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Bis Coumarin Podands and their Complexes with Na^+, K^+ and Pb^{2+} Cations

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ABSTRACT

The synthesis and characterization of some bis-7-oxabenzo-α-pyrone ended polyoxyethylenes is reported and their electronic spectra evaluated. Their fluorescence spectra showed cation specific spectral intensity changes in the presence of Na^+, K^+ *and* Pb^{2+} *in acetonitrile due to the cation complexing. Copyright © 1996 Elsevier Science Ltd*

Keywords: Coumarins, podands, K^+, Na^+, Pb^{2+}, fluorescence.

INTRODUCTION

The supramolecular chemistry of some conformationally rigid cavitands such as crown ethers indicates a relative slowness in exchanging their metal–complex solutions, with stability constants in the range 10^5–10^{10}. However, flexible podands like polyoxyethylene chains have a relatively fast cation–ligand exchange of the complex, in the range of 10^2–10^4 stability.[1–4] The lipophilicity and functionality of specific terminal groups having various polyoxyethylene backbones could be useful in enhancing the cation transport and detection properties. Similar effects can also be obtained with different types of terminals like chromophores, fluorophores and redox-responsive systems for analytical treatments.[5,6]

We have previously studied some crown ethers and their ether–esters[7–16] and we now report results on the synthesis and characteristics of some podands of coumarins (Scheme 1). The changes in the fluorescence spectra

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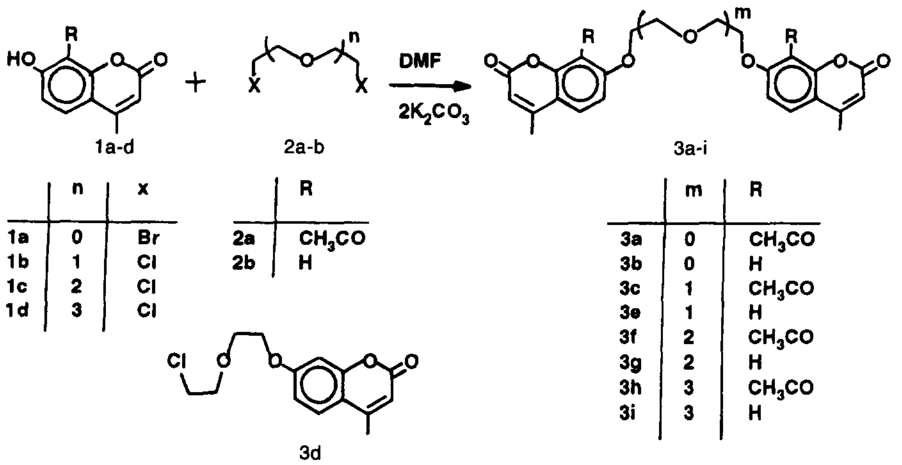

	n	x
1a	0	Br
1b	1	Cl
1c	2	Cl
1d	3	Cl

	R
2a	CH_3CO
2b	H

	m	R
3a	0	CH_3CO
3b	0	H
3c	1	CH_3CO
3e	1	H
3f	2	CH_3CO
3g	2	H
3h	3	CH_3CO
3i	3	H

Scheme 1

on complex formation has been qualitatively examined for polyoxyethylene chains with bis-7-oxabenzo-α-pyrone end groups, and Na^+, K^+ and Pb^{2+} metals were observed to preferably form their podates in acetonitrile solutions.

RESULTS AND DISCUSSION

The ion binding role of polyglycols with specific end groups (so-called podands) has been recognized.[1–6] Such systems are of particular interest with respect to polymer studies. However, the practical aspects of podands and their salt complexes (podates) as fast ion-responsive electrodes[1,2] or photosensitive detecters[4] are now better established.

Recently we initiated investigations on the design and synthesis of some macrocyclic ethers with fluorogenic coumarin moieties. The molecules obtained in our earlier work exhibited unusual fluorescence spectra in the presence of alkali and alkali earth cations, depending on the ring size and the cation radii.[7–12] The systems also displayed extreme lipophilicity, of potential interest for cation characterization and ion transport.

