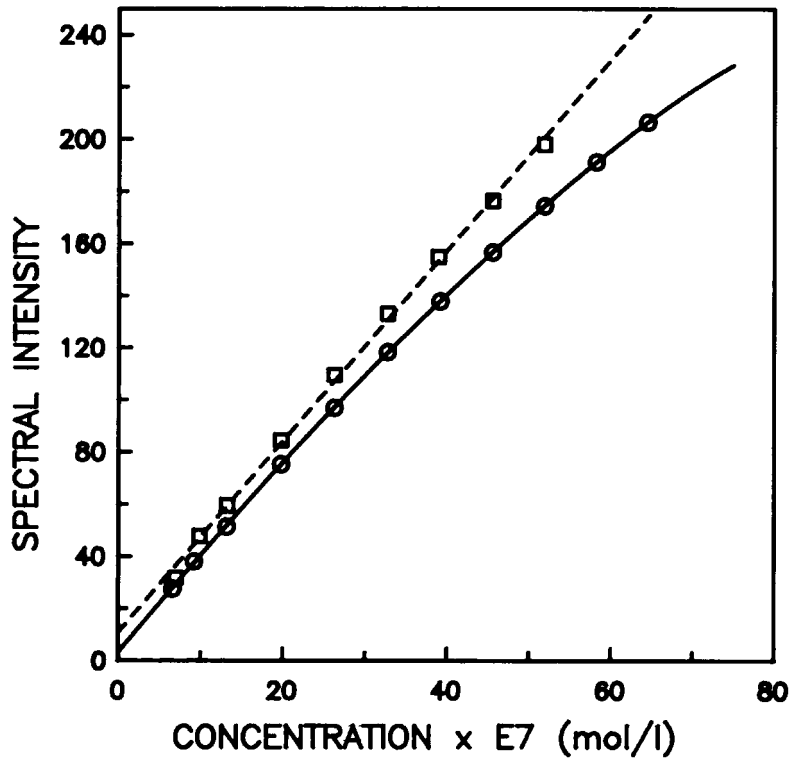


Figure 5. The plot of the fluorescence intensities of free **3d** (-□-□-□-) and **3d**/KSCN (-○-○-○-) vs the concentrations in acetonitrile at room temperature.

1.82 mmol) in DMF/water (50 ml, 90/10) were heated for 48 h while mixing at 90 °C. The acidified mixture was extracted with $CHCl_3$ and chromatography on Al_3O_3 with CH_2Cl_2 yielded **3d** (90 mg, 26%) mp 86 °C from hot water. ν_{max} (KBr)/cm^{-1} 2910 (CH_2), 1710 (C=O), 1550 (ArH), 1090 (C—O); δ_H ($CDCl_3$); 3.62 (4H, s, OC_2H_4O), 3.70 (8H, m, $O(C_2H_4O)_2$), 3.92 (2H, t, CH_2O, *J* 4.6), 3.94 (2H, t, CH_2O, *J* 5.0), 4.18 (2H, t, CH_2O, *J* 5.0), 4.20 (2H, t, CH_2O, *J* 4.6), 6.39 (1H; d, cum-H, *J* 9.5), 6.73 (1H, d, ArH, *J* 8.6), 6.93 (1H, d, ArH, *J* 8.6), 7.53 (1H, d, cum-H, *J* 9.5); m/z 380 (M^+), 204 (M^+-4 × C_2H_4O); $C_{19}H_{24}O_8$ MW = 380.39 requires, C, 59.99; H, 6.36 Found; C, 60.90, H, 6.40.

