Supramolecular Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713649759

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To cite this Article Erk, Çakil , Göçmen, Ayten and Bulut, Mustafa(1999) 'The Synthesis of Novel Macrocycles, Part V. The Coumarin Crown Ethers and Cation Binding with Fluorescence Spectra', Supramolecular Chemistry, 11: 1, 49 — 56
To link to this Article: DOI: 10.1080/10610279908048715
URL: http://dx.doi.org/10.1080/10610279908048715

SUPRAMOLECULAR CHEMISTRY, Vol. 11, pp. 49–56
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The Synthesis of Novel Macrocycles, Part V. The Coumarin Crown Ethers and Cation Binding with Fluorescence Spectra

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(Received 9 October 1998; In final form 15 March 1999)

The 4-H, 4-methyl and 4-phenyl derivatives of benzo-α-pyrone of 12-crown-4 and 15-crown-5 were synthesised starting from 4-substituted-6,7-dihydroxy- and 7,8-dihydroxybenzo-α-pyrones which reacted with dichloropolyethylene glycols in DMF/water/alkali carbonate. The coumarin-macrocycles were identified by elemental analysis, IR, EI-GC-MS as well as ^{1}H, ^{13}C NMR spectroscopy. The full experimental and spectral data is reported along with ion binding data studied in acetonitrile using fluorescence spectroscopy. The binding of the fluorogenic coumarin-crowns with Li^+, Na^+ and K^+ were recognized as specific alterations on their fluorescence spectra that strongly originated from the structures. The observed CEQFS depending on the bound cation radii and macrocycle size evidenced the rules of cationic recognition of macrocycles. Some 15-crown-5 derivatives exhibited interesting Li^+ and Na^+ binding selectivities.

Keywords: Macrocycles, coumarins, ion binding, fluorescence

INTRODUCTION

Various macrocyclic oxyethylene oligomers have been prepared since their discovery [1]. They often provide selective ion binding and recognition. The fluoroionophoric macrocycles and the role of chromo- and fluorogenic moieties upon binding have been reported [2–7].

We have reported studies of the synthesis and binding effects of crown ethers bearing fluorogenic coumarin groups fluorescence spectroscopy as well as using analytical methods [8,9]. The fluorescence of the coumarins under UV light has been utilised for the investigation of cation-macrocycle interactions.

The presented work deals primarily with the preparation of some 12-crown-4 and 15-crown-5 containing benzo-α-pyrone moieties, as well as the dihydroxy benzo-α-pyrone derivatives to observe their cation complexation properties. The coumarins were synthesised by different methods by treating trihydroxybenzenes with β-ketoesters or d,l-malic acid in the presence of a strong acid [10,11]. They were then converted to their crown ether derivatives by condensation with the dichloride derivatives of triethylene and

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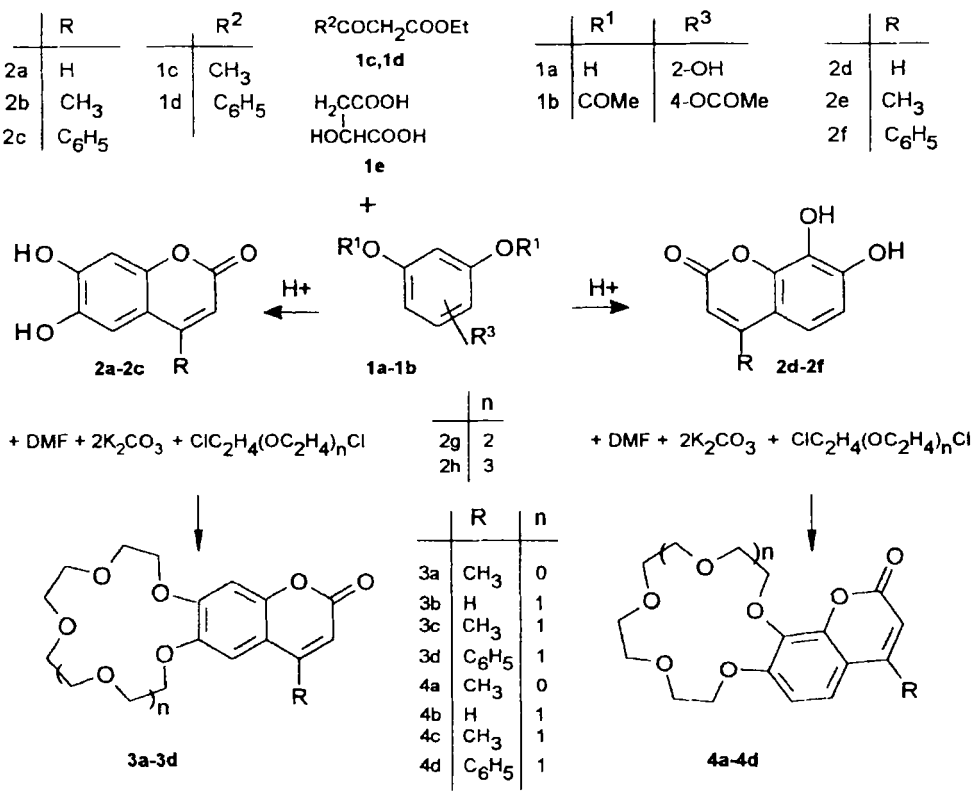
tetraethylene glycols in the presence of a base as shown in Scheme 1. The ion binding of coumarin derivatives of 18-crown-6 has been found to be quite interesting as we reported [12]. Binding was found to be cation size dependent and the compounds were very sensitive as optical sensors in solutions. We now report the binding and selectivity effects of the smaller size macrocycles.

