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The synthesis and fluorescence properties of novel chromenone-crown ethers

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o-Dihyroxy-3-phenylchromenone derivatives, namely, 6,7-dihydroxy-3-(3′,4′-dimethoxyphenyl)chromenone and 6,7-dimethoxy-3-(3′,4′-dihydroxyphenyl)chromenone, were obtained from 2,4,5-trihydroxybenzaldehyde/3,4-dimethoxyphenylacetic acid and 2-hydroxy-4,5-dimethoxybenzaldehyde/3,4-dihydroxyphenylacetic acid, respectively, in the presence of acetic anhydride and sodium acetate under an inert atmosphere, after treatment with MeOH/HCl(aq). The chromenone-crown ethers were prepared from cyclic condensation of *o*-dihydroxy-3-phenylchromenones with poly(ethylene glycol) ditosylates in the presence of CH_3CN/alkali metal carbonates. The chromatographically purified novel chromenone-crown ethers were identified by ^1H NMR, MALDI-TOF mass spectrometry and elemental analysis. The fluorescence and UV–vis spectroscopic properties of the obtained chromenone-crown ethers and their complexes with Li^+, Na^+ and K^+ perchlorate salts were estimated in acetonitrile. The quantum yields of novel chromenone-crown ethers were determined by the comparative method.

Keywords: chromenone-crown ethers; 3-phenylchromenone; quantum yield; synthesis; cation binding

Introduction

Pedersen (*1*) has shown that crown ethers have remarkable binding properties for specific metal cations. Generally, crown ethers selectively display a stable complex with metal cations which best matches the cavity; however, selectivity and stability depend on solvent properties (*2*). Much of the research involving crown ethers has focused on metal ion selectivity for the development of optical sensors due to their sensitivity and reactivity in the presence of metal cations (*3*). Crown ethers are commonly used to bind cations, catalyse phase-transfer reactions (*4*), as colorimetric reagents (*5*), in chromatographic separations (*6*) and for the photometric determination of metal cations (*7*). Spectrofluorometry is a very sensitive technique that measures both emission and excitation intensities of a fluorescent molecule, which is usually influenced by the characteristics of the environment and small changes in the positions of the energetic levels that determine the quantum yield and fluorescence decay (*8*). Chromenone-crown ethers have been used in metal ion detection (*9–11*). We have synthesised fluorogenic chromenone-crown ether derivatives of 12-crown-4, 15-crown-5 and 18-crown-6, and have examined their cation-binding effects in acetonitrile using steady-state fluorescence spectroscopy (*11–14*), conductometry (*15*, *16*) and extraction (*17*).

We now report on the synthesis (Scheme 1), spectral data and quantum yields of new 12-crown-4, 15-crown-5 and 18-crown-6 derivatives of *o*-dihydroxy-3-phenylchromenone and their complexes with Li^+, Na^+ and K^+ perchlorate salts using fluorescence spectroscopy (Table 1).

Experimental

General

The starting chemicals, 2,4,5-trimethoxybenzaldehyde, 3,4-dihydroxyphenylacetic acid and 3,4-dimethoxyphenylacetonitrile, were purchased from Acros (Geel, Belgium), Aldrich (St Louis, MO, USA) or Merck (Darmstadt, Germany), unless otherwise cited. Melting points were obtained on a Gallenkamp apparatus. ^1H NMR spectra were determined by a Brucker DPX-400, 400 MHz high-performance digital FT-NMR spectrometer. Mass spectra were obtained with a MALDI-TOF instrument, model Bruker Autoflex III. Elemental analyses were performed on a LECO CHNS 92 instrument. UV–vis and fluorescence spectra were obtained on an Agilent 8453 model UV–vis and a Hitachi F-7000 fluorescence spectrophotometer, respectively. All spectrophotometric measurements were carried out at 20°C. Fluorescence quantum yields (Φ_F) were determined by the comparative method with quinine sulphate as the standard (*18–20*).

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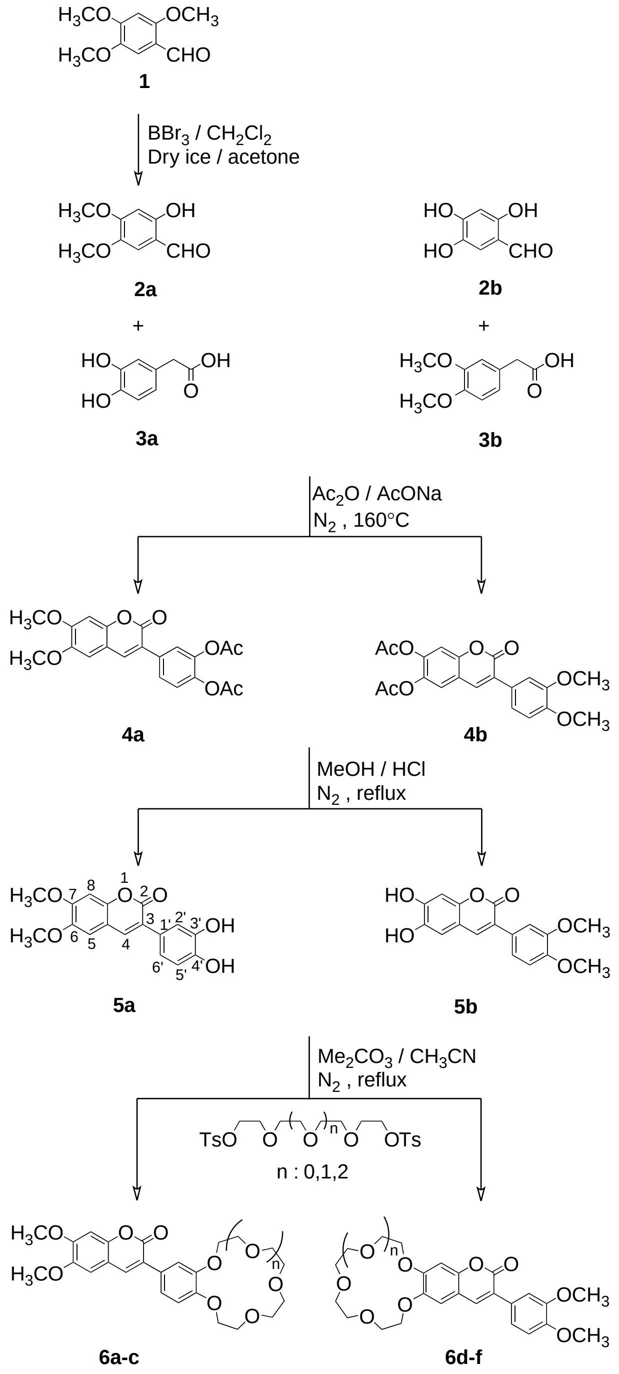

