The Synthesis of Dibenzo[3n]crown-n by Novel Methods and their Cation Binding Studied by Fluorescence Spectroscopy. Part IV *

GÖNÜL YAPAR and ÇAKIL ERK**
Technical University of Istanbul, Department of Chemistry, Maslak, 80626, Istanbul, Turkey

Abstract

The dibenzo[3n]crown-n were synthesised from 1,2-bis(*o*-hydroxyphenoxy)ethane obtained from 1,2-bis(*o*-formylphenoxy)ethane via Bayer-Williger oxidations with H_2O_2/CH_3COOH in good yields. The cyclic condensation of 1,2-bis(*o*-hydroxyphenoxy)ethane with dichlorides, and ditosylates of polyethylene glycols in DMF/Me_2CO_3 gave the macrocycles dibenzo[15]crown-5, dibenzo[18]crown-6, dibenzo[21]crown-7 and dibenzo[24]crown-8. The structures were identified using IR, mass, ^1H and ^{13}C NMR spectroscopy. The recognition of the molecules for the cations, Li^+, Na^+, K^+, Rb^+ and Zn^{2+} were conducted quantitatively with steady state fluorescence spectroscopy. The 1:1 association constants in acetonitrile showed a good relation of the appropriate size of the macrocyclic ether towards the fitting cation radii. Namely, dibenzo[15]crown-5 was the best for Li^+ binding and more than 100 times better than Na^+ and K^+. Dibenzo[21]crown-7 was excellent for Rb^+ binding while K^+ is 100 times less preferred. The largest crown ether studied, dibenzo[24]crown-8, exhibited the order of binding power, $Rb^+ > K^+ > Na^+$. Zn^{2+} displayed, however, a marked binding with only dibenzo[18]crown-6.

Introduction

The dibenzo[3n]crown-n macrocycles are well known due to the simplicity of their preparations from catechol and bisdichloro PEG following the route of Pedersen [1]. The macrocyclic ethers with different numbers of oxyethylene bridges between the o, o'-dioxydibenzo groups are less common due to limited synthesis methods [2-11]. The dibenzo groups bearing o, o'-dihydroxy terminals have been used in macrocyclic condensation with glycol bishalides or bistosylates via the template effect on cations. However, Pedersen prepared the podands with bis-*o*-hydroxyphenoxy terminals by protecting one of the phenolic dihydroxyls with the 2,3-dihydropyrano group which was then hydrolysed for crown ether condensation [1, 3–8].

However, an alternative method of preparation of mono benzyl derivatives of cathecol followed by the polyethylene glycol bridge formation and catalytic hyrogenolysis of the protecting benzyl groups to afford the o, o'-dihydroxydiphenoxy terminals has been widely used [4–11].

We prepared some dibenzo[3n]crown-n using an alternative method and studied the cationic recognition with fluorescence spectroscopy in the present work [12–16]. The high yield synthesis of the initial podand, 1,2-bis(*o*-hydroxyphenoxy)ethane, **3a** was started from *o*-hydroxybenzaldehyde, **1b** and the relevant dibenzo crown ethers were obtained [17–19]. The cationic recognition of

the macrocyclic ethers have been investigated by several analytical methods [20–23], However, we have studied such roles using steady state fluorescence spectroscopy [16]. The fluorescence and phosphorescence life time measurements of the lumophore macrocycles have shown that the aromatic macrocyclic structures with $\pi \rightarrow \pi^*$ responsive transitions are induced by cations to change triplet energy relative to excited singlet and ground state transitions [24–27]. The macrocyclic–metal interactions in AN were determined quantitatively in the present work by measuring the steady state fluorescence emission intensities of fluorophore macrocycles in the presence of various cation concentrations. The 1:1 association constants, K_a of cation, $[M^+]$ and crown ether, $[L]$ were determined using the following Equations (1)–(3) [27].

$$L + M^+ \leftrightarrow M^+L \qquad (1)$$

$$K_a = [M^+L]/[L][M^+] \qquad (2)$$

$$(I_x - I_o)/(I_{max} - I_x) = K_a[M_o], \qquad (3)$$

where I_o is the intensity of the free macrocycle and I_{max} is the intensity of the 1/1 cation complexed macrocycle. K_a values were, however, obtained from the least-squares data arising from Equation (3).

---

* Part III, Ref. [14].
** Author for correspondence.

