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A study of the metal complexing of naphthalene-2,3-crown ethers using fluorescence spectroscopy: Part III☆

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Abstract

2,3-Dioxanaphthalene derivatives of [3*n*]crown-*n* macrocycles were synthesised from 2,3-dihydroxynaphthalene and polyglycoldihalides and studied for their cationic recognition properties using steady state fluorescence spectroscopy. The association constants for the interaction of 2,3-naphtho[12]crown-4, 2,3-naphtho[15]crown-5 and 2,3-naphtho[18]crown-6 with $LiClO_4$, $NaClO_4$, NaSCN, and KSCN were measured in acetonitrile. Excellent correlation of spectroscopic, cationic charge-radii and macrocycle backbone size data was found. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Naphthalene crown ethers; Fluorescence spectroscopy; Cationic recognition; Macrocycle

1. Introduction

A large number of crown ether macrocycles containing different functional side groups have been synthesized and examined for molecular and cationic recognition, using various analytical methods [1–5]. In this regard, fluorescence spectroscopy has been a useful method for estimating the nature and strength of cation–macrocycle interactions [7–15].

Although 2,3-naphtho crown ethers are stable macrocycles [1], they have rarely been the subject matter of cation binding studies [1–3]. On the other hand, the naphthalene moiety is a well-known fluorophore, and its ability to block inter-system crossing in the first excited singlet state is remarkable. Also, it is know that the strong fluorescence induced by interactions of crown ether macrocycles with cations plays an important role in determining the nature of excited singlet and triplet states [6–14]. The complexes obtained from macrocyclic ethers and fluorescent groups have been the subject matter of studies involving the decay of excited state species [7–11].

Cations mainly cause the triplet energy arising from singlet excited and ground state energies and sometimes cause certain heavy atom effects. The changes in fluorescence emission properties caused by metal cations are determined by fluorescence, φ_f and phosphorescence, φ_p quantum yield measurements, since the computations involving

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fluorophore macrocycle cation interactions may give different results [7–14].

In the presence of metal cations, increased phosphorescence quantum yield (φ_p) of a luminescent macrocycle gives complexation enhanced quenching fluorescence spectra (CEQFS) if φ_f is decreased. However, if φ_p is decreased as φ_f is increased, CEFS is also observed. This type of behavior in naphthalene crown ethers was reported by Sousa [11–13]. On the other hand, cation-benzocrown ethers have given CEFS in alcohol [14], and their optical properties were influenced by temperature as well as the type of metal cation employed [10–14]. Anthracenes [8,10] and coumarins [9,15] have been used as stable chromophoric moieties attached to macrocyclic ethers [10.].

Pioneering studies on some naphthalene crown ethers have defined the photophysical interactions associated with their metal complex formation [11–13]. From this work, it is clear that the contribution of cations to the various types of photophysical fluorescence mechanisms can be estimated by fluorescence spectroscopy.

We recently reported macrocyclic ether structures having cation binding abilities [16–20]. This work included a quantitative assessment of the steady state fluorescence spectroscopy of oxygen donors of fluoroionophore macrocyclic ethers that exhibit a single photophysical interaction mechanism [16–20]. We also found that the open chain polyglycol derivatives (podands) were useful fluoroionophores for gauging interactions with cations [21,22].

2. Results and discussion

2.1. Synthesis

The target 2,3-naphthalene macrocycles were prepared as illustrated in Scheme 1, via cyclic condensation of 2,3-dihydroxynaphthalene with polyethylene glycol dihalides or ditosylates in DMF/Na_2CO_3 [18–20]. The reaction yields and other key analytical data are listed in Table 1.