Ionic interactions of oxygen bearing fluorophores are not great due to limited energy exchange [3,4]. However, fluorescence spectra of coumarin-crowns in the presence of alkali or alkaline earth metal salts in CH_3CN gave either a reduced or intensified fluorescence peak maximum at the same wavelength at room temperature [9,12]. Results showed that the binding of such molecules depends on the structure, size of the crown ether, and the size of cation radii as are common for a macrocyclic effect.

EXPERIMENTAL

The starting chemicals were from Merck or Fluka unless otherwise cited. IR spectra were taken as KBr pellets with a JASCO FT-IR spectrometer, model-5300. High resolution EI Mass spectra were obtained with FISONS instrument, model VG-ZABSPEC. ^1H, ^{13}C and 2D NMR spectra were taken with a BRUKER spectrometer, model AVANCE-400CPX in $CDCl_3$ or DMSO-d_6 and TMS was used as an internal standard. However, ^1H spectra of hydroxyl signals were not reported. The 100 MHz ^{13}C NMR data of the compounds **3a–3c** and **4a–4c** were separately displayed at Table III where signals were assigned to the structures using 2D HETCORR, COSY and coupled ^{13}C spectra. Combustion analyses were done with LECO-932 CHN analyser.



SCHEME 1

Fluorescence spectra of free and cation-containing coumarin-crown solutions were measured in 1.0 cm silica cells in dry acetonitrile (< 0.02 H_2O% content) as indicated in Tables I and II. The fluorescence excitation and emission spectra were recorded with a Perkin Elmer Luminescence spectrometer model LS-50 at room temperature. The data acquisition of titrations were done using standard software on a PC. The data were smoothed and then plotted for the estimation of peak maxima, see Figures 2-4.

7,8-Dihydroxy-4-methyl- and 6,7-dihydroxy-4-methylbenzo-α-pyrones were obtained by treating the relevant trihydroxybenzenes with ethyl acetoacetate in H_2SO_4 [9]. The 4-H-coumarin derivatives were obtained by condensation of d,l-malic acid with trihydroxybenzenes in a similar way. Dihydroxy-4-phenyl coumarins were prepared in CF_3COOH by treating ethyl benzoylacetate with trihydroxybenzenes.

The product, **2a** was obtained from **1e** and **1b** in the presence of H_2SO_4. **2b** was obtained from **1e** and **1b** in H_2SO_4. **2c** was obtained from **1d** and **1b** in CF_3COOH. The **2d** was obtained from **1e** and **1a** in H_2SO_4. The **2e** was obtained from **1c** and **1a** in H_2SO_4. **2f** was obtained form **1d** and **1a** in CF_3COOH. Coumarin-crown ethers were obtained by condensation of the 1,11-dichloro-3,6,9-trioxaundecane or 1,8-dichloro-3,6-dioxaoctane with dihydroxycoumarins in Na_2CO_3/DMF/water.

Namely, the reaction of **2g** with **2b** and **2e** afforded **3a** and **4a**. The reaction of **2h** with **2a** and **2d** afforded **3b** and **4b**. The reaction of **2h** with **2b** and **2e** afforded **3c** and **4c**. The reaction of **2h** with **2c** and **2f** afforded **3d** and **4d** in the presence of Na_2CO_3 in DMF/water at 90-95°C, Scheme 1.