The present paper deals with the synthesis and characterization of bis-7-coumarin ended polyoxyethylene bridges, cum-$O(C_2H_4O)_m$-cum ($m = 1$–3) as described below. These were obtained from 7-hydroxy-coumarins by reacting with polyethyleneglycol dihalides in the presence of DMF/K_2CO_3 (Scheme 1). The influence of the bis-coumarin ends of the podands on the electronic

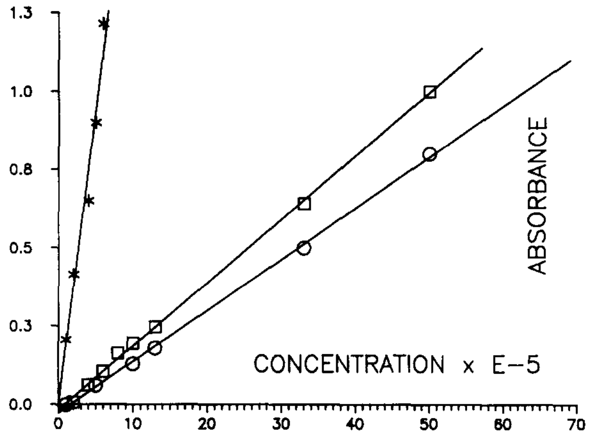

Fig. 1. Relationship between the absorbance of the UV maxima of compounds **3a** (*), **3g** (□) and **3i** (○) and their concentrations in acetonitrile at 25°C (λ_{max} = 327 nm).

spectra in CH_3CN are shown in Fig. 1. The data indicate that changes in molar absorbtivity are dependent on the molecular size.

The fluorescence spectra of the bis-coumarin-podands were examined in the presence of some cations in acetonitrile and both the excitation and emission fluorescence maxima were changed in the presence of cations. Vögtl *et al.*[5] and Ernsting *et al.*[6] have reported similar results.

The fluorescence spectral intensities of compounds **3a–3i** were affected by the cation–ligand interactions of the metal complexes in solution[12–16]

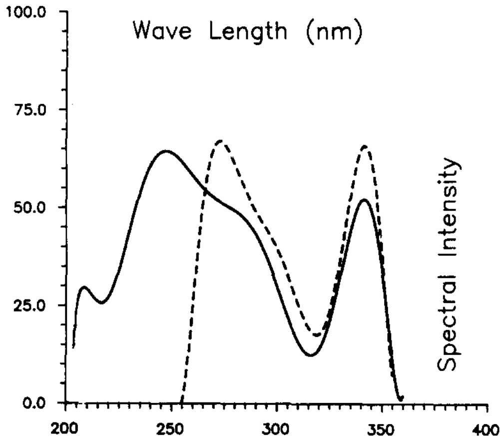

Fig. 2. The fluorescence excitation spectra of free **3e** (——) and in Pb^{2+} (- - - -) containing solutions in acetonitrile at 25°C, emission, λ_{max} = 460 nm.

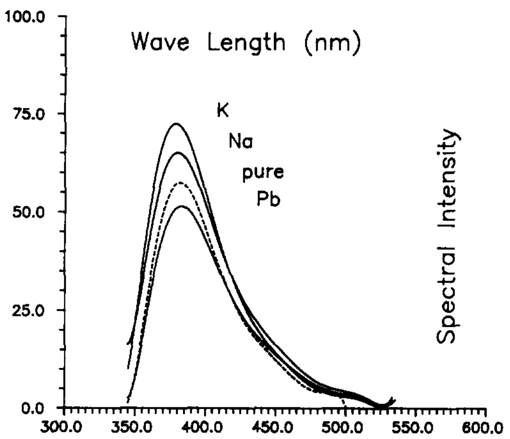

Fig. 3. The fluorescence emission spectra of free **3g** and its salt containing solutions in acetonitrile at 25°C, excitation, $\lambda_{max} = 342$ nm.

(Figs 2–4). In particular, the spectral effects were surprisingly selective for some cations, as is shown in Figs 2 and 3. A specific role of Na^+, K^+ and Pb^{2+} cations is observed, depending on the polyethylene chain length of podands.[3–5]

The alkali metal cations generally caused complexation enhanced intensity changes (Figs 3 and 4), whereas Pb^{2+} led to both complexation enhanced fluorescence intensity change for compound **3e** ($m = 1$) and complexation enhanced quenching intensity change for compounds **3g** ($m = 2$) and **3i** ($m = 3$)[16] (Figs 2–4). These effects are relatable to the influence of the length