2.2. Equilibrium constants

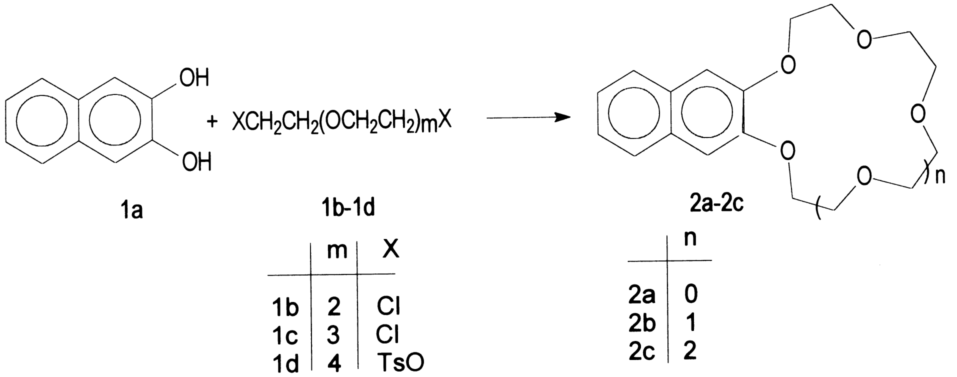
Quantitative estimations of macrocycle–metal interactions in CH_3CN were conducted with the aid of steady state fluorescence measurements of emission intensities in the presence of a cation and fluorophore macrocycle [9,10,19,20]. Equilibrium constants (K_a) for 1/1 mixtures of cation (M^+) and crown ether (L) were determined using Eqs. (1)–(3):

$$L + M^+ \leftrightarrow M^+L \tag{1}$$

$$K_a = [M^+L]/[L][M^+] \tag{2}$$

$$(I_i - I_0)/(I_{max} - I_i) = K_a[M_0] \tag{3}$$

where I_{max} is the intensity of free macrocycle and I_o is the intensity of a 1/1 cation–macrocycle complex. K_a was obtained from the least squared data arising from Eqs. (3) [9,10,16,17].



	m	X
1b	2	Cl
1c	3	Cl
1d	4	TsO

	n
2a	0
2b	1
2c	2

Scheme 1.

Table 1
Analytical data for naphthalene-2,3-crown ethers used in this study

Compound	Mp (°C)	Yield (%)	Mass (m/z)	IR spectra (cm^{-1})	^{1}H NMR spectra (ppm/TMS/CDCl$_3$)	^{13}C NMR spectra (ppm/TMS/DMSO-d_6)
2a	92	8.0	274.2, 186.1, 171.2 130.1, 102.1, 71.1	3047, 2922, 2865, 1628, 1594, 1263, 1126, 904	7.66 (2H, m), 7.34 (2H, m), 7.12 (2H,s), 4.30 (4H, t), 4.02 (4H, t), 3.85 (4H, m)	152.2, 131.3, 128.0, 125.9, 114.4, 72.7, 71.64, 70.0
2b	119	16.2	318.2, 186.1, 171.2 130.1, 102.1, 71.1	3040, 2947, 2864, 1637 1431, 1273, 1127, 958	7.68 (2H, m), 7.34 (2H, m), 7.13 (2H,s), 4.26 (4H, t), 4.00 (4H, t), 3.83 (8H, s)	150.6, 130.6, 127.8, 125.5, 109.0, 71.9, 70.9, 69.9, 69.3
2c	103	36.0	362.3, 186.1, 171.2 130.1, 102.1, 71.1	3040, 2891, 1623, 1596 1484, 1255, 1112, 950	7.75 (2H, m), 7.40 (2H, m), 7.12 (2H,s), 4.36 (4H, t), 4.07 (4H, t), 3.90 (4H, t), 3.83 (4H, t), 3.80 (4H, m)	150.3, 130.5, 127.8, 125.5, 108.7, 71.2, 71.1, 71.0, 69.83, 69.2

2.3. Cation binding

The cation binding strengths obtained from the CEQFS of 2,3-naphthalene crown ethers are affected by the macrocycle ring size and cation radii relationship (Fig. 1) [16,17]. Also, the naphthalene moiety is an excellent aromatic chromophore side group for displaying the cation selectivity of the macrocyclic ethers. It provides very high quantum yields, which permits the measurement of fluorescence emission spectra at rather low concentration ranges. This is another point that is evident from Fig. 2.

The present work included a quantitative assessment of the steady state fluorescence spectroscopy of oxygen donors of fluoroionophore macrocyclic ethers that exhibit a single photophysical interaction mechanism [16–20]. The results revealed excellent cation sensor properties in these aromatic macrocyclic ethers, and the associated binding constants showed good cation selectivity (Table 2).

