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The synthesis of novel 4-(3,4-dimethoxyphenyl)chromenone-crown ethers and their cation binding, as determined using fluorescence spectra

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o-Dihydroxy-4-(3,4-dimethoxyphenyl)-chromenones (coumarins; **3a**,**b**) were synthesised from 1,2,3-trihydroxy- or 1,2,4-triacetoxybenzenes through a reaction with ethyl 3-(3,4-dimethoxyphenyl)-3-oxopropanoate in H_2SO_4 or CF_3COOH. The chromenone-crown ethers (**4a**–**f**) were prepared from the cyclic condensation of *o*-dihydroxy-4-(3,4-dimethoxyphenyl)-chromenones (**3a**,**b**) with poly(ethylene glycol) ditosylates, in the presence of CH_3CN/alkali carbonates. The chromatographically purified original chromenone-crown ethers were identified by ^{1}H NMR, ^{13}C NMR, MALDI-TOF mass spectrometry and elemental analysis. The 1:1 binding constants of Li^+, Na^+ and K^+ with the chromenone-crown ethers were estimated in acetonitrile using fluorescence emission spectroscopy. The complexing-enhanced fluorescence spectra and complexing-enhanced quenching fluorescence spectra, along with the cationic recognition rules of the crown ethers allowed the ion binding powers to be determined.

Keywords: coumarin; chromenone-crown ether; synthesis; cation binding; fluorescence spectroscopy

Introduction

Since the discovery of crown ethers by Pedersen (*1*), their affinity for alkali and alkaline-earth cations has been established and published in several reviews (*2*–*4*). They are commonly used to bind cations, catalyse phase transfer reactions and transport ions across lipophilic membranes (*5*). Crown ethers with oxygen dipoles have been synthesised in order to investigate their alkali and alkaline-earth cations membrane transport and binding properties. These qualities have been characterised by potentiometry, optical spectroscopy as well as NMR spectroscopic methods (*6*, *7*). Although analytical methods have been used for cation determination (*8*–*11*), methods based on fluorescent sensors are advantageous because of sensitivity, selectivity, response time and cost (*12*, *13*). Fluorescence sensors contain fluorophore and ionophore moieties that are linked together. The ionophores that contain suitable light-sensitive moieties may undergo intermolecular changes at the electronic level upon cationic interactions with the donor oxygen atoms. Essentially, the fluorescence spectroscopy of fluorogenic macrocycles is a reliable method for studying cationic recognition (*14*). Crown ethers have also been used for chromatographic separation (*15*, *16*) and metal ion detection (*17*–*19*). We have recently synthesised fluorogenic [12]crown-4, [15]crown-5 and [18]crown-6 derivatives of chromenone and examined their cation binding characteristics using steady-state fluorescence spectroscopy and reported their cationic interaction in acetonitrile (*19*–*22*). Our results exhibited good agreement with the cation radii and the crown ether size as reported (*14*, *19*, *22*). However, the oxygen atom contained in the phenyl moiety in coumarin arms can potentially participate, along with the ester oxygen atoms in the analogue crown ether moiety, in the formation of a 1:1 complex with a host ion (*19*, *22*–*25*).

Here, we report the synthesis of new [12]crown-4, [15]crown-5 and [18]crown-6 derivatives of *o*-dihydroxy-4-(3,4-dimethoxyphenyl)-chromenones, as well as their spectral data and their cationic recognition capacities for Li^+, Na^+ and K^+ perchlorate salts using fluorescence spectroscopy (Scheme 1).

Experimental

General

The starting chemicals were purchased from Aldrich (St Louis, MO, USA) or Merck (Darmstadt, Germany), unless otherwise stated. Melting points were obtained on a Gallenkamp apparatus. IR spectra were taken from KBr pellets with a Schimadzu FT-IR spectrometer, model 8300. ^{1}H and ^{13}C NMR spectra were obtained with a Bruker DPX-400, 400 MHz High Performance Digital NMR spectrometer. Mass spectra were obtained with a MALDI-TOF instrument, model Bruker Autoflex III. Elemental analysis was performed on a LECO CHNS 92 instrument. UV–Vis measurements were taken with an Agilent 8453 UV–VIS spectrophotometer. Fluorescence measurements were carried out at room temperature on a Hitachi F-7000 Fluorescence Spectrophotometer.