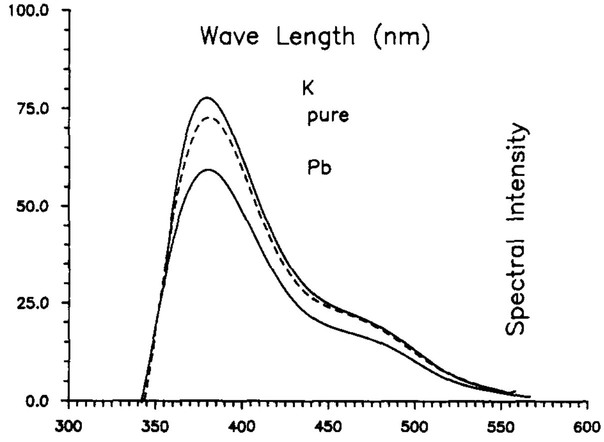

Fig. 4. The fluorescence emission spectra of free **3i** and its salt containing solutions in acetonitrile at 25°C, excitation, $\lambda_{max} = 342$ nm.

of podands. A similar effect with Pb^{2+} has also been reported with amino coumarins.[6]

EXPERIMENTAL

Melting points are uncorrected, IR spectra obtained with a Jasco FT-IR spectrometer, ^{1}H-NMR spectra were recorded on a BRUKER WA-200, using TMS as internal standard, mass spectra on a Carlo Erba mass spectrometer, model trio-1000, and electronic spectra on a Perkin-Elmer model-Lambda. Fluorescence spectra of the pure podands and in excess amount of salt solutions were obtained with a Perkin-Elmer luminescence spectrometer model LS-50, using concentrations of 10^{-4}–10^{-6} mole/litre in acetonitrile dried on P_2O_5.

The polyethyleneglycol dihalides (**1a–1d**) were sourced as in previous studies, and we have recently reported improved syntheses of the coumarin intermediates used.[13,14] The 8-H- and 8-acetyl derivatives (*3a–3i*) were obtained from 8-H- or 8-acetyl-7-hydroxycoumarins and polyethyleneglycol dihalides in DMF/K_2CO_3, namely:

1,2-Bis-(8-acetyl-7-oxa-4-methyl-2[H]-1-benzopyran-2-one)ethane; (**3a**) 8-acetyl-7-hydroxy-4-methyl-2[H]-1-benzopyran-2-one (6 g, 27 mmol), Na_2CO_3 (2.86 g, 27 mmol) and DMF (40 ml) were stirred while warming and 1,2-dibromoethane (**1a**) (3.2 g, 15 mmol) was added over 30 min and the reaction continued at 80–85°C for 24 h. The mixture was diluted with HCl (100 ml, 0.1 N) and filtered, giving pale yellow crystals from THF (5.0 g, 72%,) m.p. 265°C; IR 2920, 1730, 1700, 1600, 1380, 1290, 1100 cm^{-1}; ^{1}H-NMR (DMSO-d6) $\delta = 2.43$ ($3H,s,CH_3$), 2.51 ($3H,s,CH_3CO$), 4.54 ($4H,s,C_2H_4$), 6.26 (1H,s,Cu-H), 7.23 (1H,d,Ar-H), 7.81 (1H,d,Ar-H), MW (462), Mz (EI) 46z (M^+). Calculated for $C_{26}H_{22}O^8$C 67.53, H 4.76%. Found C 67.00, H 4.36%.

1,2-Bis-(7-oxa-4-methyl-2[H]-1-benzopyran-2-one)ethane; (**3b**) 7-hydroxy-4-methyl-2[H]-1-benzopyran-2-one (6 g, 34.mmol), K_2CO_3 (4.7 g, 34 mmol), and **1a** (3.2 g, 17 mmol) were stirred in DMF (40 ml) at 80–85°C for 24 h, giving white needles from THF (4.0 g, 62%), m.p. 240°C; IR $\nu = 2920$, 1700, 1605, 1395, 1280, 1150, 1080 cm^{-1}; ^{1}H-NMR (acetone-d6) $\delta = 2.41$ ($3H,s,CH_3$), 4.54 ($4H,s,C_2H_4$), 6.08 (1H,s,Cu-H), 6.74 (1H,d,Ar-H), 6.86 (1H,q,Ar-H), 7.61 (1H,d,Ar-H), MW (378), Mz (EI) 378 (M^+). Calculated for $C_{22}H_{18}O_6$ C 69.84, H 4.23%. Found C 70.07, H 4.14%.