6,7-(1,4,7,10,13,16-hexaoxaoctadecylene)-4-methyl-2-(H)-1-benzopyran-2-one (**3e**): **3e** was obtained from **2e** (174 mg, 91 mmol), **1a** (500 mg, 91 mmol) and K_2CO_3 (280 mg, 1.82 mmol) in DMF/water (50 ml, 90/10) as explained above. (80 mg, 22%) mp 62 °C. ν_{max} (KBr)/cm^{-1} 2910 (CH_2), 1700 (C=O), 1550 (ArH), 1090 (C—O), δ_H ($CDCl_3$) 2.48 (3H, s, Me), 3.68 (4H, m, C_2H_4O), 3.76 (4H, m,

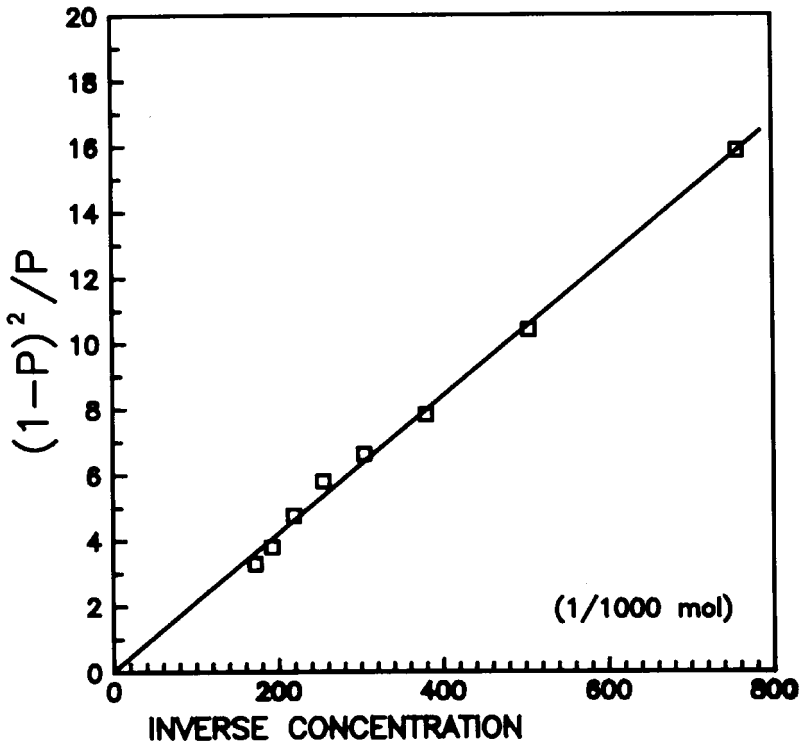


Figure 6. The dependence of the inverse of Ligand (=cation) concentration, $[1/L_0]$ vs $(1-P')^2/P'$ of complexed compound **3d** for 1 : 1 ratio of K^+ cation binding constant. The results displayed in Figure 5 are used.

C_2H_4O), 3.97 (4H, m, C_2H_4O), 4.18 (4H, m, C_2H_4O), 4.27 (4H, m, CH_2O), 6.16 (1H, s, cum-H), 6.93 (1H, s, H), 6.75 (1H, s, ArH), 6.93 (1H, s, ArH); m/z = 394 (M^+), 218 (M^+-4 × 44); $C_{20}H_{26}O_8$ MW = 394.41 requires, C, 60.95; H, 6.65 Found; C, 61.09, H, 6.79.

6,7-(1,4,7,10,13,16-hexaoxaoctadecylene)-4-pheyl-2-(H)-1-benzopyran-2-one (**3f**): The general procedure given above afforded **3f** starting from **2f** (230 mg, 0.91 mmol) and **1a** (500 mg, 0.91 mmol). Yield, 83 mg, 18% mp 118 °C, ν_{max} (KBr)/cm^{-1} 2895 (CH_2), 1720 (C=O), 1390 (ArH), 1110 (C—O), δ_H ($CDCl_3$) 3.67 (4H, s, C_2H_4O), 3.72 (8H, m, $2C_2H_4O$), 3.86 (2H, t, CH_2O, J 4.7), 3.99 (4H, m, C_2H_4O), 4.22 (2H, t, CH_2O, J 4.7), 6.22 (1H, s, cum-H), 6.82 (1H, s, ArH), 6.84 (1H, s, ArH), 7.46 (2H, m, Ph), 7.50 (3H, m, Ph); m/z = 456 (M^+) 280 (M^+-4 × 44); $C_{25}H_{28}O_8$ MW = 456.49 requires, C, 65.79; H, 6.18 Found; C, 65.69, H, 6.00.