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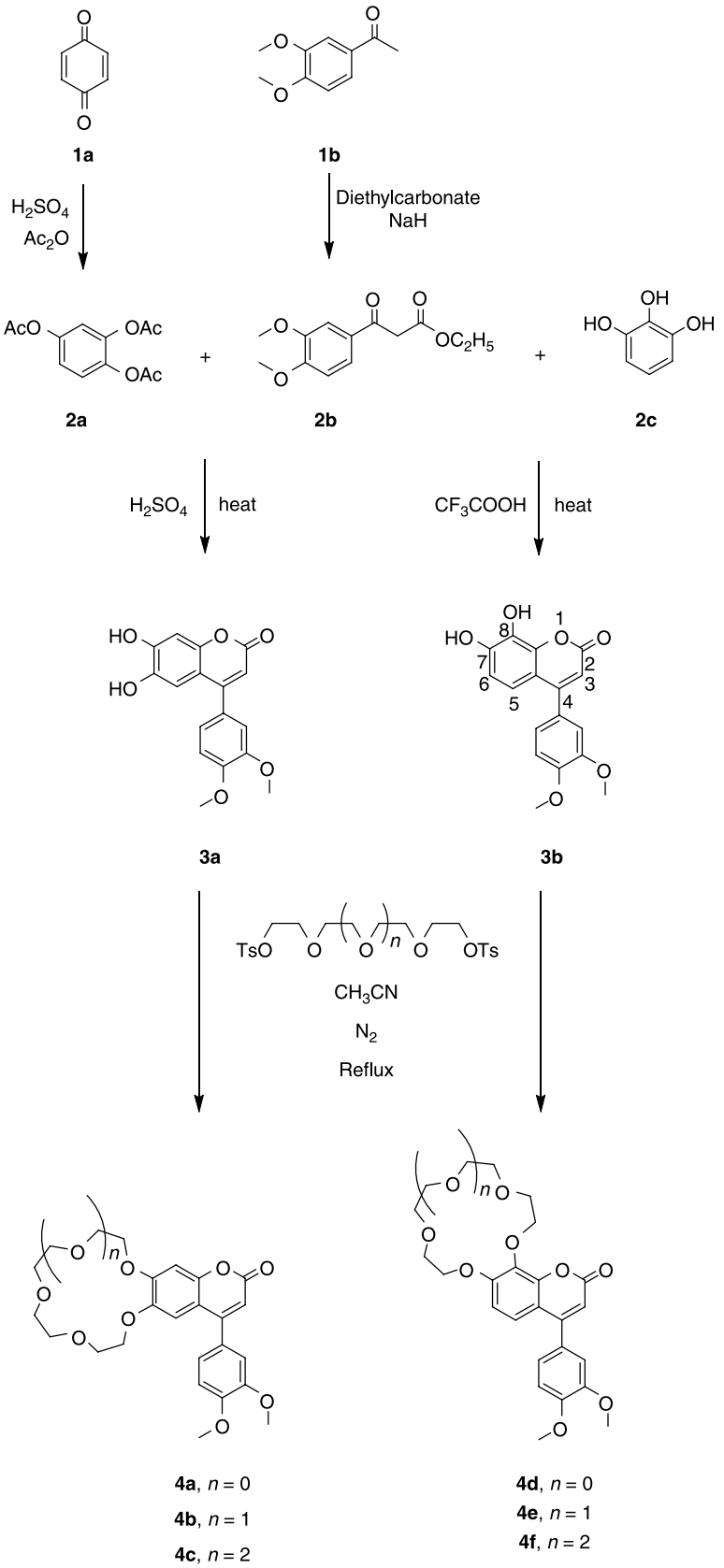

Scheme 1. Synthesis of chromenone-crown ethers.

The 1:1 binding constants, K_b, of the chromenone-crown ethers with Li^+, Na^+ and K^+ perchlorates were determined via a fluorometric method which has been previously described (*19*, *21*, *22*, *26*). Salt solutions (1.0×10^{-3} mol/l) in dry CH_3CN were added stepwise to a stirred 2.00 ml solution of the chromenone-crown ethers (1.0×10^{-5} or 3.0×10^{-5} mol/l) in dry CH_3CN. The mixture was contained in a 10-mm quartz cell, which was placed in the spectrophotometer cell compartment. The concentrations were optimised in order to prevent fluorescence quenching. Fluorescence emission intensities were recorded at 5.0 nm bandwidth.

Synthesis

*Synthesis of 1,2,4-triacetoxybenzene (**2a**)*

Concentrated sulphuric acid (2.5 ml) was added to acetic anhydride (60 ml) in a 600-ml beaker. Next, *p*-quinone (**1a**; 20.0 g, 185 mmol) was added to the stirred solution in small portions at 40–50°C. The reaction mixture was then cooled, poured into ice-water (300 ml), filtered, washed with water until neutral and dried. The product **2a** was recrystallised from ethyl alcohol and dried 40.20 g (86%); mp: 96–97°C (lit. 96–97°C (*27*)).

*Synthesis of ethyl 3-(3,4-dimethoxyphenyl)-3-oxopropanoate (**2b**; $C_{13}H_{16}O_5$)*

A solution of 3,4-dimethoxyacetophenone (**1b**; 10.0 g, 55 mmol) in diethyl carbonate (20 ml) was added dropwise to a stirred solution of sodium hydride (50% oil dispersion, 8.0 g by wt) in diethyl carbonate (20 ml), under an N_2 atmosphere. After the addition, the mixture was heated at reflux and then cooled. The mixture was poured into ice-water:HCl (10:1), extracted with $CHCl_3$ (4× 60 ml), dried over $CaCl_2$ and evaporated to give a yellow oil **2b** (*28*), 11.97 g (85%). IR [liquid, ν_{max} (cm^{-1})]: 3078 (C—H, aryl), 2977–2842 (C—H, alkyl), 1740 (C═O), 1674 (O—C═O), 1580 (C═C, aromatic), 1417 (C—O, aryl) and 1140 (C—O, alkyl).