Experimental

Salicylaldehyde and pentaethyleneglycole ditosylate, were from Fluka unless otherwise cited. The glycol dichlorides were available to us from our earlier works [14, 15]. Mass spectra was recorded on a Fisons VG-Zapspec instrument, IR spectra were recorded as KBr pellets on a Jasco FTIR spectrometer, model 5300, and 400 MHz PMR and 100 MHz ^{13}C spectra were obtained on a Bruker CPX-400 NMR spectrometer using TMS as an internal reference in CDCl$_3$. M.p. data are uncorrected and are consistent with literature values [4, 6]. Fluorescence measurements were carried out in a thermostated compartment with a magnetic stirrer of a JASCO FP-750 spectrofluorometer using the standard software at 25.0 °C (± 0.1 °C).

Cationic recognition by fluorescence spectroscopy

The 1:1 association constants, K_a, were estimated according to the method of de Silva *et al.* [25] using the equation, $K_a [M_o] = [I_x - I_o]/[I_{max} - I_x]$ with the complexation enhanced fluorescence, CEFS, data of steady state fluorescence emission spectroscopy. The fluorescence peak intensity of a macrocycle, I_x (±0.1), is observed in the presence of various cation concentrations, $[M_o]$. I_{max} is obtained in the presence of excess of a cation or better by simulation of Equation (3). The intensity of the free (uncomplexed) macrocycle is I_o, The maximum emission intensities, (307–319 nm), however, were measured with minimum quenching concentrations in solution. $[I_x - I_o]/[I_{max} - I]$ is plotted versus $[M_o]$ and the slope of the least squares line gives the association constant, K_a. The results showed interesting macrocyclic ether size-cation radii relations in Table 1.

Stock solutions of the cations, (2.5–5.0 × 10^{-4} M) in dry CH$_3$CN were added as small portions to a stirred solution of the fluorophore macrocyclic ether, (3.0–2.0 × 10^{-5} M) in dry CH$_3$CN, placed in the spectrophotometer cell compartment in 10-mm quartz cells, however, the concentrations were optimized to prevent fluorescence quenching. The spectral bandwidth was 5.0 nm at the excitation maximum, 279–280 nm. Emission peak intensities, I_x at 307–310 nm were recorded with the standard software and the data was least squared to calculate the K_a values using Equation (3) by simulating I_{max} and I_o values (see Table 1 and Figures 1 and 2).

Organic synthesis

1,2-Bis(o-formylphenoxy)ethane (**2a**): 1,2-dibromoethane, **1a** (47 g, 250.0 mmol) placed in a dropping funnel was added to a mixture of K$_2$CO$_3$ (69.0 g, 500.0 mmol), salicylaldehyde, **1b** (61.0 g, 500.0 mmol), DMF (120 mL) and water (30 mL) in a round bottom flask (500 mL) which was stirred and heated at 90 °C. The mixture was heated for 22–25 h, cooled and left for 24 h at room temperature. The solidified product was filtered and washed with water and dried before crystallization in acetone. **2a**, m.p. 130 °C 37.8 g, yield 56%, IR (KBr); ν = 3075, 2850, 1680, 1600, 1475, 1060, 950 cm^{-1} – ^{1}H-NMR (400 MHz, CDCl$_3$/TMS);

Table 1. Ratiometric titration of DB[21]crown-7, (2.5 × 10^{-4} mol L^{-1}) with RbClO$_4$ in AN. $\lambda_{excitationmaxima}$ = 279 nm, $\lambda_{emissionmaxima}$ = 307 nm, (see Figure 1)

Conc. 10^5	$(I_x - I_o)/I_{max} - I_x$	$I_{max} - I_x$	$(I_x - I_o)$	I_x
1.25	2.5	45.5	114.8	260.0
2.49	2.7	43.9	116.4	261.6
3.65	3.1	38.7	121.6	266.8
4.95	3.7	34.3	126.0	271.2
6.17	4.7	28.0	132.3	277.5
7.39	5.5	24.5	135.8	281.0
8.60	6.1	22.5	137.8	283.0
9.80	7.2	19.5	140.8	286.0
11.00	8.4	17.0	143.3	288.5
12.20	9.5	15.2	145.1	290.3
14.46	11.0	13.4	146.9	292.1
16.90	12.8	11.6	148.7	293.9
19.20	15.0	10.0	150.3	295.5
21.53	17.2	8.8	151.5	296.7
23.80	18.3	8.3	152.0	297.2
28.30	21.9	7.0	153.3	298.5
30.52	23.3	6.6	153.7	298.9
32.71	26.2	5.9	154.4	299.6
34.90	27.1	5.7	154.6	299.8