6,7-Dihydroxy-2(H)-1-benzopyran-2-one (2a)

1,2,4-triacetoxybenzene (25.2 g, 100 mmol), d,l-malic acid (13.4 g, 100 mmol) and H_2SO_4 (25 ml) were heated at 120°C for 2 h, The product was boiled in ethanol with 15 g of charcoal to give 14.00 g of **2a** 80%); m.p. 255°C; IR = 3400, 1672, 1611, 1560, 1400, 1277, 1194, 938 cm^{-1}; ^1H NMR $CDCl_3$/TMS) 200 MHz $\delta = 6.24$ (d, 1H, cum-H), 6.76(s, 1H, ArH), 6.86 (s, 1H, ArH), 7.55 (d, 1H, cum-H).

6,7-Dihydroxy-4-methyl-2(H)-1-benzopyran-2-one (2b)

A mixture of 1,2,4-triacetoxybenzene (50.4 g, 200 mmol) and ethyl acetoacetate (52 g, 400 mmol)

TABLE I Fluorescence data of free and cationic macrocycles in AN

Comp.	Ex.λ_{max}	Em.λ_{max}	I^{0a}	I^{max} (Li^+)^b	I^{max} (Na^+)^b	I^{max} (K^+)^b	I^{max} (Zn^{2+})^b
3a	340	411	34.7	28.9	21.0	20.5	32.1
3c	340	411	70.4	68.5	16.4	20.4	28.0
3d	362	460	15.9	5.9	3.0	2.9	5.8
4c	310	420	4.5	4.0	4.0	4.3	–

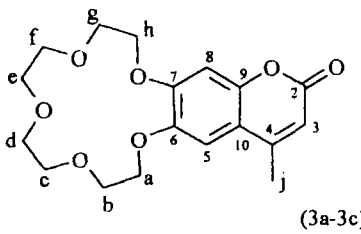
[a] Maximum intensity of macrocycles, I^0, with the maximum non-quenched concentrations, $1.5 \cdot 10^{-4}$ mol/l.
[b] The maximum intensity of ligand/cation complex, I^{max}, with the salts, $3.4-6.3 \cdot 10^{-2}$ mol/1, see Figures 1-4.

TABLE II The 1:1 binding constants of macrocycles in AN at 300 K

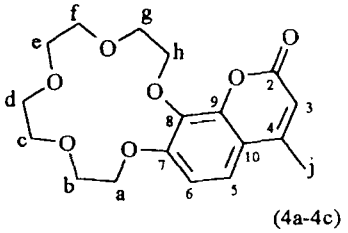
Comp.[a]	$\ln K_b$	$-\Delta G$ (Li^+)^b	$\ln K_b$	$-\Delta G$ (Na^+)^b	$\ln K_b$	$-\Delta G$ (K^+)^b	$\ln K_b$	$-\Delta G$ (Mg^{2+})^b
3a	7.77	19.29	6.55	16.26	5.11	12.03	8.72	21.65
3c	6.40	15.07	7.46	18.51	6.94	17.23	–	
3d	8.92	22.01	7.76	19.27	6.97	17.30	–	

[a] Macrocycles showing CEQFS.
[b] Free enthalpy, kJ/mol.

TABLE III ^{13}C NMR data of coumarin-crown ethers in $CDCl_3$



(3a-3c)



(4a-4c)

^{13}C	Comp. 3a	Comp. 3b	Comp. 3c	Comp. 4a	Comp. 4b	Comp. 4c
2	163.75	162.60	162.78	161.55	161.95	162.62
3	116.41	112.08	113.27	113.16	114.30	114.30
4	153.39	144.57	153.70	153.59	144.96	154.58
5	109.81	114.49	109.78	110.84	110.47	110.96
6	149.15	147.26	147.17	120.26	123.93	121.39
7	149.68	151.25	151.00	137.52	136.78	137.62
8	103.16	102.20	102.18	156.12	156.60	157.00
9	154.73	156.49	154.34	149.00	149.61	150.00
10	115.62	112.68	113.79	115.83	114.84	116.81
a	70.81	69.39	69.42	75.62	74.39	75.56
b	70.25	69.70	69.72	71.27	71.13	72.32
c	72.55	70.26	71.27	72.32	71.70	72.96
d	–	71.45	71.83	–	71.70	72.87
e	–	72.09	72.16	–	71.16	72.37
f	71.58	71.45	71.68	70.85	71.01	72.22
g	70.86	70.68	70.26	70.25	70.00	71.22
h	75.04	70.96	70.90	70.01	69.67	70.83
j	19.80	–	19.29	19.26	–	20.89