*Synthesis of 6,7-dihydroxy-4-(3,4-dimethoxyphenyl) chromenone (**3a**; $C_{17}H_{14}O_6$)*

A mixture of 1,2,4-triacetoxybenzene (**2a**; 28.26 g, 90 mmol), ethyl 3-(3,4-dimethoxyphenyl)-3-oxopropanoate (**2b**; 22.68 g, 90 mmol) and H_2SO_4 (25 ml) was heated at 120°C for 3 h under an N_2 atmosphere. The mixture was cooled and the product was collected by filtration, washed with water and dried *in vacuo* to yield **3a**, 5.6 g (25%); mp: >300°C (lit. >300°C (*29*, *30*)). IR [KBr, ν_{max} (cm^{-1})]: 3400 (OH), 3165 (C—H, aryl), 2924–2852 (C—H, alkyl), 1672 (C═O, lactone), 1618 (C═C, aromatic) and 1213 (C—O). ^{1}H NMR (CD_3OD, 400 MHz): δ (ppm) 3.79 (s, 3H, OCH_3), 3.82 (s, 3H, OCH_3), 6.01 (s, 1H), 6.70 (d, $J = 2.0$ Hz, 1H), 6.84 (d, $J = 8.2$ Hz, 1H), 6.86 (s, 1H), 7.0 (dd, $J = 8.5$, 1.6 Hz, 1H). MS (*m/z*): 314.8 $[M]^+$.

*Synthesis of 7,8-dihydroxy-4-(3,4-dimethoxyphenyl) chromenone (**3b**; $C_{17}H_{14}O_6$)*

A mixture of pyrogallol (**2c**; 5.99 g, 47 mmol), ethyl 3-(3,4-dimethoxyphenyl)-3-oxopropanoate (**2b**; 11.97 g, 47 mmol) and CF_3COOH (15 ml) was refluxed for 6 h, cooled, collected by filtration, washed with water and dried *in vacuo* to yield **3b**, 7.89 g (52%); mp: 271–272°C (lit. 274.1–274.4°C (*31*)). IR [KBr, ν_{max} (cm^{-1})]: 3436 (OH), 3200 (C—H, aryl), 2956–2839 (C—H, alkyl), 1693 (C═O, lactone), 1600 (C═C, aromatic), 1305 (C—O, aryl) and 1174 (C—O, alkyl). ^{1}H NMR (CD_3OD, 400 MHz): δ (ppm) 3.78 (s, 3H, OCH_3), 3.80 (s, 3H, OCH_3), 6.10 (s, 1H), 6.72 (d, $J = 2.0$ Hz, 1H), 6.85 (d, $J = 8.4$ Hz, 1H), 6.89 (d, $J = 8.6$ Hz, 1H), 6.92 (dd, $J = 8.5$, 1.6 Hz, 1H). MS (*m/z*): 314.7 $[M]^+$.

*General procedure for the synthesis of chromenone-crown ethers (**4a**–**f**)*

The typical procedure for the cyclisation reaction, which leads to macrocycle ethers (**4a**–**f**), is as follows. A mixture of *o*-dihydroxy-4-(3,4-dimethoxyphenyl)chromenone (**3a**,**b**; 3 mmol), poly(ethylene glycol) ditosylate (3 mmol) and metal carbonate (6 mmol) was dissolved in CH_3CN (80 ml). The mixture was heated to 80–85°C for 35–40 h. The solvent was evaporated *in vacuo.* Diluted HCl was added to the residue and the mixture was extracted with $CHCl_3$ (4× 50 ml). The combined organic layers were washed with water, dried over $CaCl_2$ and evaporated *in vacuo*. Chromatography of the crude products (silica gel 60, Merck) with chloroform gave pure chromenone-crown ethers (**4a**–**f**).

*15-(3,4-Dimethoxyphenyl)-5,6,8,9-tetrahydro-2H-[1,4,7,10]tetraoxacyclo-dodeca-[2,3-g]chromen-13(3H)-one (**4a**; $C_{23}H_{24}O_8$)*

A mixture of compound **3a** (1.0 g, 3.18 mmol), Na_2CO_3 (0.68 g, 6.37 mmol) and tri(ethylene glycol) ditosylate (1.46 g, 3.18 mmol) in CH_3CN (60 ml) reacted as described above to afford **4a**, 0.11 g (8%); mp: 181–182°C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 3.91 (s, 3H, OCH_3), 3.95 (t, $J = 4.3$ Hz, 4H), 3.96 (s, 3H, OCH_3), 4.10 (t, $J = 4.3$ Hz, 4H), 4.23 (t, $J = 4.0$ Hz, 4H), 6.23 (s, 1H), 6.93 (s, 1H), 6.94 (d, $J = 2.0$ Hz, 1H), 6.99 (s, 1H), 7.0 (d, $J = 8.2$ Hz, 1H), 7.03 (dd, $J = 8.4$, 2.0 Hz, 1H). ^{13}C NMR ($CDCl_3$): δ (ppm) 56.28 (OCH_3), 56.34 (OCH_3), 69.74, 70.19, 70.46, 71.09, 71.99, 74.37, 103.98, 111.60, 111.80, 112.38, 112.99, 117.30, 121.43, 128.29, 146.99, 149.51, 150.55, 151.56, 155.11, 155.46, 161.52. MS (*m/z*): 428.9 $[M]^+$, 450.9 $[M+Na]^+$.

