The Synthesis and the Cationic Fluorescence Role of Glycols with Aromatic End Groups, Part III *

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Abstract

Some novel bis-(substituted-phenoxy) ended glycols were synthesised using hydroxy aromatics of vanillin, *o*-vanillin, *iso*-vanillin and 4-hydroxy coumarin which reacted with bis-dihalides of polyglycols in the presence of DMSO/alkali carbonate. The novel podands, Ar-$(CH_2CH_2O)_m$-Ar, (m = 1–4), were identified with IR, ^{1}H-NMR, ^{13}C-NMR and mass spectrometry. The various (formyl-methoxy)phenyl and 4-oxycoumarin derivatives of glycols were studied to estimate the cation binding selectivity of SCN^- salts of Li^+, Na^+, K^+ and Zn^{2+} cations in acetonitrile using steady state fluorescence spectroscopy. The relevant structures of podands have shown good selectivity depending on the cation and the glycol length, although the chromophore end groups have no specific contribution on binding.

Introduction

The relevant polyethylene glycols to bind the cations were so far recognised and many of them have been synthesised and widely investigated for molecular and cationic recognition [1]. They were also known to transport the cation across the membranes as the naturally occurring precursors [1, 2]. However, their fast ligand–cation exchange rate causes limited binding power have been used for the design of the ion detectors working via potentiometry or spectroscopy [1–5]. The studies have shown that the cation–ligand interactions are also governed by the end groups as well as the conformational ability of the polyoxa-glycol chain for the cation chelation [4].

The polyethylene glycol chains, podands, binding the cation by chelation have been known since the use of pure polyethylene glycols–glymes for the salt solvating. The role of end groups may play a specific role for the chelation depending on their polarity [6]. The well known *glymes* have shown interesting cationic behaviour forming the crystalline alkali complexes [1].

The well-known lipid-soluble natural antibiotics like *peptides* and *depsipeptides* are this type of polyether molecules which are reorganised for pseudo-cyclization to complex with a cation [7]. However, the energy of chain conformation causing the maximum enthalpy of the ion binding of ionophores would be at least around 45–65 kJ/mol causing a rather fast cation–ligand exchanging equilibrium compared to macrocyclic ether complexes [8–10]. The cationic roles of such molecules have also been recently investigated by ^{1}H and ^{13}C, T_1-NMR measurements [11], as well as the fluorescence spectroscopy [12].

The synthetic podands have been recognised with the oxygen donors that are rather simple and less expensive to prepare. The structures containing oxyethylene units have been utilised as potentiometrical ion sensors in PVC matrix membranes which response with the fast ion–ligand exchange rate [13]. The additional binding site of some polar groups shows important binding effectivity likewise the calixarenes [14].

We recently synthesised bis-coumarin ended glycols and investigated their ion–ligand interactions with the fluorescence spectroscopy for the estimation of catons like Pb^{2+} [15]. Some of the mono and diethylene glycol derivatives were found to be sensitive to alkali cations in AN as we reported recently [16].
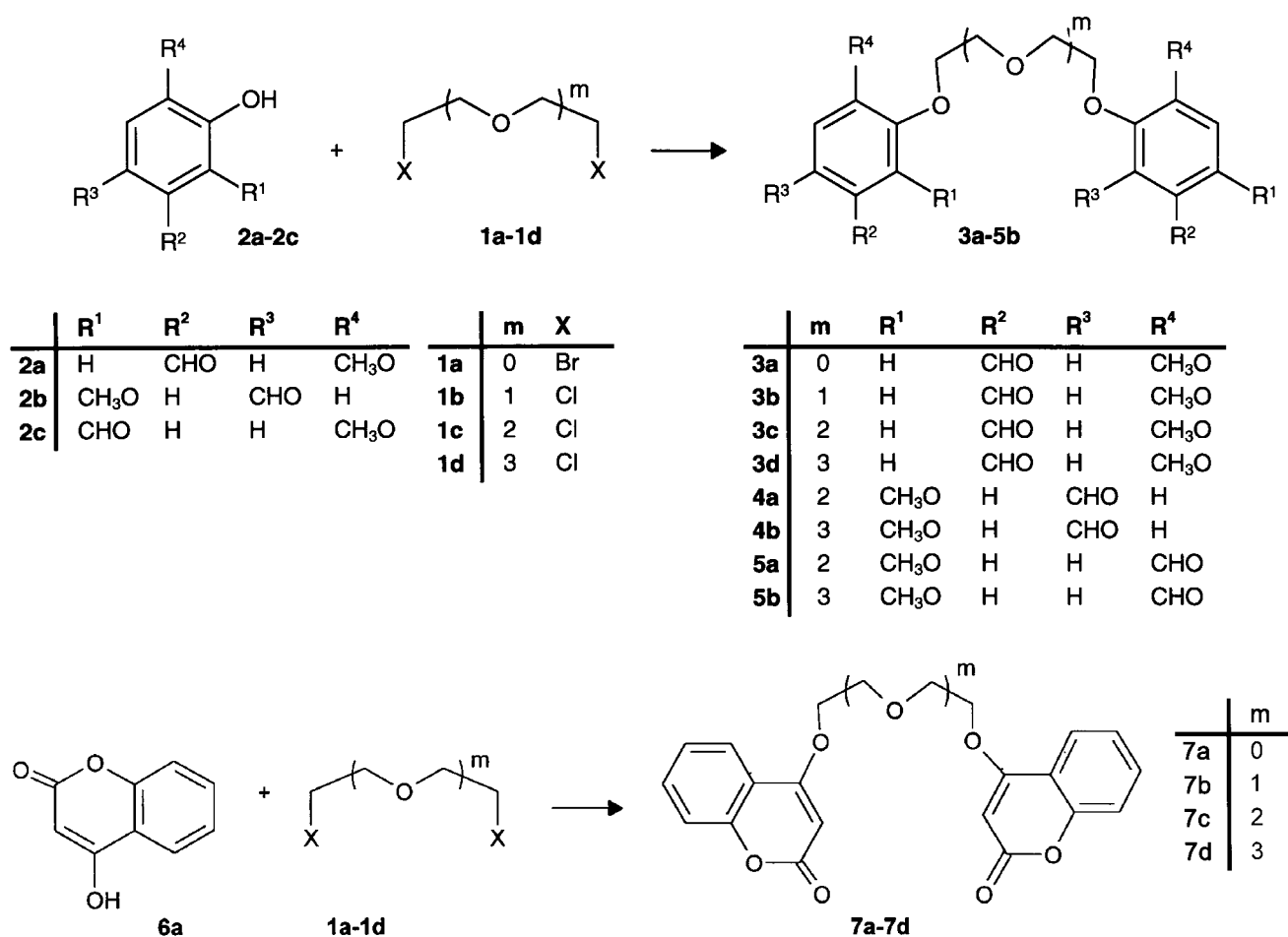
Results and discussion