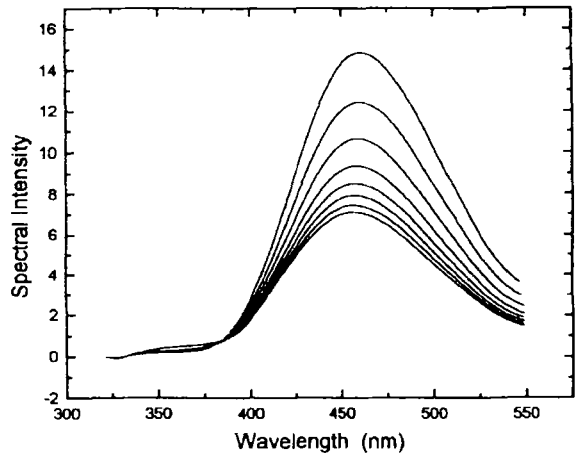


FIGURE 1 The emission CEQF spectra of **3d** ($3.3 \cdot 10^{-4}$ mol/l, top line) depending on $LiClO_4$ concentrations, (0.66, 1.33, 1.82, 2.64, 3.33, $4.66 \cdot 10^{-4}$ mol/l, reducing intensities) in AN.

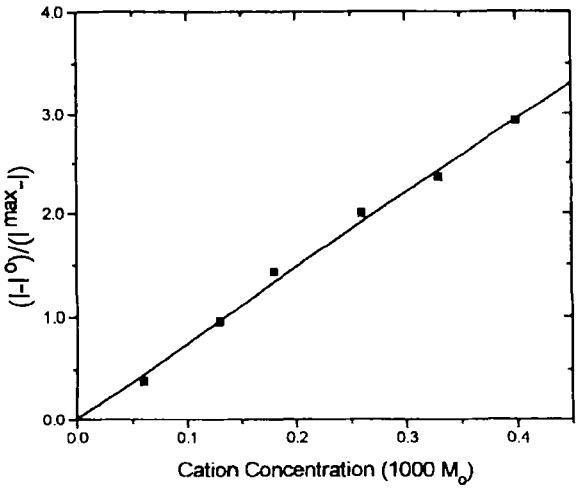


FIGURE 2 The dependence of $(I-I^0)/(I^{max}-I)$ of **3d** to $LiClO_4$ concentration in AN at room temperature.

and triethylamine (1 ml) were refluxed at 100°C for 1 h. H_2SO_4 (70 ml) was added and the mixture was heated for 3 h at 100°C to gave yellowish needles (acetone); 25 g (65%) of **2b**; m.p. 275°C; IR = 3410, 1666, 1616, 1566, 1395, 1270, 1060 cm^{-1}; ^{1}H-NMR ($CDCl_3$/TMS) 200 MHz

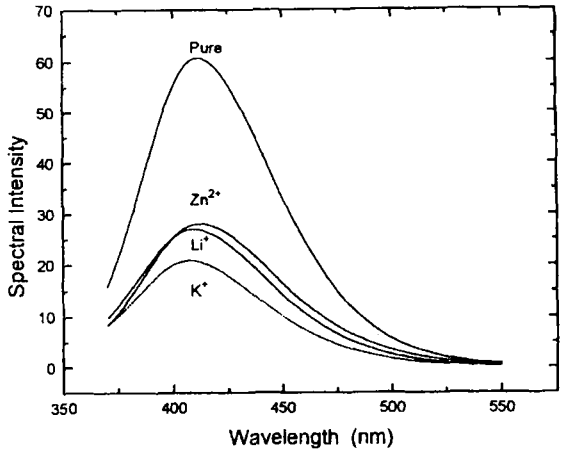


FIGURE 3 The emission CEQF spectra of **3c** ($3.4 \cdot 10^{-4}$ mol/l) and its complexes with $ZnCl_2$ ($4.9 \cdot 10^{-2}$ mol/l), KSCN ($3.5 \cdot 10^{-2}$ mol/l) and $LiClO_4$ ($2.9 \cdot 10^{-2}$ mol/l) in AN.

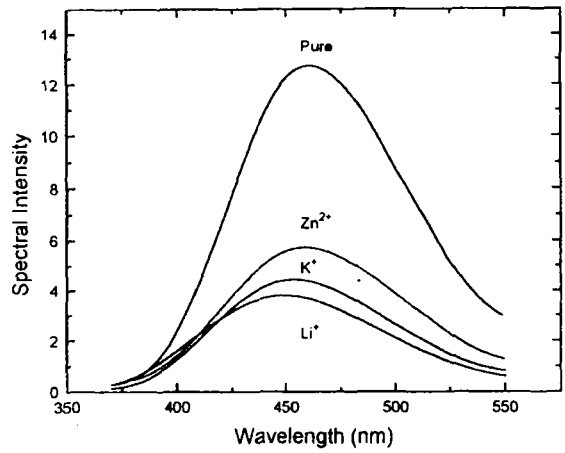


FIGURE 4 The emission CEQF spectra of **3c** ($3.4 \cdot 10^{-4}$ mol/l) and its complexes with $ZnCl_2$ ($3.0 \cdot 10^{-2}$ mol/l), KSCN ($3.4 \cdot 10^{-2}$ mol/l) and $LiClO_4$ ($2.6 \cdot 10^{-2}$ mol/l) in AN.