We found that the [18]crown-6 naphthalene derivative **2c** exhibited the best binding with K^{+} (K_a= 85.819) and its selectivity for Na^{+} (K_a= 21.162) was 4:1. However, the [15]crown-5 naphthalene derivative (**2b**) exhibited greater selectivity for Na^{+} (K_a= 27.446) than for K^{+} (K_a= 3.904), which is consistent with the size of the macrocycle [2–5]. However, the smallest macrocycle (**2a**) gave the lowest association constants with Na^{+} and Li^{+}, which is normal for interactions between such macrocycles and cations having smaller radii [16,17]. We also found that the naphthalene crown ethers generally exhibited relatively higher binding strengths than the benzocrown ethers [2,20]. This is probably due to less intense interactions between the solvent medium (CH$_3$CN) and the complexing naphthalene crown ethers. Similar results have been obtained with coumarin crown ether derivatives in CH$_3$CN, where the fluorescence quantum yields were also high [18–20].

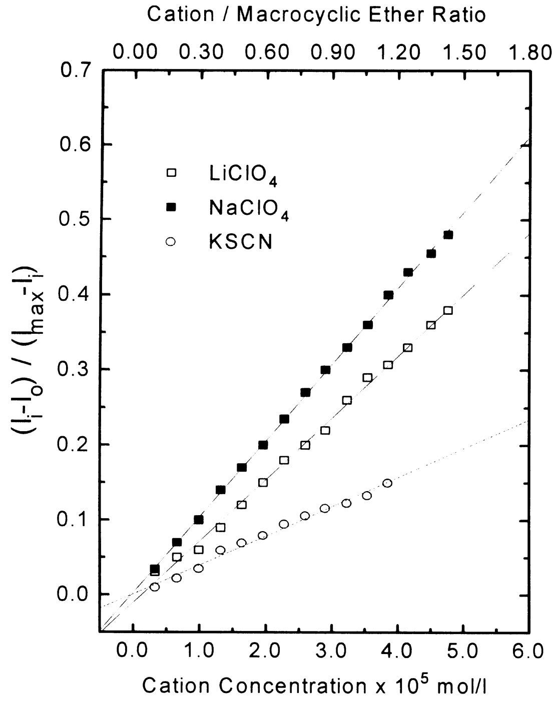


Fig. 1. The binding of 2,3-naphthalene[15]-crown-5 (**2c**) with Li^{+}, Na^{+} and K^{+} in CH$_3$CN.

However, the previous benzo crown ethers we reported gave lower quantum yields than the present 2,3-naphthalene crown ethers. Consequently, our earlier studies of benzo crown ethers required much higher macrocycle and cation concentrations [17].

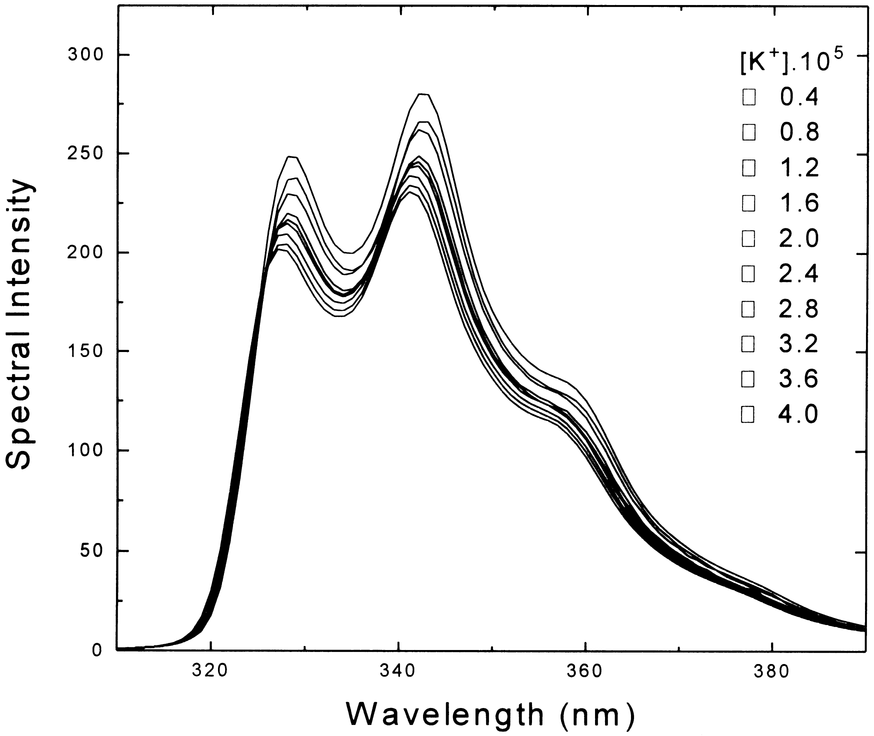


Fig. 2. Effects of KSCN on the fluorescence emission spectra of 2,3-naphtho[18]crown-6 in CH_3CN.