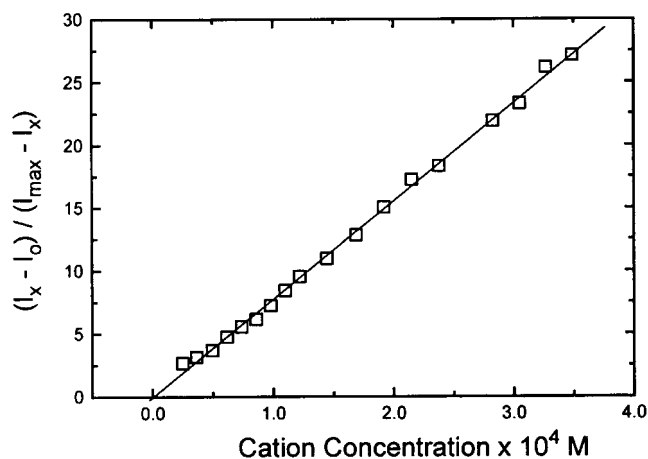*Figure 1.* The plot of association constant for RbClO$_4$/DB[21]crown-7, **4c** according to Equation (3).

δ = 4.58 (s, 4H, C$_2$H$_4$O), 7.08 (m, 4 H, Ar), 7.58 (m, 2 H, Ar), 7.83 (m, 2 H, Ar), 10.44 (s, 2H, CHO) ppm; ^{13}C-NMR (100 MHz, CDCl$_3$/TMS); δ = 137.9, 162.7, 130.7, 127.2, 123.5, 114.8, 69.1, 191.3 ppm; MS (*m/z*): 270 (M$^+$), 149, 120.

1,2-Bis(o-hydroxyphenoxy)ethane (**3a**): Acetic acid (20 mL) and 1,2-bis(o-formylphenoxy)ethane (**2a**) (2.0 g, 7.0 mmol) in a flask (250 mL) were heated at 40 °C on a water bath. H$_2$O$_2$ (Fluka, 30%, 15 mL) was added to the stirred solution of **2a** carefully whilst the temperature was kept at 40 °C steadily for 8–9 h. The cooled mixture was diluted with NaHSO$_3$ (40%, 25 mL) solution while stirring then the solid product was filtered and crystallised from CHCl$_3$. **3a**, m.p. 114 °C, 1.21 g, yield 67%, IR (KBr); ν = 3420, 3045, 2925, 1600, 1500, 720 cm^{-1}; ^{1}H-NMR (400
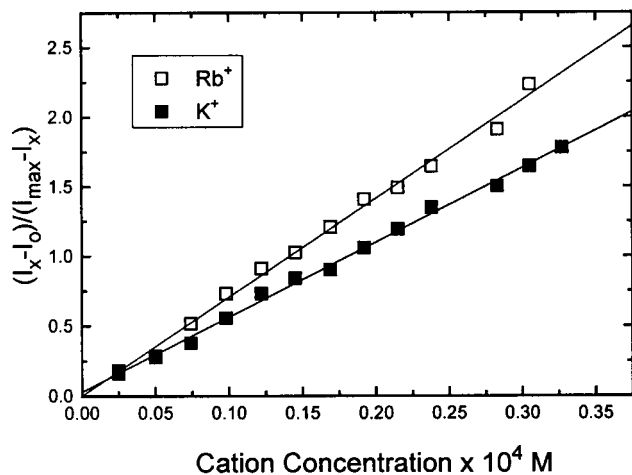
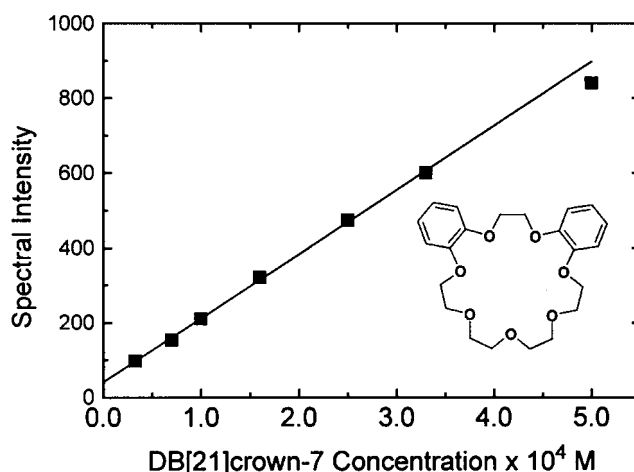*Figure 2*. The plot of association constant for Rb$^+$ and K$^+$/DB[24]crown-8, **4d** according to Equation (3).