Scheme 1. Synthesis of chromenone-crown ethers.

Table 1. Absorption, excitation, emission wavelengths (nm), Stokes' shifts (nm) and quantum yields of chromenone-crown ethers in CH_3CN at 20°C.

Compound	Ligand	Complexes		
		Li^+	Na^+	K^+
6a				
$\lambda_{absorption}$ (nm)	362	360	361	362
$\lambda_{excitation}$ (nm)	370	370	370	370
$\lambda_{emission}$ (nm)	457	456	456	457
Δ_{Stokes} (nm)	95	96	95	95
Φ_F	0.45	0.38	0.30	0.41
6b				
$\lambda_{absorption}$ (nm)	367	366	367	366
$\lambda_{excitation}$ (nm)	371	371	371	371
$\lambda_{emission}$ (nm)	461	461	462	460
Δ_{Stokes} (nm)	94	95	95	94
Φ_F	0.58	0.36	0.47	0.34
6c				
$\lambda_{absorption}$ (nm)	367	367	367	367
$\lambda_{excitation}$ (nm)	371	371	371	371
$\lambda_{emission}$ (nm)	461	459	460	459
Δ_{Stokes} (nm)	94	92	93	92
Φ_F	0.52	0.52	0.39	0.53
6d				
$\lambda_{absorption}$ (nm)	359	360	357	357
$\lambda_{excitation}$ (nm)	367	367	367	367
$\lambda_{emission}$ (nm)	466	466	466	466
Δ_{Stokes} (nm)	107	106	109	109
Φ_F	0.24	0.32	0.30	0.31
6e				
$\lambda_{absorption}$ (nm)	368	368	367	367
$\lambda_{excitation}$ (nm)	371	371	371	371
$\lambda_{emission}$ (nm)	463	463	463	462
Δ_{Stokes} (nm)	95	95	96	95
Φ_F	0.30	0.37	0.31	0.42
6f				
$\lambda_{absorption}$ (nm)	368	367	367	367
$\lambda_{excitation}$ (nm)	371	371	371	371
$\lambda_{emission}$ (nm)	462	462	463	463
Δ_{Stokes} (nm)	94	95	96	96
Φ_F	0.61	0.46	0.35	0.47

Synthesis

*Synthesis of 2-hydroxy-4,5-dimethoxybenzaldehyde (**2a**)*

Boron tribromide (5.0 g, 20 mmol) was slowly added to a stirring solution of 2,4,5-trimethoxybenzaldehyde (5.0 g, 25 mmol) in CH_2Cl_2 in a dry ice/acetone bath. After 1 h, the reaction mixture was warmed to room temperature and stirred for 3 h, and then a HCl (10%; 20 ml) aqueous solution was added. The mixture was extracted with CH_2Cl_2 (3 × 100 ml). The organic layers were washed with NaCl solution (2 × 100 ml) and water (100 ml). The product was dried over Na_2SO_4 and evaporated to produce **2a** (4.3 g, 91%). Mp 103–104°C (lit. 104°C (*21*)). MS (MALDI-TOF): $m/z = 182.6$ $[M]^+$. $C_9H_{10}O_4$ (182.06).

*General procedure for the synthesis of o-diacetoxy-3-phenylchromenones (**4a** and **4b**)*

In a typical reaction, a mixture of benzaldehyde (**2a** and **2b**) (20 mmol), phenylacetic acids (**3a** and **3b**) (20 mmol) and sodium acetate (50 mmol) was stirred in acetic anhydride (40 ml) at 160°C under N_2 atmosphere for 6 h.

The reaction mixture was cooled, poured into ice-cold water (200 ml) and then filtered. The crude products were purified via crystallisation from ethanol.