1,5-Bis-(8-acetyl-7-oxa-4-methyl-2[H]-1-benzopyran-2-one)-3-oxapentane); (**3c**) 8-acetyl-7-hydroxy-4-methyl-2[H]-1-benzopyran-2-one (0.7 g, 3.2 mmol), K_2CO_3 (0.86 g, 3.2 mmol), water (3 ml) and DMF (30 ml) were stirred while warming and β,β'-dichlorodiethyl ether (**1b**) (0.22 g, 1.6 mmol) was then added and the reaction continued at 80–85°C for 20 h. The liquor was diluted with HCl (50 ml, 0.1 N) and filtered. The product was crystallized from THF (0.15 g, 18%), m.p. 233°C; IR $\nu=2940$, 1720, 1610, 1440, 1380, 1290, 1060 cm^{-1}; ^1H-NMR (DMSO-d6) $\delta=2.38$ ($3H,s,CH_3$), 2.56 ($3H,s,CH_3CO$), 3.87 ($4H,t,C_2H_4$), 4.25 ($4H,t,C_2H_4$), 6.26 (1H,s,Cu-H), 7.23 (1H,d,Ar-H), 7.81 (1H,d,Ar-H), MW (507). Calculated for $C_{28}H_{26}O_9$ C 66.27, H 5.12%. Found C 66.00, H 5.42%.

1-(7-oxa-4-methyl-2[H]-1-benzopyran-2-one)-3-oxa-5-chloropentane; **(3d)** 7-hydroxy-4-methyl-2[H]-1-benzopyran-2-one (6.0 g, 34 mmol), K_2CO_3 (4.7 g, 34 mmol), water (5 ml), DMF (50 ml) and β,β'-dichlorodiethyl ether **(1b)** (2.4 g, 17 mmol) were heated at 80–85°C for 40 h, giving yellow crystals from THF (3.0 g, 62%), m.p. 108°C; IR $\nu=2900$, 1720, 1610, 1390, 1280, 1070, 840 cm^{-1}; ^1H-NMR ($CDCl_3$) $\delta=2.38$ ($3H,s,CH_3$), 3.70 ($8H,m,C_2H_4$), 3.88 ($4H,t,C_2H_4$), 4.17 ($4H,t,C_2H_4$), 6.11 (1H,s,Cu-H), 6.79 (1H,d,ArH), 6.87 (1H,q,ArH), 7.47 (1H,d,ArH), MW (282.5), Mz (EI) 283 (M^+). Calculated $C_{14}H_{15}O_4Cl$ C 59.46, H 4.97%. Found C 58.60, H 5.30%.

1,5-Bis-(7-oxa-4-methyl-2[H]-1-benzopyran-2-one)-3-oxapentane; **(3e)** 7-hydroxy-4-methyl-2[H]-1-benzopyran-2-one (3.0 g, 17 mmol), Na_2CO_3 (1.8 g, 17 mmol), water (5 ml), DMF (50 ml) and β,β'-dichlorodiethyl ether **(1b)** (1.21 g, 8.5 mmol) were heated at 80–85°C for 40 h then diluted with HCl (50 ml, 0.1 N) and filtered, giving white crystals from THF (2.87 g, 40%), m.p. 185°C; IR $\nu=2940$, 1720, 1610, 1440, 1380, 1290, 1060 cm^{-1}; ^1H-NMR (DMSO-d6) $\delta=2.38$ ($3H,s,CH_3$), 3.87 ($4H,t,C_2H_4$), 4.25 ($4H,t,C_2H_4$), 6.17 (1H,s,Cu-H,) 6.97 (1H,d,Ar-H), 6.85 (1H,q,Ar-H), 7.53 (1H,d,Ar-H), Mz (EI) 422 (M^+). Calculated for $C_{30}H_{30}O_{10}$ C 68.25, H 5.12%. Found C 67.66, H 5.40%.

1,8-Bis-(8-acetyl-7-oxa-4-methyl-2[H]-1-benzopyran-2-one)-3,6-dioxaoctane; **(3f)** 8-acetyl-7-hydroxy-4-methyl-2[H]-1-benzopyran-2-one (2.0 g, 9.2 mmol), Na_2CO_3 (1.0 g, 9.2 mmol), water (2 ml), DMF (50 ml) and 1,8-dichloro-3,6-dioxaoctane **(1c)** (1.71 g, 4.6 mmol) were reacted at 80–85°C for 20 h and the liquor diluted with HCl (50 ml, 0.1 N) and filtered. The crude product was purified on an Al_2O_3 column using CH_2Cl_2 as eluant, giving pale yellow crystals from THF (1.5 g, 60%) m.p. 233°C; IR $\nu=2940$, 1720, 1610, 1440, 1380, 1290, 1060 cm^{-1}; ^1H-NMR (DMSO-d6) $\delta=2.38$ ($3H,s,CH_3$), 2.56 ($3H,s,CH_3CO$), 3.47 ($4H,m,C_2H_4$), 3.87 ($4H,t,C_2H_4$), 4.25 ($4H,t,C_2H_4$), 6.26 (1H,s,Cu-H), 7.23 (1H,d,Ar-H), 7.81 (1H,d,Ar-H), Mz (EI) 550 (M^+). Calculated for $C_{24}H_{22}O_7$ C 65.45, H 5.45%. Found C 66.07, H 5.90%.