Figure 3. The dependence of the spectral intensity of dibenzo[21]crown-7, **4c** on the concentration in AN, excitation λ_{max} = 280 nm and emission λ_{max} = 310 nm.

MHz, CDCl$_3$/TMS); δ = 4.39 (s, 4 H, C$_2$H$_4$O), 5.80 (s, 2 H, OH), 6.95 (m, 6H, Ar), 8.89 (2 H, m, Ar) ppm; ^{13}C-NMR (100 MHz, CDCl$_3$/TMS); δ = 115.1, 117.4, 122.3, 124.7, 147.5, 148.3, 70.1 ppm; MS (*m/z*): 246 (M$^+$), 136, 121, 109.

Dibenzo[b,h]6,7,9,10,17,18-hexahydro-1,4,7,10,13-pentaoxacyclopentadesin (Dibenzo-15 -crown-5) (**4a**): (**3a**) (0.71 g, 2.88 mmol), DMF (20 mL), Na$_2$CO$_3$ (0.61 g, 5.76 mmol) and water (5 mL) placed in a flask (100 mL) were heated while stirring at 65–70 °C. To this solution, β, β-dichlorodiethyl ether (**1c**) (0.42 g, 2.89 mmol) in DMF (10 mL) was added in 2 h and the reaction mixture was heated at 80 °C for 60–70 h. The mixture was acidified with HCl, extracted with CH$_2$Cl$_2$ (2 × 40 mL) and the organic layer was dried with Al$_2$O$_3$ (5.0 g, basic) and chromatographed on Al$_2$O$_3$ (50 g, Fluka, basic) with CH$_2$Cl$_2$ (2 × 25 mL), **4a**, m.p. 112 °C, 0.31 g, yield 34%, IR (KBr): ν = 3050, 2925, 1600, 1500, 1265, 1140, 940, 740 cm^{-1}; ^{1}H-NMR (400 MHz, CDCl$_3$/TMS); δ = 3.99 (t, 4H, CH$_2$OCH$_2$), 4.23 (t, 4H, CH$_2$OCH$_2$), 4.41 (s, 4H, C$_2$H$_4$O), 6.92 (8 H, m, Ar) ppm; ^{13}C-NMR (100 MHz, CDCl$_3$/TMS): δ = 116.4, 117.4, 123.2, 123.1, 150.8, 150.9, 69.0, 70.7, 71.2 ppm; MS (*m/z*): 316 (M$^+$), 216, 136, 121.

Dibenzo[b,h]6,7,9,10,12,13,20,21-octahydro-1,4,7,10, 13,16-hexaoxacyclooctodecin (Dibenzo-18-crown-6) (**4b**); (**3a**) (1.0 g, 4.06 mmol), DMF (25 mL), Na$_2$CO$_3$ (0.87 g, 8.20 mmol) placed in a flask (250 mL) were heated while stirring at 70–75 °C. To this solution, 1,8-dichloro-3,6-dioxaoctane (**1d**) (0.76 g, 4.08 mmol) in DMF (10 mL) was added in 2 h and the reaction mixture was heated for 60–70 h. The mixture was acidified with HCl extracted with CH$_2$Cl$_2$ (3 × 25 mL) and the organic layer was dried with Al$_2$O$_3$ (basic, 5.0 g) and chromatographed on Al$_2$O$_3$ (70 g, Fluka, basic) with CH$_2$Cl$_2$ (3 × 25 mL), **4b**, m.p. 113 °C, 0.16 g, yield 11%, IR (KBr); ν = 3046, 2925, 1600, 1250, 1125, 940, 740 cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$/TMS); δ = 3.83 (s, 4H, CH$_2$OCH$_2$), 3.93 (m, 4H, CH$_2$OCH$_2$), 4.21 (m, 4H, C$_2$H$_4$O), 4.44 (s, 4H, C$_2$H$_4$O) 6.95 (m, 8H, Ar) ppm; ^{13}C-NMR (100 MHz, CDCl$_3$/TMS); δ = 115.8, 117.4, 123.1, 122.7, 150.2, 150.8, 69.0, 70.3, 70.4, 71.7 ppm; MS (*m/z*): 360 (M$^+$), 136, 121, 109.