δ = 2.37 (s, 3H, CH_3), 6.04(s, 1H, cum-H), 6.85 (s, 1H, ArH), 7.08 (s, 1H, ArH).

6,7-Dihydroxy-4-phenyl-2(H)-1-benzopyran-2-one (2c)

1,2,4-Triacetoxy-benzene (15.8 g, 62.5 mmol), ethyl benzoylacetate (12 g, 62.5 mmol) and CF_3 COOH (Merck, 40 ml) were refluxed for 5 h. The product was crystallised from ether to give 11.0 g (69%) of **2c**; m.p. 222°C; IR = 3410, 1690, 1655, 1450, 1266, 1238, 1044, 855 cm^{-1}; ^{1}H-NMR ($CDCl_3$/TMS) 200 MHz δ = 6.23 (s, 1H, cum-H), 6.97 (s, 1H, ArH), 6.99 (s, 1H, ArH), 7.52 (m, 5H, Ph).

7,8-Dihydroxy-2(H)-1-benzopyran-2-one (2d)

Pyrogallol (12.6 g, 100 mmol), d,l-malic acid (13.4 g, 100 mmol) and H_2SO_4 (25 ml) were heated at 130°C for 2 h while stirring to give pink needles (methanol), 14.5 g (83%) **2d**; m.p. 255°C; IR = 3150, 1610, 1580, 1450, 1140, 940 cm^{-1}; ^{1}H-NMR ($CDCl_3$/TMS) 200 MHz δ = 6.28 (d, 1H, cum-H), 6.85 (d, 1H, ArH), 7.14 (d, 1H, ArH), 7.61 (d, 1H, cum-H).

7,8-Dihydroxy-4-methyl-2(H)-1-benzopyran-2-one (2e)

Pyrogallol (19.0 g, 150 mmol), ethyl acetoacetate (39 g, 300 mmol) and triethylamine (1 ml) were refluxed at 99°C for 1 h and heated with H_2SO_4 (35 ml) at 100°C for 1 h (pink needles, methanol), 25.0 g (88%) of **2e**; m.p. 244°C; IR = 3400, 1690, 1570, 1060, 1000 cm^{-1}; ^{1}H-NMR ($CDCl_3$/TMS) 400 MHz δ = 2.37 (s, 3H, CH_3), 6.14 (s, 1H, cum-H), 6.80 (d, 1H, ArH), 7.21 (d, 1H, ArH).

7,8-Dihydroxy-4-phenyl-2(H)-1-benzopyran-2-one (2f)

Pyrogallol (19.0 g, 150 mmol), benzoyl acetoacetate (29 g, 150 mmol), CH_3COOH (Merck, 50 ml) were refluxed for 5 h, cooled and 50 ml ether was added to give grey leafs, methanol, 19.0 g (66%) **2f**; m.p. 134°C; IR = 3450, 1700, 1610, 1460, 800 cm^{-1}; ^{1}H-NMR ($CDCl_3$/TMS) 400 MHz δ = 6.22 (s, 1H, cum-H), 6.87 (d, 1H, ArH), 6.99 (d, 1H, ArH), 7.45 (m, 5H, Ph).

6,7-(1,4,7,10-tetraoxadecylene)-4-methyl-2(H)-1-benzopyran-2-one (3a)

In a flask (250 ml), Na_2CO_3 (4.25 g, 40 mmol), **2g** (3.80 g, 20 mmol), **2b** (3.84 g, 20 mmol), DMF

(45 ml) and water (5 ml) were heated at 90°C for 40 h. The product was chromatographed on Al_2O_3/CH_2Cl_2 to give 1.48 g (24%) of **3a**; m.p. 126°C; IR = 2920, 1720, 1615, 1450, 1120 cm^{-1}; ^{1}H-NMR ($CDCl_3$/TMS) 400 MHz δ = 2.34 (s, 3H, CH_3), 3.82 (m, 4H, OC_2H_4O), 3.84 (t, 2H, OCH_2), 3.94 (t, 2H, OCH_2), 4.14 (m, 4H, 2(OCH_2)), 6.06 (s, 1H, cum-H), 6.88 (s, 1H, ArH), 7.20 (s, 1H, ArH); MS m/z 306.11 (M^+), 218.06 (M^+-$2C_2H_4O$), 190.06 (218-CO).