Anal. calcd for $C_{23}H_{24}O_8$ (%): C, 64.48; H, 5.65; found: C, 64.35; H, 5.57.

*18-(3,4-Dimethoxyphenyl)-5,6,8,9,11,12-hexahydro-2H-[1,4,7,10,13]-pentaoxacyclo-pentadeca[2,3-*g *]chromen-16(3H)-one (***4b***; $C_{25}H_{28}O_9$)*

A mixture of compound **3a** (1.0 g, 3.18 mmol), Na_2CO_3 (0.68 g, 6.37 mmol) and tetra(ethylene glycol) ditosylate (1.60 g, 3.18 mmol) in CH_3CN (60 ml) was reacted as described above to produce **4b**, 0.31 g (20%); mp: 159–160°C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 3.86 (t, $J = 4.3$ Hz, 4H), 3.90 (s, 3H, OCH_3), 3.94 (t, $J = 4.0$ Hz, 4H), 3.96 (s, 3H, OCH_3), 4.0 (t, $J = 4.3$ Hz, 4H), 4.20 (t, $J = 4.0$ Hz, 4H), 6.22 (s, 1H), 6.86 (s, 1H), 6.94 (d, $J = 2.0$ Hz, 1H), 6.98 (s, 1H), 6.99 (d, $J = 8.0$ Hz, 1H), 7.03 (dd, $J = 8.2$, 2.0 Hz, 1H). ^{13}C NMR ($CDCl_3$): δ (ppm) 56.27 (OCH_3), 56.34 (OCH_3), 68.98, 69.17, 69.62, 70.16, 70.43, 70.71, 71.22, 71.33, 101.70, 111.09, 111.61, 111.77, 111.99, 112.08, 121.38, 128.47, 146.02, 149.45, 150.48, 150.73, 153.36, 155.55, 161.70. MS (*m/z*): 472.9 $[M]^+$, 494.9 $[M+Na]^+$, 510.9 $[M+K]^+$.

Anal. calcd for $C_{25}H_{28}O_9$ (%): C, 63.55; H, 5.97; found: C, 63.42; H, 5.83.

*21-(3,4-Dimethoxyphenyl)-5,6,8,9,11,12,14,15-octahydro-2H-[1,4,7,10,13,16]hexaoxacyclooctadeca[2,3-*g *]chromen-19(3H)-one (***4c***; $C_{27}H_{32}O_{10}$)*

A mixture of compound **3a** (1.0 g, 3.18 mmol), K_2CO_3 (0.88 g, 6.37 mmol) and penta(ethylene glycol) ditosylate (1.67 g, 3.18 mmol) in CH_3CN (60 ml) was reacted as described above to give **4c**, 0.13 g (8%); mp: 106–107°C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 3.69 (t, $J = 4.0$ Hz, 4H), 3.81 (t, $J = 4.0$ Hz, 4H), 3.84 (s, 3H, OCH_3), 3.89 (t, $J = 4.0$ Hz, 4H), 3.90 (s, 3H, OCH_3), 3.96 (t, $J = 4.0$ Hz, 4H), 4.16 (t, $J = 4.0$ Hz, 4H), 6.16 (s, 1H), 6.81 (s, 1H), 6.88 (d, $J = 2.0$ Hz, 1H), 6.91 (s, 1H), 6.94 (d, $J = 8.4$ Hz, 1H), 6.96 (dd, $J = 8.2$, 2.0 Hz, 1H). ^{13}C NMR ($CDCl_3$): δ (ppm) 56.27 (OCH_3), 56.34 (OCH_3), 69.25, 69.59, 70.12, 70.40, 70.68, 70.80, 70.91, 71.12, 71.23, 71.30, 101.62, 111.52, 111.66, 111.72, 111.90, 112.09, 121.37, 128.42, 145.96, 149.42, 150.44, 150.58, 155.42, 155.58, 161.90. MS (*m/z*): 539.0 $[M+Na]^+$, 555.0 $[M+K]^+$.

Anal. calcd for $C_{27}H_{32}O_{10}$ (%): C, 62.78; H, 6.24; found: C, 62.58; H, 6.50.