Table II. Na^+ association constants of coumarin crowns in water with different stoichiometries.

Comp	$\log K_{11}$	$-\Delta G_{11}$	$\log K_{12}$	$-\Delta G_{12}$	$\log K_{21}$	$-\Delta G_{21}$
3a	2.07	5938	4.66	13368	4.99	14315
3b	2.10	6024	5.00	14343	5.34	15319
3d	1.83	5250	4.67	13393	5.00	14344
3e	1.92	5508	4.77	13684	5.11	14659

[a] For 1 : 1 (n : m) ratio of complexing in J/mol at 278 K.
[b] For 1 : 2 (n : m) complexing in J/mol at 278 K.
[c] For 2 : 1 (n : m) complexing in J/mol at 278 K.

3. Results and Discussion

3.1. Synthesis of coumarin [18]crown-6 derivatives

The synthesis of coumarin [18]crown-6 derivatives were conducted as outlined in Scheme 1. The reaction of **1a** with **2a**, **2b** and **2c** afforded **3a**, **3b**, and **3c** within the yield of 15–55%. The reaction of **1a** with **2d**, **2e** and **2f** afforded **3d**, **3e** and **3f** in 18–25% yields.

3.2. Potentiometric Na^+ association constants in water

The water soluble products **3a,b** and **3d,e** obtained were purified once more to determine their association constants with potentiometry using a Na^+ selective glass electrode in water. The samples with appropriate NaCl concentrations, $[A_0^+]$ were used for the electrode calibrations. However, the concentration of the initial macrocylic ether complexed solution with the equivalent amount of salt, $[A_0^+]$ = $[L_0]$ was varied to change the mole fraction of the complex, P versus cation concentration and the mV values observed were recorded via the PC, Equations (1, 2).

The Na^+ ion association constants were estimated in water for different complexing ratios, (n : m) using Equations (1, 2), Table II, [11]. However, Na^+ complexes of such compounds were found to be more stable then their benzocrown analogues in water [1, 2]. The experimental and calculated data are displayed in Table II and thermodynamic K_a values were obtained form the linear regression of the data.

3.3. Fluorescence spectroscopy for cation binding

Interesting results were obtained from the fluorescence spectra of coumarin crowns in the presence of alkali and alkaline earth cations in dry CH_3CN confirming that the cationic ion-dipole interactions of coumarin[18]crown-6 caused polarisations at the electronic level which alter the fluorescence quantum yields significantly upon

Table III. The fluorescence emission spectral data for the cationic complexes of compound **3b** in acetonitrile.

Salts	Conc (mol/l)	λ^{em}_{max} (nm)	λ^{ex}_{max} (nm)	l_f	l_c/l_f
Free ligand	3.3×10^{-7}	460	379	3.3	1.00
$LiClO_4$	10.0×10^{-7}	460	379	27.6	8.36
KSCN	12.0×10^{-7}	460	379	64.5	19.54
$Ba(NO_3)_2$	$\approx 10.0 \times 10^{-7}$	460	379	45.9	13.91
$Sr(NO_3)_2$	$\approx 10.0 \times 10^{-7}$	460	379	128.9	39.06
$Pb(CH_3COO)_2$	$\approx 10.0 \times 10^{-7}$	460	379	188.1	57.00

complex formation. Complexing of such compounds, therefore, showed remarkable changes in the spectral intensities of emission and excitation maxima depending on the cationic radii and the size of the macrocycle [6, 8]. The results also proved that the origin of cationic ion dipole interactions of the macrocycles is the distance between the ions and dipoles.