Anal. For $C_{16}H_{18}O_6$. Calcd: C, 62.74; H, 5.92. Found: C, 62.63; H, 5.71.

6,7-(1,4,7,10,13-pentaoxatridecylene)-2(H)-1-benzopyran-2-one (3b)

Na_2CO_3 (4.25 g, 40 mmol), **2h** (4.6 g, 20 mmol), **2a** (3.56 g, 20 mmol), DMF (45 ml) and water (15 ml) were heated at 80°C for 96 h to give 0.75 g (11.0%) **3b**; m.p. 118°C; IR = 2895, 1710, 1550, 1130 cm^{-1}; ^{1}H-NMR ($CDCl_3$/TMS) 400 MHz δ = 3.65 (m, 4H, 2(OCH_2)), 3.69 (m, 4H, 2 (OCH_2)), 3.87 (m, 4H, 2 (OCH_2)), 4.10 (m, 4H, 2 (OCH_2)), 6.20 (s, 1H, cum-H), 6.73 (d, 1H, ArH), 6.81 (s, 1H, ArH), 7.51 (d, 1H, cum-H); MS m/z 336.12 (M^+), 248.07 (M^+-$2C_2H_4O$), 204.04 (M^+-$3C_2H_4O$).

Anal. Calcd. for $C_{17}H_{20}O_7$. C, 60.71; H, 5.99. Found: C, 60.81; H, 5.94.

6,7-(1,4,7,10,13-pentaoxatridecylene)-4-methyl-2(H)-1-benzopyran-2-one (3c)

In a flask (250 ml), Na_2CO_3 (4.25 g, 40 mmol), **2h** (4.6 g, 20 mmol), **2b** (3.84 g, 20 mmol), DMF (45 ml) and water (5 ml) were heated at 80°C for 50 h. The product was purified on Al_2O_3 (Basic)/CH_2Cl_2 to give 2.2 g (31%) of **3c**; m.p. 126°C; IR = 2920, 1700, 1420, 1125 cm^{-1}; ^{1}H-NMR ($CDCl_3$/TMS) 500 MHz δ = 2.34 (s, 3H, CH_3), 3.72 (m, 8H, $O(C_2H_4)_2$), 3.90 (m, 4H, 2(OCH_2)), 4.14 (m, 4H, 2(OCH_2)), 6.10 (s, 1H, cum-H), 6.76 (s, 1H, ArH); 6.95 (s, 1H, ArH); MS m/z 350.37 (M^+), 262.09 (M^+-$2C_2H_4O$), 218.06 (M^+-$3C_2H_4O$).

Anal. Calcd. for $C_{18}H_{22}O_7$. C, 61.71; H, 6.33. Found: C, 61.77; H, 6.38.

6,7-(1,4,7,10,13-pentaoxatridecylene)-4-phenyl-2(H)-1-benzopyran-2-one (3d)

Na_2CO_3 (4.25 g, 40 mmol), **2h** (4.6 g, 20 mmol), **2c** (5.08 g, 20 mmol), DMF (45 ml) and water (5 ml) were heated at 80°C for 48 h to give 4.15 g (50%) (white needles, methanol), **3d**; m.p. 130°C; IR = 2910, 1710, 1605, 1225, 1120, 970 cm^{-1}; ^{1}H-NMR ($CDCl_3$/TMS) 200 MHz δ = 3.75 (m, 8H, $O(C_2H_4)_2$), 3.87 (t, 2H, OCH_2), 3.96 (m, 4H, 2(OCH_2)), 4.21 (t, 2H, OCH_2), 6.24 (s, 1H, cum-H), 6.87 (s, 1H, ArH); 6.90 (s, 1H, ArH), 7.52 (m, 5H, Ph); MS m/z 412.15 (M^+), 280.07 (M^+-$3C_2H_4O$), 252.08 (280-CO).

Anal. Calcd. for $C_{23}H_{24}O_7$: C, 66.99; H, 5.87. Found: C, 66.69; H, 5.80.