*13-(3,4-Dimethoxyphenyl)-5,6,8,9-tetrahydro-2H-[1,4,7,10]tetraoxacyclo-dodeca[2,3-*h *]chromen-15(3H)-one (***4d***; $C_{23}H_{24}O_8$)*

A mixture of compound **3b** (1.0 g, 3.18 mmol), Na_2CO_3 (0.68 g, 6.37 mmol) and tri(ethylene glycol) ditosylate (1.46 g, 3.18 mmol) in CH_3CN (60 ml) was reacted as described above to give **4d**, 0.31 g (23%); mp: 194–195°C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 3.91 (s, 3H, OCH_3), 3.96 (s, 3H, OCH_3), 3.97 (t, $J = 4.3$ Hz, 4H), 4.22 (t, $J = 4.3$ Hz, 4H), 4.41 (t, $J = 4.0$ Hz, 4H), 6.22 (s, 1H), 6.80 (d, $J = 8.9$ Hz, 1H), 6.94 (d, $J = 1.6$ Hz, 1H), 6.98 (d, $J = 8.2$ Hz, 1H), 7.02 (dd, $J = 8.2$, 2.0 Hz, 1H), 7.24 (d, $J = 8.6$ Hz, 1H). ^{13}C NMR ($CDCl_3$): δ (ppm) 56.27 (OCH_3), 56.34 (OCH_3), 69.75, 70.01, 70.66, 71.03, 72.34, 75.37, 110.22, 111.53, 111.93, 112.12, 114.42, 121.53, 122.40, 128.35, 137.20, 148.91, 149.42, 150.53, 155.41, 156.02, 160.90. MS (*m/z*): 428.9 $[M]^+$, 450.9 $[M+Na]^+$, 466.9 $[M+K]^+$.

Anal. calcd for $C_{23}H_{24}O_8$ (%): C, 64.48; H, 5.65; found: C, 64.40; H, 5.76.

*16-(3,4-Dimethoxyphenyl)-5,6,8,9,11,12-hexahydro-2H-[1,4,7,10,13]-pentaoxacyclo-pentadeca[2,3-*g *]chromen-16(3H)-one (***4e***; $C_{25}H_{28}O_9$)*

A mixture of compound **3b** (1.0 g, 3.18 mmol), Na_2CO_3 (0.68 g, 6.37 mmol) and tetra(ethylene glycol) ditosylate (1.60 g, 3.18 mmol) in CH_3CN (60 ml) was reacted as described above to give **4e**, 0.48 g (32%); mp: 144–145°C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 3.78 (t, $J = 4.0$ Hz, 4H), 3.91 (s, 3H, OCH_3), 3.95 (s, 3H, OCH_3), 3.96 (t, $J = 4.3$ Hz, 4H), 4.22 (t, $J = 4.3$ Hz, 4H), 4.36 (t, $J = 4.7$ Hz, 4H), 6.21 (s, 1H), 6.79 (d, $J = 8.9$ Hz, 1H), 6.94 (d, $J = 1.6$ Hz, 1H), 6.98 (d, $J = 8.2$ Hz, 1H), 7.02 (dd, $J = 8.2$, 2.0 Hz, 1H), 7.22 (d, $J = 8.6$ Hz, 1H). ^{13}C NMR ($CDCl_3$): δ (ppm) 56.27 (OCH_3), 56.34 (OCH_3), 69.04, 69.43, 70.41, 70.52, 70.64, 71.12, 71.16, 73.85, 109.10, 111.52, 111.94, 112.07, 114.18, 121.53, 122.27, 128.39, 136.11, 148.93, 149.41, 150.49, 155.29, 155.94, 160.99. MS (*m/z*): 473.0 $[M]^+$, 495.0 $[M+Na]^+$, 511.0 $[M+K]^+$.

Anal. calcd for $C_{25}H_{28}O_9$ (%): C, 63.55; H, 5.97; found: C, 63.62; H, 5.90.

*19-(3,4-Dimethoxyphenyl)-5,6,8,9,11,12,14,15-octahydro-2H-[1,4,7,10,13,16]hexaoxacyclooctadeca[2,3-*g *]chromen-19(3H)-one (***4f***; $C_{27}H_{32}O_{10}$)*

A mixture of compound **3b** (1.0 g, 3.18 mmol), K_2CO_3 (0.88 g, 6.37 mmol) and penta(ethylene glycol) ditosylate (1.67 g, 3.18 mmol) in CH_3CN (60 ml) was reacted as described above to give **4f**, 0.18 g (11%); mp: 151–152°C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 3.70 (t, $J = 4.3$ Hz, 4H), 3.84 (s, 3H, OCH_3), 3.88 (t, $J = 5.0$ Hz, 4H), 3.89 (s, 3H, OCH_3), 3.94 (t, $J = 5.4$ Hz, 4H), 4.17 (t, $J = 5.4$ Hz, 4H), 4.28 (t, $J = 5.0$ Hz, 4H), 6.14 (s, 1H), 6.74 (d, $J = 8.9$ Hz, 1H), 6.87 (d, $J = 2.0$ Hz, 1H), 6.91 (d, $J = 8.6$ Hz, 1H), 6.95 (dd, $J = 8.2$, 2.0 Hz, 1H), 7.16 (d, $J = 8.9$ Hz, 1H). ^{13}C NMR ($CDCl_3$): δ (ppm) 56.27