Table 2
Binding data for 1:1 cation–naphthalene-2,3-crown ether interactions in CH_3CN

Compound	Salt	λ_{max} (nm)	I_{max}	I_o[c]	ln K_a	ΔG[d]	Correlation coefficient[e]	Y-intercept[e]
2a	$LiClO_4$	343	372[a]	220	6.60	16.32	0.998	0.009
	$NaClO_4$	343	370[a]	155	7.07	17.49	0.997	0.009
2b	KSCN	343	388[a]	150	8.27	20.41	0.994	0.008
	NaSCN	343	383[a]	227	10.22	25.34	0.998	0.007
	$NaClO_4$	343	384[a]	221	9.23	22.76	0.999	0.009
	$LiClO_4$	343	372[a]	145	9.01	22.22	0.998	−0.001
2c	KSCN	342	276[b]	218	11.36	28.01	0.990	−0.001
	NaSCN	342	260[b]	180	9.96	24.58	0.991	0.004
	$NaClO_4$	342	272[b]	159	9.64	23.77	0.988	0.001

[a] 3.0×10^{-5} mol/l crown ether.
[b] 2.0×10^{-5} mol/l crown ether.
[c] Values from the least squares simulation of Eq. (3).
[d] kJ/mol.
[e] For estimating the K_a from the slope of Eq. (3) (see Fig. 2).

3. Experimental

3.1. General

All chemicals, including 2,3-dihydroxynaphthalene and pentaethylene glycol ditosylate, were obtained from Fluka unless otherwise indicated. The polyethylene dichlorides were available to us from our earlier studies. Mass spectra were recorded on a Fisons VG-Zapspec instrument, IR spectra were recorded in KBr pellets on a Jasco FTIR spectrometer, model 5300, and NMR spectra were obtained on a Bruker CPX-400 spectrometer using TMS as an internal reference. M.p. data are uncorrected and are consistent with literature values [1,3]. Fluorescence measurements were carried out at room temperature on a JASCO FP-750 spectrofluorimeter in dry CH_3CN in 10-mm quartz cells. A spectral bandwidth of 5.0 nm at the excitation maximum (275 nm) was used with optimized concentrations (2.0×10^{-5} or 3.0×10^{-5} mol/l) in order to prevent spectral quenching.

3.2. Metal complexation

Stock solutions of the cations prepared in dry CH_3CN at concentrations of 0.4×10^{-5}–4.0×10^{-5} mol/l were added gradually to a stirred solution of the free macrocyclic fluorophores (3.0–2.0×10^{-5} mol/l) in dry CH_3CN, in the spectrophotometer compartment. Emission peak intensities (I_I) at 343 nm were recorded on the resultant complexed macrocycles, and least squared data were used to calculate the K_a values using Eq. (3).

3.3. Crown ether synthesis

The naphthalene crown ethers were prepared by the method of Pedersen [1], except that Na_2CO_3 was used as the base and DMF or DMSO was used as the solvent [2,20]. To a solution of **1a** (50 mmol) and Na_2CO_3 (100 mmol) in DMF (20 ml) and water (10 ml) was added polyglycol dichloride (50 mmol), and the mixture was stirred at 90–95°C. After 3 days the reaction the mixture was cooled, acidified with HCl (0.1 N, 500 ml), and extracted with $CHCl_3$ (3×50 ml). The contents of the evaporated $CHCl_3$ solutions were chromatographed on Al_3O_3 (30 g) with $CHCl_3/CH_2Cl$ (50/50, 250–300 ml). The products were recrystallised from ethanol (**2a**) or methanol (**2b,c**). Spectral data, product yields and mp values are listed in Table 1.

Acknowledgements

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