7,8-(1,4,7,10-tetraoxadecylene)-4-methyl-2(H)-1-benzopyran-2-one (4a)

Na_2CO_3 (4.25 g, 40 mmol), **2g** (3.80 g, 20 mmol), **2e** (3.85 g, 20 mmol), DMF (45 ml) and water (5 ml) were heated at 80°C for 48 h to give 0.92 g (15%) of **4a**, white crystals; m.p. 64°C; IR = 2930, 1720, 1420, 1120 cm^{-1}; ^{1}H-NMR ($CDCl_3$/TMS) 400 MHz δ = 2.37 (s, 3H, CH_3), 3.82 (m, 4H, OCH_2), 3.84 (t, 2H, OCH_2), 3.97(t, 2H, OCH_2), 4.24(t, 2H, OCH_2), 4.36 (t, 2H, OCH_2), 6.15 (s, 1H, cum-H), 6.88 (d, 1H, ArH), 7.29(d, 1H, ArH); MS m/z 306.11(M^+), 218.06 (M^+-$3C_2H_4O$), 190.06 (218-CO).

Anal. Calcd. for $C_{16}H_{18}O_6$: C, 62.75; H, 5.92. Found: C, 62.90; H, 5.67.

7,8-(1,4,7,10,13-pentaoxatridecylene)-2(H)-1-benzopyran-2-one (4b)

Na_2CO_3 (4.25 g, 40 mmol), **2h** (4.6 g, 20 mmol), **2d** (3.56 g, 20 mmol), DMF (45 ml) and water (5 ml) were heated at 85°C for 48 h. Product was chromatographed on Al_2O_3/CH_3OH gave 1.35 g (20%), **4b**; m.p. 113°C; IR: 2920, 1720, 1600, 1125 cm^{-1}; ^{1}H-NMR (DMSO-d_6/TMS) 400 MHz δ = 3.59 (m, 8H, $O(C_2H_4)_2$), 3.84 (m, 4H, 2(OCH_2)), 4.16 (t, 4H, 2(OCH_2)), 6.15(d, 1H, cum-H), 6.92(d, 1H, ArH), 7.27 (d, 1H, ArH), 7.78 (d, 1H, cum-H);

MS m/z 336.12(M^+), 248.07 (M^+-2C_2H_4O), 204.05(M^+-3C_2H_4O), 176.05 (204-CO).

Anal. Calcd. for $C_{17}H_{20}O_7$: C, 60.71; H, 5.99. Found: C, 60.95; H, 6.08.

7,8-(1,4,7,10,13-pentaoxatridecylene)-4-methyl-2(H)-1-benzopyran-2-one (4c)

Na_2CO_3 (4.25 g, 40 mmol), 2h (4.60 g, 20 mmol), 2e (3.85 g, 20 mmol), DMF (45 ml), water (5 ml) were heated at 80°C for 48 h to give 2.5 g (36%) **4c**, white crystals; m.p. 114°C; IR = 2920, 1720, 1350, 1125 cm^{-1}; ^{1}H-NMR ($CDCl_3$/TMS) 400 MHz δ = 2.32 (s, 3H, CH_3), 3.68 (m, 8H, O(C_2H_4)$_2$), 3.85 (t, 2H, OCH_2), 3.90 (t, 2H, OCH_2), 4.16 (t, 2H, OCH_2), 4.25 (t, 2H, OCH_2), 6.04 (s, 1H, cum-H), 6.80 (d, 1H, ArH), 7.21 (d, 1H, ArH); MS m/z 350.13 (M^+), 262.09 (M^+-2C_2H_4O), 218.06 (M^+-3C_2H_4O).

Anal. Calcd. for $C_{18}H_{22}O_7$: C, 61.71; H, 6.28. Found: C, 61.57; H, 6.32.

7,8-(1,4,7,10,13-pentaoxatridecylene)-4-phenyl-2(H)-1-benzopyran-2-one (4d)

Na_2CO_3 (4.25 g, 40 mmol), **4b** (4.60 g, 20 mmol), **2c** (5.08 g, 20 mmol), DMF (45 ml) and water (15 ml) were heated at 80°C for 50 h to give 2.10 g (25%) of **4d**; m.p. 94°C; IR = 2940, 1720, 1440, 1115 cm^{-1}; ^{1}H-NMR ($CDCl_3$/TMS) 200 MHz δ = 3.72 (m, 8H, O(C_2H_4)$_2$), 3.95, (m, 4H, 2(OCH_2)), 4.18 (t, 2H, OCH_2), 4.27 (t, 2H, OCH_2), 6.23 (s, 1H, cum-H), 6.44, (d, 1H, ArH), 6.85 (d, 1H, ArH), 7.29 (m, 5H, Ph); MS m/z 412.15 (M^+), 280.07 (M^+-3C_2H_4O), 252.08 (280-CO).

Anal. Calcd. for $C_{23}H_{24}O_7$: C, 66.99; H, 5.87. Found: C, 67.07; H, 6.01.