Dibenzo[b,h]6,7,9,10,12,13,15,16,23,24-decahydro-1, 4,7,10,13,16,19-heptaoxacycloheneicosin (Dibenzo-21-crown-7) (**4c**); (**3a**) (1.33 g, 5.4 mmol), DMSO (35 mL) and Na$_2$CO$_3$ (1.15 g, 10.8 mmol) mixed in a flask (250 mL) were reacted with 1,11-dichloro-3,6,9-trioxaundecane (**1e**) (1.25 g, 5.41 mmol) in DMSO (5 mL) while heating at 80 °C for 4 days. The acidified mixture diluted with water (100 mL) was extracted with CH$_2$Cl$_2$ (4 × 25 mL) and dried on Al$_2$O$_3$ (basic, 4 g). The raw product was eluted from Al$_2$O$_3$ (Fluka, basic, 50 g) with CH$_2$Cl$_2$ (2 × 35 mL), **4c**, m.p. 49–50 °C, 0.91 g, yield 42%, IR (KBr); ν = 3068, 2947, 1613, 1500, 1273, 1152, 958, 763 cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$/TMS): δ = 3.69 (m, 8H, 2CH$_2$OCH$_2$), 4.12 (m, 4H, m, CH$_2$OCH$_2$), 4.21 (m, 4H, CH$_2$OCH$_2$), 4.37 (m, 4H, C$_2$H$_4$O), 6.94 (8 H, m, Ar) ppm; ^{13}C-NMR (100 MHz, CDCl$_3$/TMS); δ = 117.3, 116.2, 123.2, 122.7, 150.3, 150.8, 69.5, 69.5, 70.3, 71.6, 71.7 ppm; MS (*m/z*): 404 (M$^+$), 136, 121, 80.