1,8-Bis-(7-oxa-4-methyl-2[H]-1-benzopyran-2-one)-3,6-dioxaoctane; **(3g)** 7-hydroxy-4-methyl-2[H]-1-benzopyran-2-one (0.7 g, 3.9 mmol), K_2CO_3 (0.54 g, 4 mmol), water (3 ml), DMF (30 ml) and 1,8-dichloro-3,6-dioxaoctane **(1c)** (0.36 g, 1.95 mmol) were heated at 80–85°C for 40 h and the liquor then diluted with HCl (50 ml, 0.1 N) and filtered, giving pale yellow crystals from $CHCl_3$ (0.54 g, 59%), m.p. 146°C; IR $\nu=2900$, 1720, 1610, 1390, 1280, 1125, 1065 cm^{-1}; ^{1}H-NMR (DMSO-d6) $\delta=2.38$ (3H,s,CH_3), 3.47 (4H,m,C_2H_4), 3.87 (4H,t,C_2H_4), 4.25 (4H,t,C_2H_4), 6.17 (1H,s,Cu-H,), 6.67 (1H,d,Ar-H), 6.95 (1H,q,Ar-H), 7.45(1H,d,Ar-H). Mz (EI) 466 (M^+). Calculated for $C_{26}H_{26}O_8$ C 66.95, H 5.58%. Found C 66.09, H 5.18.

1,11-Bis-(8-aceto-7-oxa-4-methyl-2[H]-1-benzopyran-2-one)-3,6,9-trioxaundecane; **(3h)** 8-acetyl-7-hydroxy-4-methyl-2[H]-1-benzopyran-2-one (3.3 g, 15 mmol), Na_2CO_3 (1.6 g, 15 mmol), water (2 ml), DMF (50 ml) and 1,11-dichloro-3,6,9-trioxaundecane **(1d)** (1.75 g, 7.5 mmol) were reacted at 80–85°C for 72 h, giving light brown crystals from THF (1.45 g, 34%), m.p. 104°C: IR $\nu=2940$, 1720, 1600, 1450, 1380, 1290 1090 cm^{-1}; ^{1}H-NMR ($CDCl_3$) $\delta=2.38$ (3H,s,CH_3), 2.56 (3H,s,CH_3CO), 3.70 (8H,m,$(C_2H_4)_20$), 3.87 (4H,t,C_2H_4), 4.25 (4H,t,C_2H_4), 6.26 (1H,s,Cu-H), 7.23 (1H,q,Ar-H), 7.81 (1H,d,Ar-H). Calculated for $C_{32}H_{34}O_{11}$ C 64.65, H 5.72%. Found C 65.07, H 5.90%.

1,11-Bis-(7-oxa-4-methyl-2[H]-1-benzopyran-2-one)-3,6,9-trioxaundecane; **(3i)** 7-hydroxy-4-methyl-2[H]-1-benzopyran-2-one (3.5 g, 19 mmol), Na_2CO_3 (2.04 g, 19 mmol), water (3 ml), DMF (50 ml) and 1,11-dichloro-3,6,9-trioxaundecane **(1d)** (2.2 g, 9.5 mmol) were reacted at 80–85°C for 70 h and the liquor was then diluted with HCl (50 ml, 0.1 N) and filtered, giving pale yellow crystals from $CHCl_3$ (1.0 g, 20%), m.p. 74°C; IR $\nu=2930$, 1710, 1610, 1520, 1390, 1130, 1070 cm^{-1}; ^{1}H-NMR ($CDCl_3$); $\delta=2.38$ (3H,s,CH_3), 3.71 (8H,m,$(C_2H_4)_20$), 3.88 (4H,t,C_2H_4), 4.16 (4H,t,C_2H_4), 6.11 (1H,s,Cu-H), 6.63 (1H,d,Ar-H), 6.91 (1H,q,Ar-H), 7.51 (1H,d,Ar-H), Mz (EI) 570 (M^+). Calculated for $C_{28}H_{30}O_9$ C 65.88, H 5.88%. Found C 66.07, H 5.90%.

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