Therefore the power of cationic interactions were observed from the relationship between the quantum yields of free and complexed fluorophore, φ_f and φ_c respectively (see appendix). The binding effect of compound **3b** observed via complexation enhanced fluorescence spectroscopy is in the order of $Pb^{2+} \approx Sr^{2+} > Ba^{2+} > K^+ > Li^+ \gg Ca^{2+} \approx Na^+$ which is partly displayed in Figures 2–4, (see Table III and appendix).

The fluorescence of such complexing ionophore probes, influenced with cations observed without any isoemissive spectral peaks has been first reported by Sousa, [5] with naphthalene crowns in the presence of cations with the dicotomus behaviour depending on the macrocycle structure. However, much attention has been paid to this topic since then for molecular recognition and building chemosensors for analytical purposes although the different physical interaction mechanisms involved depend on the donor nature of the sensor [6–8].

In the present work, we have observed both the complexation enhanced fluorescence spectra (CEFS) and the complexation enhanced quenching fluorescence spectra (CEQFS) for coumarin-crown ethers. CEFS is observed if the fluorescence rate is increased while CEFQS is observed when the fluorescence rate is reduced in the presence of a cation. We noticed the dicotomus role of the coumarin crowns of oxygen donors which exhibited CEFS from 7,8-macrocyclic ring substituted coumarins such as **3a-c** while the 6,7-substituded macrocylic derivatives such as **3d-f** exhibited CEQFS upon cationic interactions. Both cases could be evaluated for the molecular and cationic recognition, Figures 2–4 and Tables I and IV.

There are various methods for the determination of cationic interactions using optical spectroscopy. The intensities at the peak maxima of free and complexed fluorophore being proportional to fluorescence quantum yields is a good measure for quantitative treatments, (see appendix). We, therefore, determined the role of compounds **3a**, **3d** and **3e** on Na^+ and K^+ in acetonitrile from the peak intensities

Table IV. The thermodynamic 1 : 1 interaction data of some coumarin[18]crown-6 with Na^+ and K^+.

Compound	Na^+		K^+	
	log K	$-\Delta G_{11}$	log K	$-\Delta G_{11}$
3a	4.19	12.02	4.86	13.93
3b	4.90	14.07	4.68	13.42
3e	4.77	13.69	4.62	13.25

using the similar formalism of Equations (1, 2) so that we calculated the least squares 1 : 1 ratio of association constants, Table IV. Rather rigid benzo[18]crown-6 like macrocycles did not exhibit good selectivity between the Na^+ and K^+ cations but compound **3d** displayed good results, Table III, for heavy cations for which we are still looking for more suitable solvent and counter ion systems. No such work was tried for the alkaline earth cations due to poor solubility in acetonitrile [4, 11]. This solvent is also capable of strong inclusion complexes particularly with [18]crown-6 derivatives [2].

Appendix

The following is considered for the notation of fluorescence parameters. The fluorescence intensity of the free ionophore is $I_f = I_0 > \xi_f \varphi_f b[L_0]$ with the concentration of $[L_0]$ where ξ_f and φ_f are the extinction coefficient and quantum yield of the free fluorophore respectively. The fluorescence intensity of the cation complexed fluorophore is $I_C = I_0 \xi_f \varphi_f b[L] + I_0 \xi_C \varphi_C b[A^+L]$ where ξ_C and φ_C are the extinction coefficient and quantum yield of the complexed $[A^+L]$ fluorophore respectively. [L] is the uncomplexed fluorophore in the equilibrium. Thus the relative intensities of the free and complexed fluorophore ligand, $(I_f - I_C)/I_f = P[1 - (\xi_C \varphi_0 / \xi_f \varphi_f)]$ could give the mole fraction of the complexed fluorophore ligand. However, mostly $(\xi_C \varphi_0 / \xi_f) < 1$ if the $\varphi_C \xi_f \ll \varphi_f \xi_f$ particularly for CEQFS of complex formation. Therefore, $P = (I_f - I_C)/I_f$ observed is used for the mole fraction ratios of the 1 : 1 ratio complex, Tables I, IV.

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