RESULTS AND DISCUSSION

The coumarin derivatives of some 12-crown-4 and 15-crown-5 macrocycles were synthesised in good yields and used for cationic recognition with fluorescence spectroscopy. Mostly, the practical fluorescence ligand probes are affected in the presence of cations involving a change in fluorescent quantum yield without a shift in the emission and excitation spectra [2–7].

Interesting results were obtained with the fluorescence spectra of the cation-ligand solutions in our work, although, the complex formation detected *via* fluorescence is known also for oxygen bearing macrocycles [4–7]. Likewise, the naphthalene-crowns exhibit detectable fluorescence intensity changes upon the cation complex formation [4, 6].

Pioneering studies in other laboratories, have shown cation responses of some aromatic nitrogen pivot macrocycles. However, such fluorophores may display different roles due to different photophysical effects [2–5]. The oxygen-bearing macrocycles studied by us for cationic recognition possess uncompensated charges; this imparts a strong electric effect to the system. However, cation concentrations need to be increased for remarkable effects to be observed.

We demonstrated that the fluorescence spectra of coumarin-crowns have been altered by the addition of anhydrous Li^+, Mg^{2+}, Na^+ and K^+ salts. The emission and excitation intensities of cationic macrocycles were mostly reduced due to polarisation of electrons on fluoroionophore affected by a cation [3, 4].

The role of actonitril solvent, AN, is important in cationic fluorescence spectra due to perturbation of the excited states depending on solvent polarity, particularly, in non-stoichiometric cation-ligand interactions, Table I, Figures 3, 4. However, we observed the stoichiometric 1:1 cation-ligand interactions of Compounds **3a**, **3c** and **3d** as shown on Table II, Figure 1.

Some coumarin-macrocycles, compounds **3b**, **4a** and **4b** exhibited interesting cationic fluorescence which was quenched after the concentration of 10^{-3} mol/l. The least quenching complex structures are the most suitable cation sensors with the widest concentration ranges to detect the ion as shown on Figures 1, 3, 4.

The compound **3d** is the best ligand we observed in this work. It is followed by compound **3c**, see Figures 1, 2. The ring sizes are significant as well as the *R* groups bearing at coumarin position-4, see Scheme 1. However, compounds **3a–3d** displayed complexing enhanced quenching fluorescence spectra, CEQFS, showing a wide concentration range of spectral changes, Table I, Figure 1. The Na^+ selectivity found for compound **3c** as 15-crown-5 derivative is better than K^+ but not so good for Li^+ or Mg^{2+}, Table I. The binding of compound **3d** is quite selective for Li^+ but not so selective for Na^+ and K^+ as expected. However, the role of excess cation is more clear, Table I, Figures 3, 4. The 7,8-dioxo-coumarin terminal crown compounds, **4a–4d**, did not allow us to estimate their properties in AN since a strong quenching was observed. No fluorescence roles in water were observed.

Cations having larger radii were less effective, than Na^+, K^+, Mg^{2+} for the coumarin 12-crown-4 and 15-crown-5 derivatives, suggesting a role of the macrocyclic size in these systems. The anions, SCN^- and ClO_4^- are much more effective in acetonitrile compared to Cl^- indicating the role of ion pairs.

The 1 : 1 binding constants, K_b, were estimated according to Valeur, [2] and de Silva, [3] using steady state fluorescence spectroscopy and the equation; $K_b.[M_0] = [I - I^0]/[I^{max} - I]$, in which I, is the fluorescence peak intensity of a macrocycle in the presence of different cation concentrations, $[M_0]$. I^{max} is obtained in the presence of excess of a cation. The intensity of the constant free macrocycle is I^0, The maximum intensities were measured with minimum quenching concentrations in solution, Table I, Figures 1–4. The $[I - I^0]/[I^{max} - I]$ is plotted *versus* $[M_0]$ and the slope of the least squared line gives the binding constant, K_b. The results shows a macrocycle size-cation radius relationships (see Tabs. I, II).

The coumarin moieties are excellent for use in a cation sensor since the fluorescence extinction of benzo-α-pyronecrowns is at least, 100-fold higher, than observed for benzocrowns such as, benzo-15-crown-5 in acetonitrile [9, 12]. The effectiveness of the coumarin macrocycles also depends on substituents such as R(H, CH_3, C_6H_5) attached to the coumarin 4-position.

Acknowledgements

We thank the, Research Foundation of ITU, Turkey for support of initiations of the serial work, Turkish Scientific and Technological Council, TÜBİTAK, is acknowledged for the support of project, TBAG-1681, covering this work.

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