*Synthesis of 6,7-dimethoxy-3-(3′,4′-diacetoxyphenyl)chromenone (**4a**; $C_{21}H_{18}O_8$)*

The mixture of 2-hydroxy-4,5-dimethoxybenzaldehyde (**2a**) (3.6 g, 20 mmol), 3,4-dihydroxyphenylacetic acid (**3a**) (3.4 g, 20 mmol) and sodium acetate (4.1 g, 50 mmol) in acetic anhydride (40 ml) was treated as described above to yield **4a** (7.7 g, 97%). Mp 207–208°C. ^{1}H NMR (400 MHz, $CDCl_3$, 25°C): $\delta = 2.31$ (s, 6H, $COCH_3$), 3.93 (s, 3H, OCH_3), 3.96 (s, 3H, OCH_3), 6.87 (s, 1H), 6.91 (s, 1H), 7.26 (d, $J = 8.2$ Hz, 1H), 7.61 (dd, $J = 8.2$, 2 Hz, 1H), 7.63 (d, $J = 2$ Hz, 1H) and 7.77 (s, 1H) ppm. MS (MALDI-TOF): $m/z = 398.9$ $[M]^+$. $C_{21}H_{18}O_8$ (398.10).

*Synthesis of 6,7-diacetoxy-3-(3′,4′-dimethoxyphenyl)chromenone (**4b**; $C_{21}H_{18}O_8$)*

The mixture of 2,4,5-trihydroxybenzaldehyde (**2b**) (3.0 g, 20 mmol), 3,4-dimethoxyphenylacetic acid (**3b**) (3.9 g, 20 mmol) and sodium acetate (4.1 g, 50 mmol) in acetic anhydride (40 ml) was treated as described above to produce **4b** (4.8 g, 60%). Mp 220°C. ^{1}H NMR (400 MHz, CD_3OD, 25°C): $\delta = 2.33$ (s, 3H, $COCH_3$), 2.34 (s, 3H, $COCH_3$), 3.93 (s, 3H, OCH_3), 3.95 (s, 3H, OCH_3), 6.94 (d, $J = 8.2$ Hz, 1H), 7.25 (dd, $J = 8.2$, 2.3 Hz, 1H), 7.27 (d, $J = 2.3$ Hz, 1H), 7.28 (s, 1H), 7.39 (s, 1H) and 7.71 (s, 1H) ppm. MS (MALDI-TOF): $m/z = 397.8$ $[M]^+$. $C_{21}H_{18}O_8$ (398.10).

*General procedure for the synthesis of o-dihydroxy-3-phenylchromenones (**5a** and **5b**)*

The *o*-diacetoxy-3-phenylchromenone derivatives (**4a** and **4b**) were refluxed with MeOH/HCl(aq) for 3 h, methanol was removed using distillation and the precipitates were collected by filtration. The crude products were purified by crystallisation from ethanol.

*Synthesis of 6,7-dimethoxy-3-(3′,4′-dihydroxyphenyl)chromenone (**5a**; $C_{17}H_{14}O_6$)*

Compound **4a** (6.4 g, 16 mmol) was treated as described above to yield **5a** (3.2 g, 64%). Mp 220–221°C. ^{1}H NMR (400 MHz, CD_3OD, 25°C): $\delta = 3.79$ (s, 3H, OCH_3), 3.81 (s, 3H, OCH_3), 6.74 (d, $J = 8.4$ Hz, 1H), 6.78 (s, 1H), 6.90 (dd, $J = 8.2$, 1.8 Hz, 1H), 7.10 (d, $J = 1.8$ Hz, 1H), 7.15 (s, 1H) and 7.58 (s, 1H) ppm. MS (MALDI-TOF): $m/z = 314.7$ $[M]^+$. $C_{17}H_{14}O_6$ (314.08).

*Synthesis of 6,7-dihydroxy-3-(3′,4′-dimethoxyphenyl)chromenone (**5b**; $C_{17}H_{14}O_6$)*

Compound **4b** (4.7 g, 12 mmol) was treated as described above to yield **5b** (3.1 g, 82%). Mp 255–256°C. ^{1}H NMR (400 MHz, CD_3OD, 25°C): $\delta = 3.86$ (s, 3H, OCH_3), 3.87 (s, 3H, OCH_3), 6.77 (s, 1H), 6.98 (d, $J = 8.9$ Hz, 1H), 7.0 (s, 1H), 7.26 (dd, $J = 8.4$, 2 Hz, 1H), 7.32 (d, $J = 2$ Hz, 1H) and 7.89 (s, 1H) ppm. MS (MALDI-TOF): $m/z = 314.7$ $[M]^+$. $C_{17}H_{14}O_6$ (314.08).

*General procedure for the synthesis of 3-phenylchromenone-crown ethers (**6a–6f**)*

The typical procedure for the cyclisation reaction leading to macrocycle ethers (**6a–6f**) is as follows. A mixture of *o*-dihydroxy-3-phenylchromenones (**5a** and **5b**) (3 mmol), poly(ethylene glycol) ditosylate (3 mmol) and alkali metal carbonate (6 mmol) was dissolved in CH_3CN (60 ml). The mixture was heated for 35–40 h at 80–85°C. 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 (**6a–6f**).

*6,7-Dimethoxy-3-(2,3,5,6,8,9-hexahydrobenzo[b][1,4,7,10]tetraoxacyclododecin-12-yl)-2H-chromen-2-one (**6a**; $C_{23}H_{24}O_8$)*

The mixture of compound **5a** (1.0 g, 3.2 mmol), Na_2CO_3 (0.7 g, 6.4 mmol) and tri(ethylene glycol) ditosylate (1.5 g, 3.2 mmol) in CH_3CN (60 ml) was reacted as described above to produce **6a** (0.21 g, 15%). Mp 178–179°C. ^{1}H NMR (400 MHz, $CDCl_3$, 25°C): $\delta = 3.69$ (t, $J = 4$ Hz, 4H), 3.80 (s, 6H, OCH_3), 3.96 (t, $J = 4$ Hz, 4H), 4.20 (t, $J = 4$ Hz, 4H), 6.88 (s, 1H), 6.90 (s, 1H), 6.93 (d, $J = 8.2$ Hz, 1H), 7.28 (dd, $J = 8.2$, 2.3 Hz, 1H), 7.31 (d, $J = 2.3$ Hz, 1H) and 7.70 (s, 1H) ppm. MS (MALDI-TOF): $m/z = 427.9$ $[M]^+$, 450.9 $[M + Na]^+$. $C_{23}H_{24}O_8$ (428.15): calcd C = 64.48, H = 5.65; found C = 64.37, H = 5.54.