Dibenzo[b, h]6,7,9,10,12,13,15,16,18,19,26,27-dodeca-hydro-1,4,7,10,13,16,19,22-octaoxacyclotetracosin (Dibenzo-24-crown-8) (**4d**); (**3a**) (0.5 g, 2.03 mmol), DMF (10 mL), K$_2$CO$_3$ (0.56 g, 4.05 mmol) were reacted with bis(*p*-toluenesulfonyl) pentaethylene glycol (**1f**) (1.12 g, 2.04 mmol) and DMF (10 mL) at 95–105 °C for 70–80 h. Treatments given above afforded **4d**, m.p. 111-112 °C, 0.33 g, yield 36%. IR (KBr) ν = 3065, 2918, 2874, 1585, 1496, 1253, 1120, 936, 745 cm^{-1}; ^{1}H-NMR (400 MHz, CDCl$_3$/TMS): δ = 3.63 (m, 8H, 2C$_2$H$_4$O), 3.86 (s, 4H, CH$_2$OCH$_2$), 3.91 (t, 4H, CH$_2$OCH$_2$), 4.19 (t, 4H, CH$_2$OCH$_2$), 4.42 (s, 4H, CH$_2$OCH$_2$) ppm; ^{13}C-NMR (100 MHz, CDCl$_3$/TMS): δ = 117.3, 116.2, 123.2, 122.8, 150.3, 150.8, 69.5, 70.2, 70.5, 71.6, 71.6, 71.8 ppm; MS (*m/z*): 448 (M$^+$), 279, 149, 121.
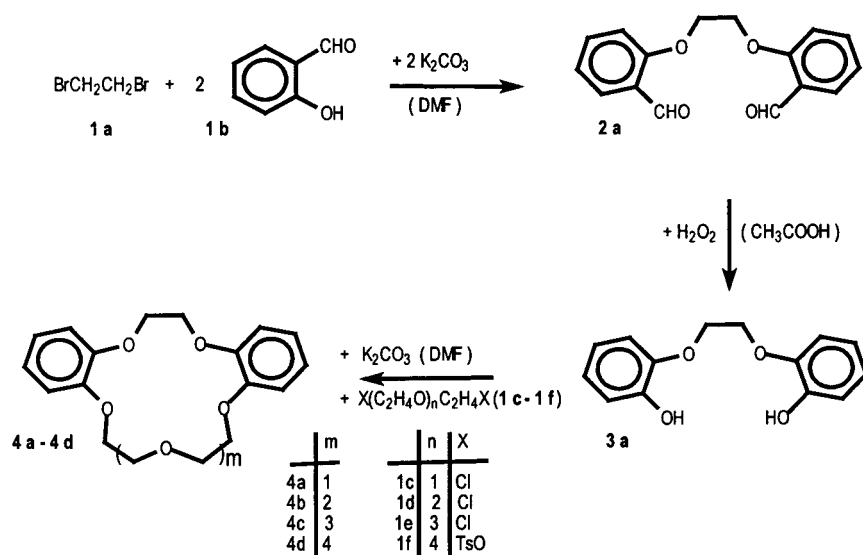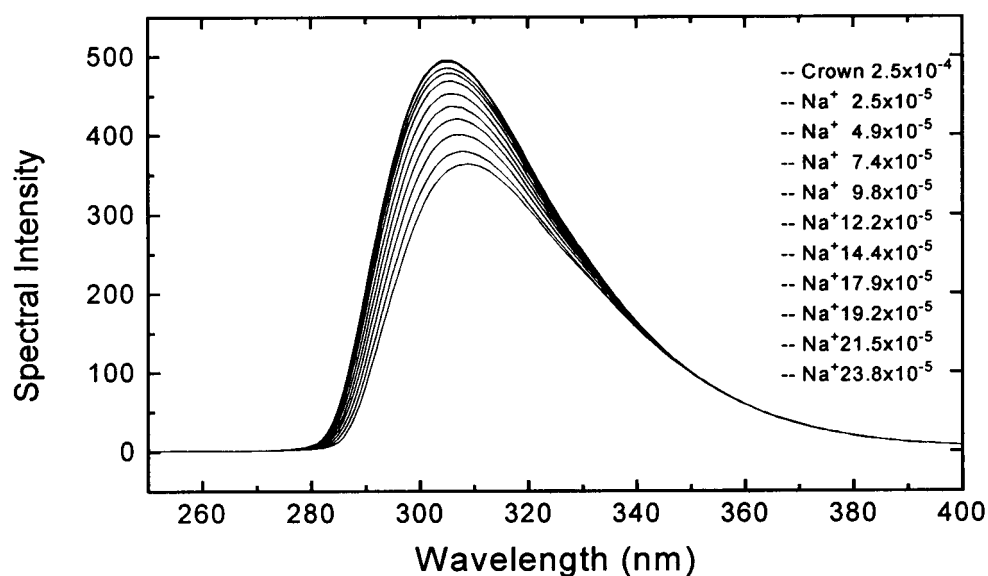
Scheme 1.

Figure 4. The plot of CEFS complexed DB[18]crown-6 in various concentrations of NaClO$_4$ where the increasing concentrations are from the bottom to top of the spectral lines.

Table 2. The K$_a$ (± 1.0), ln K$_a$ (± 0.10) and $-\Delta G$ (± 0.10) values of dibenzo[3n]crown-n with cation perchlorates in AN using Equation (3), $\lambda_{\text{excitationmaxima}}$ = 279–280 nm, $\lambda_{\text{emissionmaxima}}$ = 308–306 nm

Crown	Cation	K$_a$	ln K$_a$	$-\Delta G$ (kJ M^{-1})	Corell. C.	Intercept	I$_o$/I$_{max}$
4a	Li$^+$	1006.4	6.1	15.62	0.992	< 1E-05	260/410
4a	Na$^+$	> 55	> 4.0				
4a	K$^+$	> 55	> 4.0				
4b	Na$^+$	7250.5	8.89	20.08	0.996	> 1E-06	320/600
4b	K$^+$	928.5	6.89	3.69	0.994	1E-06	340/550
4b	Rb$^+$	>55	> 4.0				
4b	Zn$^+$	277.9	5.63	12.71	0.998	− 3E-05	238/096
4c	Na$^+$	> 55	> 4.0				
4c	K$^+$	824.8	6.72	15.17	0.997	1E-06	261/330
4c	Rb$^+$	78130.2	11.27	25.45	0.999	1E-06	145/305
4d	Na$^+$	2270.9	7.73	17.46	0.998	> 1E-05	201/240
4d	K$^+$	5367.1	8.59	19.40	0.998	> 1E-05	230/180
4d	Rb$^+$	7333.8	8.89	20.10	0.996	> 1E-05	220/156