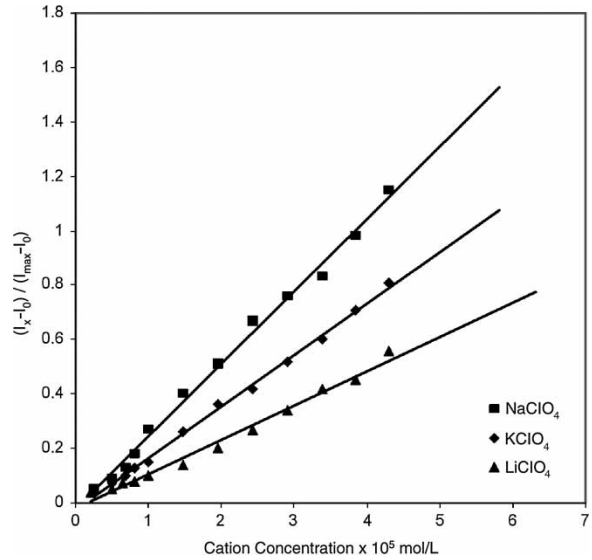

Figure 1. The estimation of K_b of **4e**/$LiClO_4$, $NaClO_4$ and $KClO_4$ complexes based on Equation (3).

(OCH_3), 56.34 (OCH_3), 69.29, 69.74, 70.56, 70.71, 70.96, 71.03, 71.04, 71.23, 71.45, 73.28, 109.71, 111.52, 111.93, 112.18, 114.32, 121.53, 122.29, 128.36, 136.13, 148.90, 149.42, 150.51, 155.12, 155.89, 160.99. MS (*m/z*): 517.0 $[M]^+$, 539.0 $[M+Na]^+$, 555.0 $[M+K]^+$.

Anal. calcd for $C_{27}H_{32}O_{10}$ (%): C, 62.78; H, 6.24; found: C, 62.65; H, 6.13.

Results and discussion

o-Dihydroxy-4-(3,4-dimethoxyphenyl)-chromenone-crown ether derivatives (**4a**–**f**) were synthesised from the poly(ethylene glycol) ditosylates and corresponding

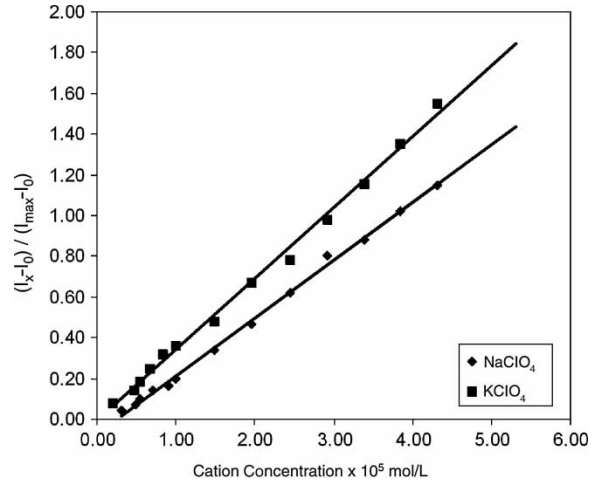

Figure 2. The estimation of the K_b of **4f**/$KClO_4$ and $NaClO_4$ complexes based on Equation (3).

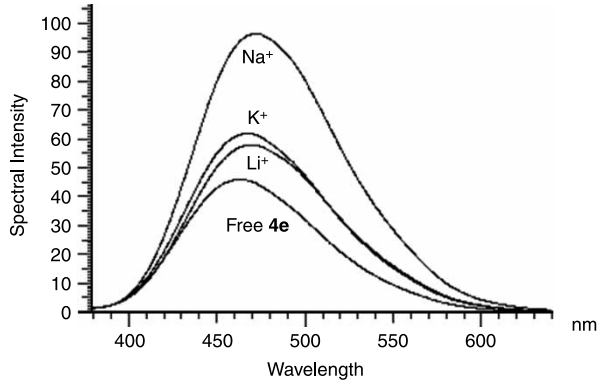

Figure 3. The CEF emission spectra of **4e** (1×10^{-5} mol/l, bottom line) and its complexes with Li^+, Na^+ and K^+ perchlorates (2×10^{-4} mol/l) in acetonitrile.

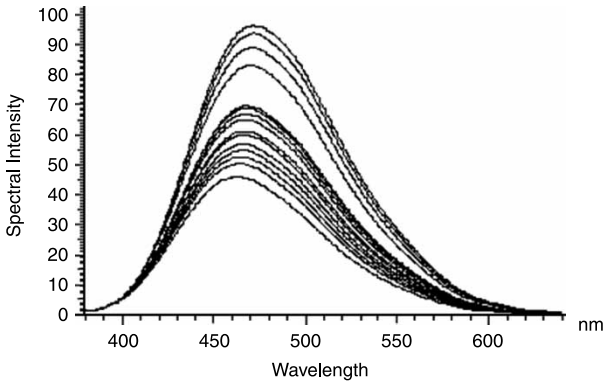

Figure 4. The CEF emission spectra of **4e** (1×10^{-5} mol/l, bottom line) as a function of $NaClO_4$ concentration increasing 0–2×10^{-4} mol/l.