*6,7-Dimethoxy-3-(2,3,5,6,8,9,11,12-octahydrobenzo[b][1,4,7,10,13]pentaoxacyclopentadecin-15-yl)-2H-chromen-2-one (**6b**; $C_{25}H_{28}O_9$)*

The mixture of compound **5a** (1.0 g, 3.2 mmol), Na_2CO_3 (0.7 g, 6.4 mmol) and tetra(ethylene glycol) ditosylate (1.6 g, 3.2 mmol) in CH_3CN (60 ml) was reacted as described above to produce **6b** (0.31 g, 20%). Mp 161–162°C. ^{1}H NMR (400 MHz, $CDCl_3$, 25°C): $\delta = 3.69$ (t, $J = 4$ Hz, 4H), 3.77 (t, $J = 4$ Hz, 4H), 3.81 (s, 6H, OCH_3), 3.96 (t, $J = 5$ Hz, 4H), 4.20 (t, $J = 5$ Hz, 4H), 6.87 (s, 1H), 6.90 (s, 1H), 6.93 (d, $J = 8.9$ Hz, 1H), 7.28 (dd, $J = 8.9$, 2.3 Hz, 1H), 7.31 (d, $J = 2.3$ Hz, 1H) and 7.70 (s, 1H) ppm. MS (MALDI-TOF): $m/z = 495.0$ $[M + Na]^+$. $C_{25}H_{28}O_9$ (472.17): calcd C = 63.55, H = 5.97; found C = 63.44, H = 5.86.

*6,7-Dimethoxy-3-(2,3,5,6,8,9,11,12,14,15-decahydrobenzo[b][1,4,7,10,13,16]hexaoxacyclo octadecin-18-yl)-2H-chromen-2-one (**6c**; $C_{27}H_{32}O_{10}$)*

The mixture of compound **5a** (1.0 g, 3.2 mmol), K_2CO_3 (0.9 g, 6.4 mmol) and penta(ethylene glycol) ditosylate (1.7 g, 3.2 mmol) in CH_3CN (60 ml) was reacted as described above to produce **6c** (0.26 g, 16%). Mp 122–123°C. ^1H NMR (400 MHz, $CDCl_3$, 25°C): $\delta = 3.69$ (t, $J = 4$ Hz, 4H), 3.73 (t, $J = 4$ Hz, 4H), 3.77 (t, $J = 4$ Hz, 4H), 3.81 (s, 6H, OCH_3), 3.96 (t, $J = 4$ Hz, 4H), 4.22 (t, $J = 5$ Hz, 4H), 6.87 (s, 1H), 6.91 (s, 1H), 6.93 (d, $J = 8.9$ Hz, 1H), 7.28 (dd, $J = 8.9$, 2.3 Hz 1H), 7.31 (d, $J = 2.3$ Hz, 1H) and 7.70 (s, 1H) ppm. MS (MALDI-TOF): $m/z = 538.9$ $[M + Na]^+$, 554.9 $[M + K]^+$. $C_{27}H_{32}O_{10}$ (516.20): calcd C = 62.78, H = 6.24; found C = 62.63, H = 6.36.

*14-(3,4-Dimethoxyphenyl)-5,6,8,9-tetrahydro-2H-[1,4,7,10]tetraoxacyclododeca[2,3-g]chromen-13(3H)-one (**6d**; $C_{23}H_{24}O_8$)*

The mixture of compound **5b** (1.0 g, 3.2 mmol), Na_2CO_3 (0.7 g, 6.4 mmol) and tri(ethylene glycol) ditosylate (1.5 g, 3.2 mmol) in CH_3CN (60 ml) was reacted as described above to produce **6d** (0.31 g, 23%). Mp 182–183°C. ^1H NMR (400 MHz, $CDCl_3$, 25°C): $\delta = 3.77$ (t, $J = 4$ Hz, 4H), 3.92 (t, $J = 4$ Hz, 4H), 3.94 (s, 6H, OCH_3), 4.22 (t, $J = 4$ Hz, 4H), 6.89 (s, 1H), 6.93 (d, $J = 8.2$ Hz, 1H), 7.12 (s, 1H), 7.25 (dd, $J = 8.6$, 2.3 Hz, 1H), 7.29 (d, $J = 2.3$ Hz, 1H) and 7.66 (s, 1H) ppm. MS (MALDI-TOF): $m/z = 427.8$ $[M]^+$, 450.8 $[M + Na]^+$. $C_{23}H_{24}O_8$ (428.15): calcd C = 64.48, H = 5.65; found C = 64.37, H = 5.74.