Results and discussion

The novel method of synthesis of bis(o-hydroxyphenoxy)ethane and crown ethers

We recently aimed to study macrocyclic ethers with chromophore and fluorophore moieties and prepared several types of chromo- and fluoroionophores of macrocyclic ethers and investigated their cation binding and selectivity effects using steady state fluorescence spectroscopy at room temperature, in particular, in acetonitrile [16].

The organic synthesis of some dibenzo[3n]crown-n (n = 5–8) with an (o, o′-dioxydiphenoxy)ethane bridge in good overall yields, were achieved in the present work, (see Scheme 1). This type of crown ethers were only characterized from the X-ray work on their cationic complexes [4, 6].

The macrocyclic ethers with different length of oxyethylene bridges between the o, o′-dioxydibenzo groups, **4a–4d**, were synthesized with a novel method [12, 13]. The podand, **2a**, with (o, o′-diformyl)diphenoxy terminals was obtained from 1,2-dibromoethane, **1a** and salicylaldehyde, **1b**, in Me_2CO_3/DMF [12, 13] (Scheme 1). Bishalides and bistosylates ended polyglycols, **1c–1f**, were condensed in Me_2CO_3/DMF with 1,2-bis(o-hydroxyphenoxy)ethane, **3a** which was obtained from 1,2-bis(o-formylphenoxy)ethane, **2a**, via Baeyer–Villiger oxidation of aromatic –CHO using H_2O_2 in AcOH at 40 °C [18]. The alternative methods given in the literature have given lower yield of end products, therefore, we had to develop a new method to prepare the glycols with bis-o-hydroxyphenoxy terminals [12, 13]. The procedures, yields, structural and spectral data of the products are given in the experimental section.

Cationic recognition with steady state fluorescence spectroscopy

The cationic recognition of the dibenzo[3n]crown-n molecules (n = 5, 6, 7, 8) have not been widely investigated before, (see Scheme 1) [2, 4–6]. The fluorophoric effect of dibenzo moieties in cation sensing is practical to investigate the cationic recognition of **4a**-**4d**, although, the fluorescence quantum yields of benzocrowns are, at least, a hundred times less compared to those of coumarin crowns in acetonitrile as we recently reported [16, 26, 27].

In general the association constants in acetonitrile displayed good 1/1 selectivity of the appropriate size of macrocyclic ether towards the fitting radii of cations, (see Table 2). The observed cationic recognition of such macrocycles using steady state fluorescence showed that the large macrocycles are strongly complexed with large radii of cations of K^+ and, in particular, with Rb^+. Accordingly, Li^+ cation has too small fluorescence responses with seven and eight oxygen member macrocyclic ethers in AN. However, reported association constants are only for a 1/1 cation-macrocyclic ratio using Equation (3).

Dibenzo[15]crown-5, **4a**, however, was the best for Li^+ binding which is more than 20 times better than those of Na^+ and K^+ since m = 1 and the (o, o′-dioxydiphenoxy)ethane bridge is rather rigid (Scheme 1) [28]. Na^+ and K^+ displayed marked results of complexing with dibenzo[18]crown-6, **4b**, However, Na^+ showed better selectivity than K^+, Figure 4, due to the limited conformational flexibility of the macrocycle even for m = 2 (Scheme 1) [4, 6, 29]. The results indicate that the encapsulated alkali cations are not completely centralized by the macrocycles. Zn^{2+} displayed a marked binding with only **4b** which interestingly showed complexation enhanced quenching fluorescence spectra, CEQFS. However, dibenzo[21]crown-7, **4c**, was found to exhibit the highest Rb^+ selectivity whilst K^+ was 90 times less preferred and Na^+ was really poor to bind [2, 30]. The largest crown studied dibenzo[24]crown-8, **4d**, exhibited a cation binding power order of $Rb^+ > K^+ > Na^+$. This molecule, probably, has no ability to wrap around the cations studied in the present work due to the rigid diphenoxy ethane link [5, 6].