o-dihydroxy-4-(3,4-dimethoxyphenyl)-chromenone, 6,7-dihydroxy-4-(3,4-dimethoxyphenyl)chromenone (**3a**) and 7,8-dihydroxy-4-(3,4-dimethoxyphenyl)-chromenone (**3b**). These chromenones were prepared from 1,2,4-

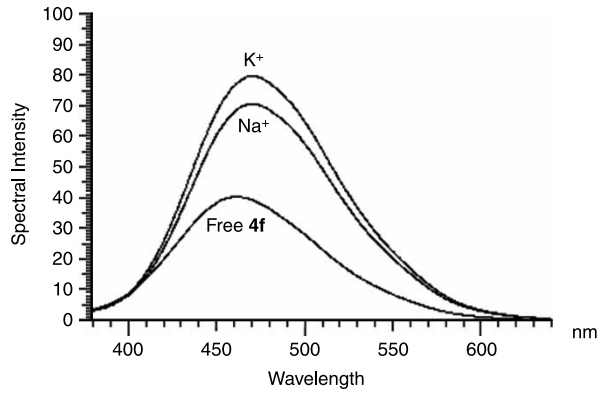

Figure 5. The CEF emission spectra of **4f** (1×10^{-5} mol/l, bottom line) and its complexes with Na^+ and K^+ perchlorates (2×10^{-4} mol/l) in acetonitrile.

Table 1. The 1:1 cation binding constants, K_b, extracted from CEQFS acquired at room temperature in acetonitrile.

Compound	Ex λ_{max} (nm)	Em λ_{max} (nm)	Salt	I_f	ln K_b	$-\Delta G$ (kJ/mol)
4a[a]	337	454	$LiClO_4$	25.5	9.88 ± 0.13	24.49 ± 0.33
			$NaClO_4$	25.5	10.09 ± 0.27	25.00 ± 0.49
			$KClO_4$	25.5	10.00 ± 0.18	24.80 ± 0.25
4b[a]	346	450	$LiClO_4$	41.9	9.28 ± 0.07	22.98 ± 0.19
			$NaClO_4$	41.9	9.00 ± 0.25	22.30 ± 0.62
			$KClO_4$	41.9	8.66 ± 0.10	21.45 ± 0.26
4c[b]	340	451	$NaClO_4$	70.8	9.34 ± 0.10	23.14 ± 0.25
			$KClO_4$	70.8	9.54 ± 0.26	23.64 ± 0.47
4d[a]	332	462	$LiClO_4$	66.9	9.34 ± 0.12	23.14 ± 0.31
			$NaClO_4$	66.9	9.42 ± 0.18	23.33 ± 0.25
			$KClO_4$	66.9	9.27 ± 0.09	22.96 ± 0.13

[a] 1×10^{-5} mol/l.
[b] 3×10^{-5} mol/l.

Table 2. The 1:1 cation binding constants, K_b, extracted from CEFS acquired at room temperature in acetonitrile.

Compound	Ex λ_{max} (nm)	Em λ_{max} (nm)	Salt	I_f	ln K_b	$-\Delta G$ (kJ/mol)
4e[a]	328	463	$LiClO_4$	45.9	9.66 ± 0.23	23.94 ± 0.46
			$NaClO_4$	45.9	10.87 ± 0.34	26.93 ± 0.74
			$KClO_4$	45.9	9.95 ± 0.17	24.65 ± 0.42
4f[a]	327	462	$NaClO_4$	40.2	10.66 ± 0.13	26.41 ± 0.32
			$KClO_4$	40.2	10.95 ± 0.22	27.12 ± 0.22

[a] 1×10^{-5} mol/l.

triacetoxy- or 1,2,3-trihydroxybenzenes condensing with ethyl 3-(3,4-dimethoxyphenyl)-3-oxopropanoate (**2b**) in H_2SO_4 or CF_3COOH, respectively (Scheme 1).

Compounds **3a** and **b** were reacted with tri-/tetra- and penta(ethylene glycol) ditosylate to give the corresponding chromenone-crown ethers **4a**–**c** and **4d**–**f**, respectively. The residues were subjected to chromatography over a silica gel column eluted with $CHCl_3$. This produced the chromenone-crown ethers (**4a**–**f**) in 8–32% yields. The novel compounds have been characterised by elemental analysis, ^{1}H NMR, ^{13}C NMR and MALDI-TOF mass spectroscopy.

The binding constants, K_b, for a 1:1 mixture of cation (M^+) and chromenone-crown ether (L) were determined using the following equations (*19*, *21*, *22*, *26*):

$$L + M^+ \rightleftharpoons M^+L \quad (1)$$

$$K_b = [M^+L]/[L][M^+] \quad (2)$$

$$K_b[M_o] = (I_x - I_o)/(I_{max} - I_x) \quad (3)$$

where I_o is the intensity of free chromenone-crown ether and I_x is the peak fluorescence intensity of a complexed

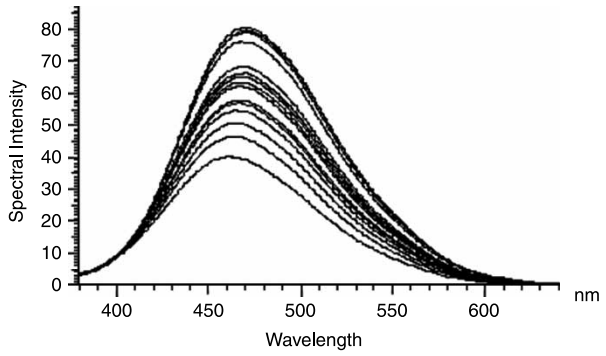

Figure 6. The CEF emission spectra of **4f** (1×10^{-5} mol/l, bottom line) depending on $KClO_4$ concentration increasing from 0 to 2×10^{-4} mol/l.