*17-(3,4-Dimethoxyphenyl)-5,6,8,9,11,12-hexahydro-2H-[1,4,7,10,13]pentaoxacyclopentadeca[2,3-g]chromen-16(3H)-one (**6e**; $C_{25}H_{28}O_9$)*

The mixture of compound **5b** (1.0 g, 3.2 mmol), Na_2CO_3 (0.7 g, 6.4 mmol) and tetra(ethylene glycol) ditosylate (1.6 g, 3.2 mmol) in CH_3CN (60 ml) was reacted as described above to produce **6e** (0.48 g, 32%). Mp 164–165°C. ^1H NMR (400 MHz, $CDCl_3$, 25°C): $\delta = 3.77$ (t, $J = 4$ Hz, 8H), 3.92 (t, $J = 4$ Hz, 4H), 3.94 (s, 6H, OCH_3), 4.18 (t, $J = 5$ Hz, 4H), 6.84 (s, 1H), 6.93 (d, $J = 8.2$ Hz, 1H), 7.12 (s, 1H), 7.24 (dd, $J = 8.6$, 2.3 Hz, 1H), 7.30 (d, $J = 2.3$ Hz, 1H) and 7.68 (s, 1H) ppm. MS (MALDI-TOF): $m/z = 495.0$ $[M + Na]^+$. $C_{25}H_{28}O_9$ (472.17): calcd C = 63.55, H = 5.97; found C = 63.64, H = 5.88.

*20-(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 (**6f**; $C_{27}H_{32}O_{10}$)*

The mixture of compound **5b** (1.0 g, 3.2 mmol), K_2CO_3 (0.9 g, 6.4 mmol) and penta(ethylene glycol) ditosylate (1.7 g, 3.2 mmol) in CH_3CN (60 ml) was reacted as described above to produce **6f** (0.36 g, 22%). Mp 148–149°C. ^1H NMR (400 MHz, $CDCl_3$, 25°C): $\delta = 3.77$ (t, $J = 4$ Hz, 8H), 3.92 (t, $J = 4$ Hz, 8H), 3.94 (s, 6H, OCH_3), 4.22 (t, $J = 5$ Hz, 4H), 6.85 (s, 1H), 6.92 (d, $J = 8.2$ Hz, 1H), 7.12 (s, 1H), 7.24 (dd, $J = 8.6$, 2.3 Hz, 1H), 7.30 (d, $J = 2.3$ Hz, 1H) and 7.67 (s, 1H) ppm. MS (MALDI-TOF): $m/z = 517.0$ $[M]^+$, 539.0 $[M + Na]^+$. $C_{27}H_{32}O_{10}$ (516.20): calcd C = 62.78, H = 6.24; found C = 62.64, H = 6.16.

Results and discussion

The novel chromenone-crown ethers (**6a–6f**) were prepared in the presence of CH_3CN/metal carbonates from the cyclic condensation of poly(ethylene glycol) ditosylates and the corresponding chromenones. The chromenones, 6,7-dimethoxy-3-(3′,4′-dihydroxyphenyl)-chromenone and 6,7-dihydroxy-3-(3′,4′-dimethoxyphenyl)-chromenone (**5a** and **5b**), were prepared from 2-hydroxy-4,5-dimethoxybenzaldehyde/3,4-dihydroxyphenylacetic acid and 2,4,5-trihydroxy benzaldehyde/3,4-dimethoxyphenylacetic acid, respectively, in the presence of acetic anhydride and sodium acetate under an inert atmosphere, after being treated with MeOH/HCl (Scheme 1).

Compounds **5a** and **5b** were reacted with tri-/tetra- or penta(ethylene glycol) ditosylate in the presence of Me_2CO_3 in CH_3CN to produce the chromenone-crown ethers (**6a–6c**) and (**6d–6f**), respectively. Chromatographic separation over a silica gel column eluted with $CHCl_3$ residue resulted in chromenone-crown ethers **6a–6f** at 15–32% yields. The novel compounds were

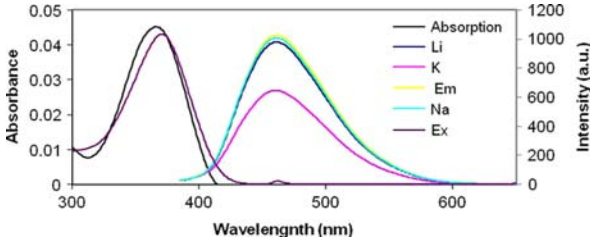

Figure 1. Absorption, excitation and emission spectra of the compound **6b** and its 1:1 complex emission spectra with Li^+, Na^+ and K^+ perchlorate salts in CH_3CN.

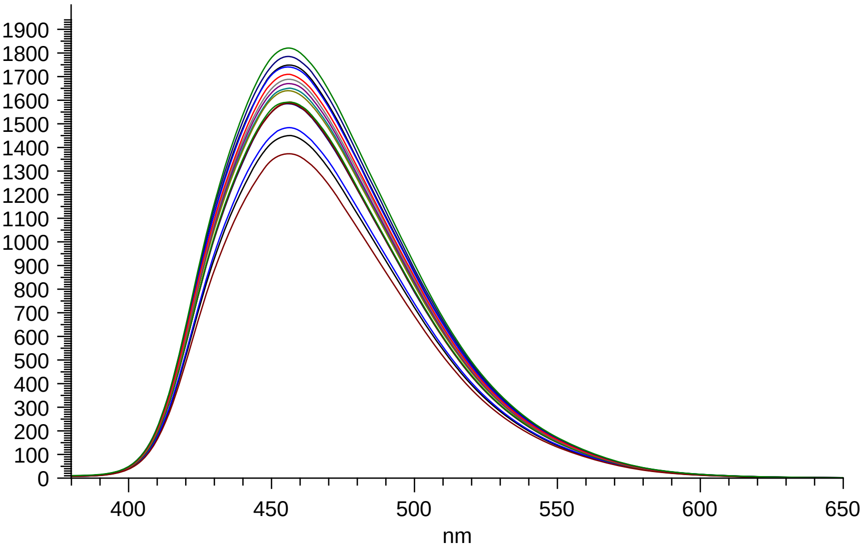

Figure 2. The emission spectra of **6a** (3×10^{-6} mol/l, top line) depending on $LiClO_4$ concentration increasing from 0 to 2.3×10^{-5} mol/l.

characterised using elemental analysis, ^1H NMR and MALDI-TOF mass spectroscopy.