References

1. C.J. Pedersen: *J. Am. Chem. Soc.* **92**, 391 (1970).
2. R.M. Izatt, G.A. Clark, J.D. Lamb, J.E. King and J.J. Christensen: *Thermochim. Acta* **97**, 115 (1986).
3. G.W. Gokel, D.J. Cram, C.L. Liotta and F.L. Cook: *J. Org. Chem.* **74**, 2445 (1974).
4. D.G. Parsons, M.R. Truter and J.N. Wingfield: *Inorg. Chim. Acta* **14**, 45 (1975).
5. M. Shamsipur and A.I. Popov: *J. Am. Chem. Soc.* **101**, 4051 (1979).
6. J.N. Wingfield: *Inorg. Chim. Acta* **45**, 1157 (1980).
7. E. Weber, F. Vögtle, H.-P. Josef, G. Newkome and W.E. Puckett: *Chem. Ber.* **116**, 1906 (1983).
8. E. Weber: *Chem. Ber.* **118**, 4439 (1985).
9. M.C. Howard, E.P. Goodings, J.M. Maud, J.F. Stoddart, J.B. Wolstenholme and D.J. Williams: *J. Chem. Soc. Perkin Trans. 2* 607 (1985).
10. J.F. Stoddart: *Pure Appl. Chem.* **4**, 467 (1988).
11. F. Vögtle and E. Weber: *Angew. Chem. Int. Ed. Engl.* **18**, 753 (1979).
12. G. Yapar, S. Akyüz, and Ç. Erk: Abstracts, *4th Int. Summer School on Supramolecular Chemistry*, Sobleszwo, Poland (1993).
13. G. Yapar and Ç. Erk: Abstracts, *7th Metal-Macromolecule Complexes*, Leiden, Holland (1997).
14. G. Yapar, and Ç. Erk: *Dyes Pigments* **48**, 173 (2001).
15. H. Tuncer and Ç. Erk: *Dyes Pigments* **44**, 81 (2000).
16. Ç. Erk: *Ind. Eng. Chem. Res.* **39**, 3582 (2000).
17. J. Tirado-Rives, R.D. Gandour and F.R. Fronczek: *Tetrahedron Lett.* **23**, 1639 (1982).
18. C.H. Hassal: in *The Baeyer-Villiger-Oxidation of Aldehydes and Ketones, Organic Reactions*, Vol. XI, Wiley, New York (1957), pp. 73–106.
19. J.A. de Boer, J.W.H.M. Uterwijk, J. Geevers, S. Harkema and D.N. Reinhoudt: *J. Org. Chem.* **48**, 2821 (1983).
20. R.M. Izatt, K. Pawlak, J.S. Bradshaw and R.L. Bruening: *Chem. Rev.* **91**, 1721 (1991).
21. R.M. Izatt, K. Pawlak, J.S. Bradshaw and R.L. Bruening: *Chem. Rev.* **95**, 2529 (1995).
22. J.S. Bradshaw and R.M. Izatt: *Acc. Chem. Res.* **30**, 338 (1997).

23. J.E.D. Davies and J.A. Ripmeester (eds.): Physical Methods in Supramolecular Chemistry, in *Comprehensive Supramolecular Chemistry*, Vol. 8, Pergamon, New York (1996).

24. S. Ghosh, M. Petrin, M. Maki and L.R.J. Sousa: *J. Chem. Phys.* **88**, 2913 (1988).

25. A.P. de Silva, Q.N. Gunaratne, T. Gunnlaugsson, A.J.M. Huxley, C.P. McCoy, J.T. Rademacher and T.E. Rice: *Chem. Rev.* **97**, 1515 (1997).

26. (a) A. Göçmen and Ç. Erk: *J. Incl. Phenom.* **26**, 67 (1996). (b) Ç. Erk and A. Gömen: *Talanta* **53**, 137 (2000).

27. Ç. Erk, A. Gömen and M. Bulut: *J. Incl. Phenom.* **37**, 411 (2000).

28. G.W. Buchanan, S. Mathias Y. Lear and C. Bensimon: *Can. J. Chem.* **69**, 404 (1991).

29. H.J. Buschmann: *J. Solution Chem.* **17**, 177 (1988).

30. J.W. Steed and J.L. Atwood (eds.): *Supramolecular Chemistry*, Wiley, New York (2000), pp. 118–119.