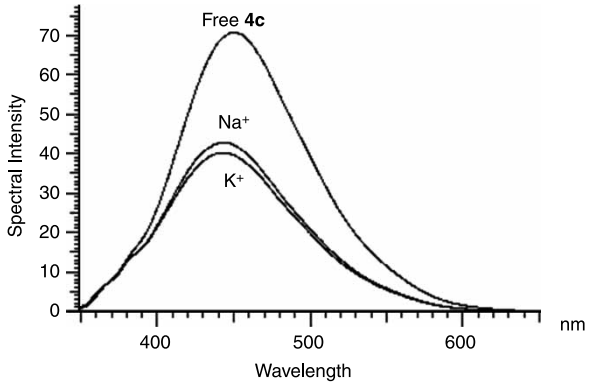

Figure 7. The CEQF emission spectra of **4c** (3×10^{-5} mol/l, bottom line) and its complexes with Na^+ and K^+ perchlorates (2×10^{-4} mol/l) in acetonitrile.

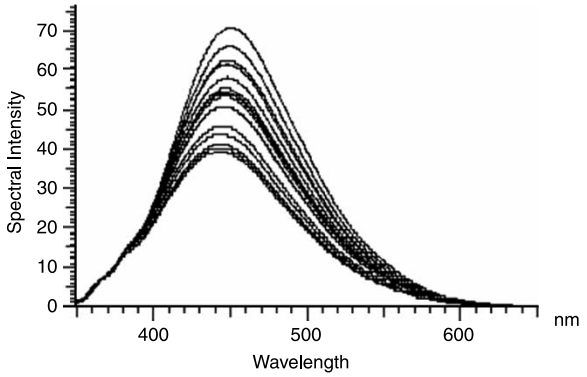

Figure 8. The CEQF emission spectra of **4c** (3×10^{-5} mol/l, top line) as a function of $KClO_4$ concentration increasing 0–2×10^{-4} mol/l.

chromenone-crown ether for a given cation concentration, $[M_o]$. I_{max} is the intensity observed in the presence of excess cation at room temperature. The binding constant, K_b, was calculated with MS Office (Excel) using least squared data according to Equation (3). The $(I_x - I_o)/(I_{max} - I_x)$ values were plotted versus $[M_o]$ using the recorded intensity data (Figures 1 and 2). The resulting values of $\ln K_b$ and Gibbs enthalpy (ΔG) are displayed in Tables 1 and 2.

The binding constant, K_b, was estimated from the emission fluorescence spectra of chromenone-crown ether complexes in acetonitrile (Tables 1 and 2). However, [15]crown-5 and [18]crown-6 derivatives of 7,8-dihydroxy-4-(3,4-dimethoxyphenyl)chromenone (**4e**, **f**) have exhibited complexing-enhanced fluorescence spectra (CEFS) upon cation complexation (Figures 3–6), whereas the [12]crown-4 derivative of 7,8-dihydroxy-4-(3,4-dimethoxyphenyl)chromenone and 6,7-dihydroxy-4-(3,4-dimethoxyphenyl)-chromenone-crown ether derivatives (**4a**–**d**) exhibited complexing-enhanced quenching fluorescence spectra (CEQFS) as they became complexed with Li^+, Na^+ and K^+ perchlorate salts in acetonitrile (Figures 7 and 8). These results are similar to the results we observed for other derivatives of these chromophore structures (*14*, *19*, *21*, *22*).

We found that the chromenone-crown ether derivative **4a** was not selective for Na^+, K^+ and Li^+. Its binding affinity was $Na^+ > K^+ > Li^+$. The Li^+ selectivity of compound **4b** as a [15]crown-5 derivative was greater than its selectivity for Na^+ and K^+. Compound **4c** was quite selective for Na^+ and K^+, but had higher affinity for K^+. The selectivity order of **4d** was $Na^+ > Li^+ > K^+$. Compound **4e** exhibited the best binding with Na^+, with a binding order of $Na^+ > K^+ > Li^+$. Its selectivity for Na^+:K^+ and Na^+:Li^+ were 2.5:1 and 3.5:1, respectively. Compound **4f** was quite selective for K^+ as compared to Na^+. No significant interaction was observed between Li^+ and **4c** or **f**. This was because of the large ring size of the crown ether and small radii of cation. This result showed that the binding of such molecules depends on the structure, ring size of crown ether and the cation radii.

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