The ^1H NMR spectra of **6a–6f** showed characteristic signals for etheral (—O—CH_2—CH_2—O—) protons at $\delta = 3.69–4.22$ ppm for each triplet. The peak at $\delta = 3.80–3.94$ ppm indicated the presence of the $-OCH_3$ group. The chemical shifts of the aromatic protons could be observed at $\delta = 6.84–7.31$ ppm. In addition, the chemical shifts of the coumarin lacton ring proton (H-4) could be observed at $\delta = 7.68–7.70$ ppm. MALDI-TOF spectrum and elemental analysis confirmed the formation of chromenone-crown ether derivatives.

The fluorescence quantum yields (Φ_F) of the chromenone-crown ethers were calculated by the comparative method with the following equation (*18–20*):

$$\Phi_{F(x)} = \Phi_{F(s)} \frac{A_s}{A_x} \frac{F_x}{F_s} \left(\frac{\eta_x}{\eta_s} \right)^2.$$

Here, subscripts *s* and *x* denote the reference and samples, respectively; $\Phi_{F(x)}$ and $\Phi_{F(s)}$ are quantum yields of the samples and reference, respectively; F_x and F_s are the areas under the fluorescence emission curves of the samples and reference, respectively; A_x and A_s are the absorbances of the samples and reference, respectively, at the excitation

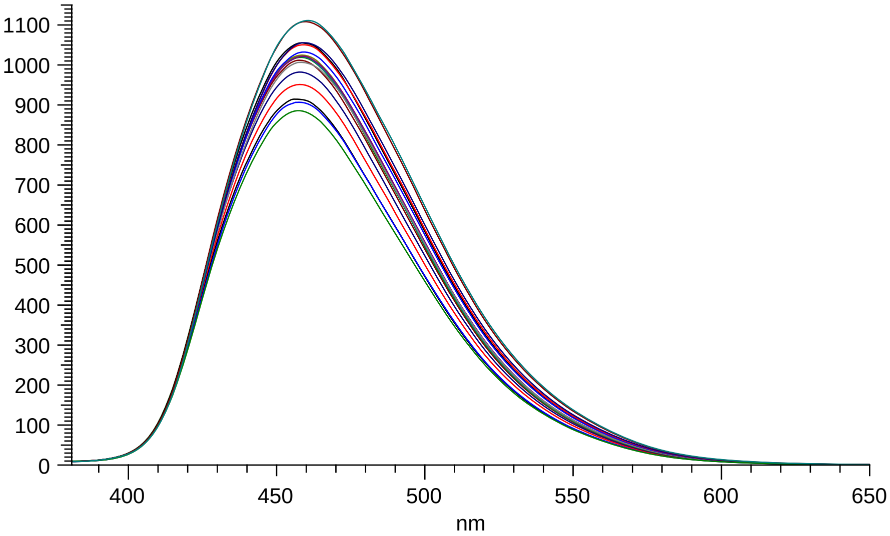

Figure 3. The emission spectra of **6c** (3×10^{-6} mol/l, top line) depending on $NaClO_4$ concentration increasing from 0 to 2.3×10^{-5} mol/l.

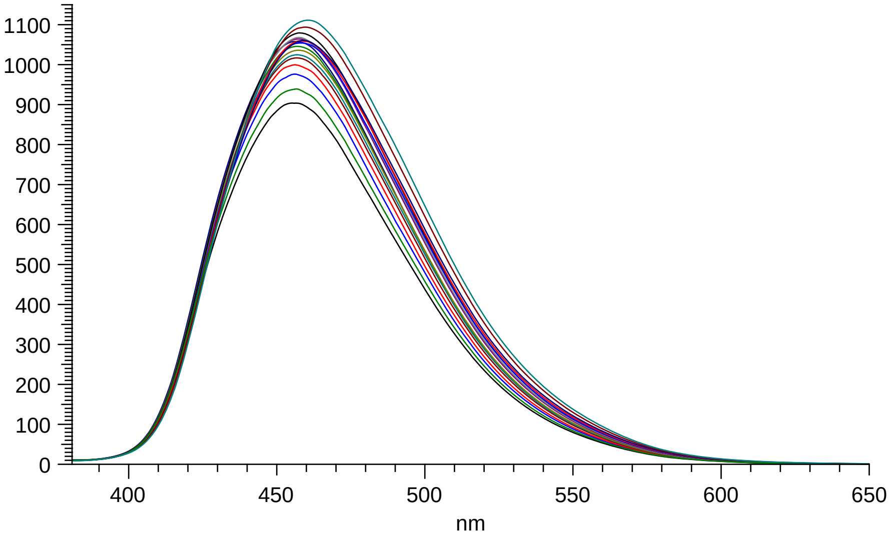

Figure 4. The emission spectra of **6c** (3×10^{-6} mol/l, top line) depending on $KClO_4$ concentration increasing from 0 to 2.3×10^{-5} mol/l.

wavelength and η_x and η_s are the refractive indices of the solvents used for the samples and reference, respectively. Quinine sulphate (in 0.5 M H_2SO_4, $\Phi_F = 0.546$) was used as a reference for calculating the fluorescence quantum yields. The absorbance of the solutions at the excitation wavelength was less than 0.05.

Figure 1 depicts the fluorescence emission for complexes and free ligand, in addition to the excitation and absorption spectra for compound **6b**. Figures 2–7 depict the fluorescence emission spectra for compounds **6a**–**6f** depending on the perchlorate salts. All of the complexes (**6a**–**6f**) demonstrated similar fluorescence behaviour in acetonitrile.

Table 1 shows that larger bathochromic shifts occurred for the chromenone-crown ethers (**6a**–**6f**) and their metal complexes, as expected. The emission peaks of **6a** for Li^+, Na^+ and K^+ complexes were observed at 456 nm in acetonitrile.

Ligands **6d**–**6f** displayed larger Stokes' shifts when compared to **6a**–**6c**. The fluorescence quantum yield (Φ_F) values of compounds **6a**, **6b** and **6f** with Li^+, Na^+ and K^+ perchlorate salt complexes, respectively, were lower than those of the ligands in acetonitrile. A comparison of the Φ_F values for the complexes of compound **6a** showed that the K^+ complex was larger than the Li^+ and Na^+ complexes. A similar comparison of Φ_F values for the

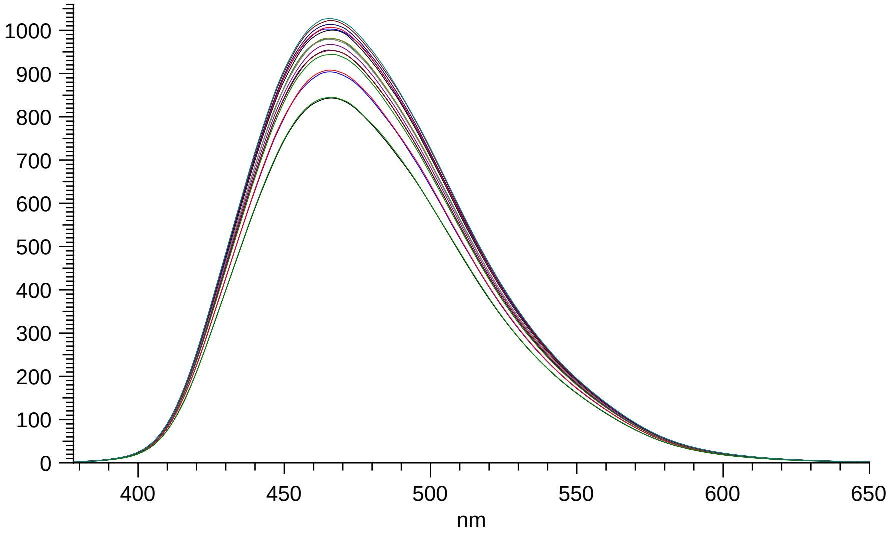

Figure 5. The emission spectra of **6d** (3×10^{-6} mol/l, top line) depending on $NaClO_4$ concentration increasing from 0 to 2.3×10^{-5} mol/l.

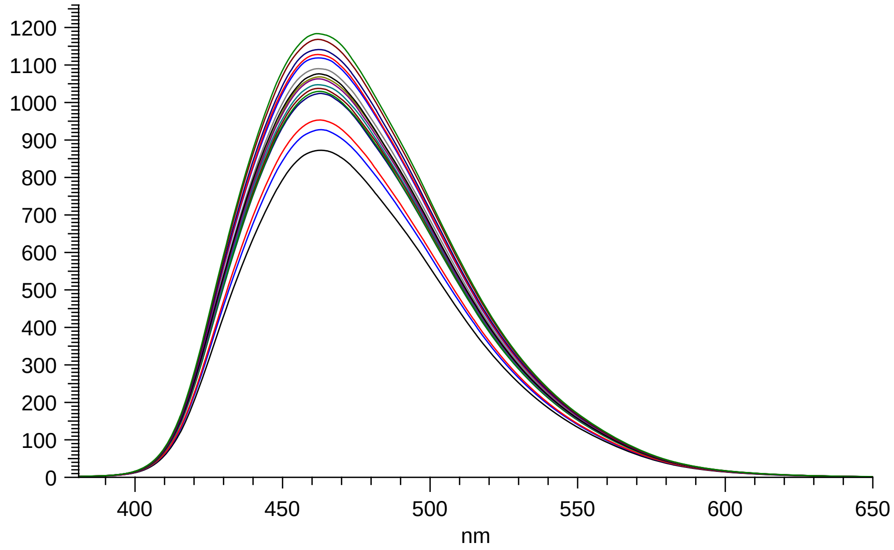

Figure 6. The emission spectra of **6e** (3×10^{-6} mol/l, top line) depending on $NaClO_4$ concentration increasing from 0 to 2.3×10^{-5} mol/l.

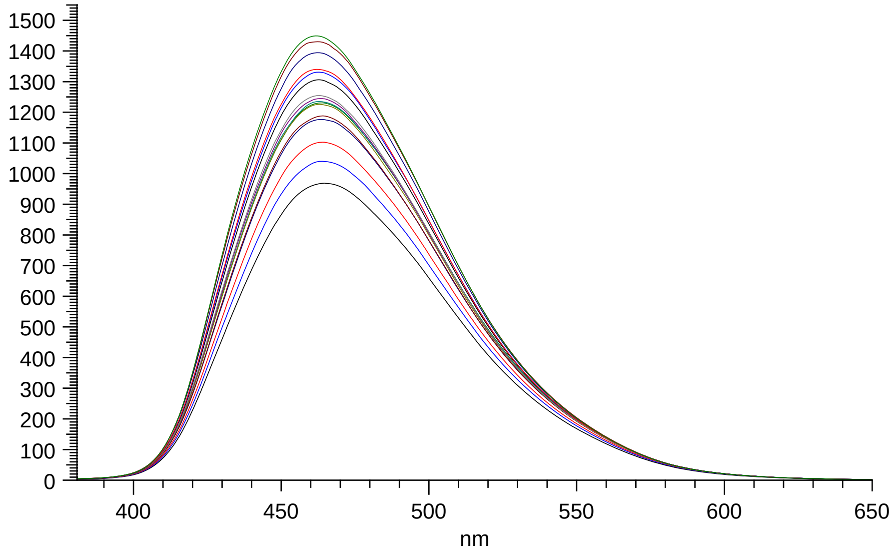

Figure 7. The emission spectra of **6f** (3×10^{-6} mol/l, top line) depending on $KClO_4$ concentration increasing from 0 to 2.3×10^{-5} mol/l.

complexes of compounds **6b** and **6f** showed the relationships $Na^+ > Li^+ > K^+$ and $K^+ > Li^+ > Na^+$, respectively.

The Φ_F values of the complexes of compound **6c** compared to those of the ligand in acetonitrile showed that $K^+ >$ **6c** $= Li^+ > Na^+$; however, the Φ_F values of the metal perchlorate salt complexes of compounds **6d** and **6e** were higher than those of the ligands in acetonitrile. A comparison of Φ_F values for the complexes of compounds **6d** and **6e** showed the relationship $Li^+ > K^+ > Na^+$ and $K^+ > Li^+ > Na^+$, respectively.

These results demonstrate that the binding of such molecules depends on the structure, crown-ether ring size and size of the cation radii, which are common for a macrocyclic effect.

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References

(1) Pedersen, C.J. *J. Am. Chem. Soc.* **1967**, *89*, 7017–7036.
(2) Takeda, Y.; Tanaka, M.; Yamada, H.; Katsuta, S. *J. Coord. Chem.* **2002**, *55*, 459–468.
(3) De Silva, A.P.; Gunaratne, H.Q.N.; Gunnlaugsson, T.; Huxley, A.J.M.; McCoy, C.P.; Rademacher, J.T.; Rice, T.E. *Chem. Rev.* **1997**, *97*, 1515–1566.
(4) Stott, P.E.; Bradshaw, J.S.; Parish, W.W.; Cooper, J.W. *J. Org. Chem.* **1980**, *45*, 4716–4720.
(5) Pacey, G.E.; Bubnis, B.P. *Anal. Lett.* **1980**, *13*, 1085–1091.
(6) Kimura, K.; Shano, T. *J. Liq. Chromatogr.* **1982**, *5*, 223–255.
(7) Shiga, M.; Nakamura, H.; Takagi, M.; Ueno, K. *Chem. Soc. Jpn.* **1984**, *57*, 412–415.
(8) Erk, Ç. *Ind. Eng. Chem. Res.* **2000**, *39*, 3582–3588.
(9) Alonso, M.T.; Brunet, E.; Juanes, O.; Rodriguez-Ubis, J.C. *J. Photoch. Photobiol. A* **2002**, *147*, 113–125.
(10) Alonso, M.T.; Brunet, E.; Hernandez, C.; Rodriguez-Ubis, J.C. *Tetrahedron Lett.* **1993**, *34*, 7465–7468.
(11) Erk, Ç.; Göçmen, A.; Bulut, M. *J. Incl. Phenom. Macro.* **1998**, *31*, 319–331.
(12) Göçmen, A.; Bulut, M.; Erk, Ç. *Pure Appl. Chem.* **1993**, *65*, 447–450.
(13) Bulut, M.; Erk, Ç. *J. Heterocyclic Chem.* **2001**, *38*, 1291–1295.
(14) Erk, Ç.; Göçmen, A.; Bulut, M. *Supramol. Chem.* **1999**, *11*, 49–56.
(15) Abdurrahmanoglu, S.; Gündüz, C.; Çakır, Ü.; Çiçek, B.; Bulut, M. *Dyes Pigments* **2005**, *65*, 197–204.
(16) Gündüz, C.; Salan, Ü.; Özkul, N.; Başaran, İ.; Çakır, Ü.; Bulut, M. *Dyes Pigments* **2006**, *71*, 161–167.
(17) Çakır, Ü.; Özer, M.; Içen, M.A.; Uğraş, H.I.; Bulut, M. *Dyes Pigments* **2004**, *60*, 177–185.
(18) Rurack, K.; Dekhyar, M.L.; Bricks, J.L.; Resch-Genger, U.; Rettig, W. *J. Phys. Chem. A* **1999**, *103*, 9626–9635.
(19) Fery-Forgues, S.; Lavabre, D. *J. Chem. Edu.* **1999**, *76*, 1260–1264.
(20) Valeur, B. *Molecular Fluorescence Principles and Applications*; Wiley-VCH: Weinheim, 2002; pp 159–161.
(21) Kelkar, S.L.; Phadke, S.; Marina, S. *Indian J. Chem.* **1984**, *23B*, 458–459.