The bis-(formyl-methoxy)phenyl and bis-(4-oxa)coumarin ended polyglycols were synthesised using vanillin, *o*-vanillin, *iso*-vanillin and 4-hydroxy coumarin. The hydroxy groups of those phenols reacted with bis-dihalides of polyglycols in the presence of DMF or DMSO/alkali carbonate to afford the bis-substituted aromatic podands, Scheme 1, [16]. The synthesised original products were identified with IR, ^{1}H-NMR, ^{13}C-NMR and mass spectrometry as displayed on Table 1 with the yields. The purity of the products was good enough to study on the cation selectivity in AN using fluorescence spectroscopy.

Aromatic bis-methoxy-carbonyl derivatives as well as the bis-4-oxycoumarin derivatives of glycols were studied in

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	R^1	R^2	R^3	R^4
2a	H	CHO	H	CH$_3$O
2b	CH$_3$O	H	CHO	H
2c	CHO	H	H	CH$_3$O

	m	X
1a	0	Br
1b	1	Cl
1c	2	Cl
1d	3	Cl

	m	R^1	R^2	R^3	R^4
3a	0	H	CHO	H	CH$_3$O
3b	1	H	CHO	H	CH$_3$O
3c	2	H	CHO	H	CH$_3$O
3d	3	H	CHO	H	CH$_3$O
4a	2	CH$_3$O	H	CHO	H
4b	3	CH$_3$O	H	CHO	H
5a	2	CH$_3$O	H	H	CHO
5b	3	CH$_3$O	H	H	CHO

	m
7a	0
7b	1
7c	2
7d	3

Scheme 1.

the present work for the estimation of the binding selectivity of SCN$^-$ salts of the Li$^+$, Na$^+$, K$^+$ and Zn^{2+} in AN using the steady state fluorescence spectroscopy. The fluorescence data of the maximum emission intensity ratios of free and cation chelated podands at 25 °C are displayed in Table 2. The podands, **3a–5b** and **7a–7d**, are strongly quenched even at low concentrations in AN. The fluorescence effectivity, E_{eff}, obtained from quantum yields, of free and complexed molecules referring the intensities of free, I_{max} and complexed lumophore, I_o, according to Equations (1) and (2), are displayed in Table 2.

$$E_{\text{eff}} = \varphi_o - \varphi_{\text{max}}/\varphi_{\text{max}}, \qquad (1)$$

$$E_{\text{eff}} = I_o - I_{\text{max}}/I_{\text{max}} = E_{\text{eff}}, \qquad (2)$$

where $I_i = \xi_i C_i I_i \varphi_i$ and ξ_i of both free and complexed macrocycle are supposed to be close to each other to cancel in the ratio of Equation (1).

Fluorophores are promoted to high energy levels by absorbing photon energy in one region so in the excited state there is a rapid radationless energy transfer to the lowest excited state and then a return to the ground state by the emission of the photone at a longer wavelength depending on the cationic interactions. The strength of the cation–podand interactions depending on the chelation ability of

the podand and the cation radii as well as the cation electropositivity displayed mostly the complexation enhanced fluorescence, CEFS, of the 1:1 molar ratio of cation–podand mixtures in acetonitrile solutions, Table 2. A few of them, however, exhibited the complexation enhanced quenching spectra, CEQFS, although the results are mostly due to the challenges between the phosphorescence and fluorescence decay rates of the excited cation complexes as was discussed recently in our reports [17–19].

Accordingly, **3b**, (m = 2) exhibited the best interaction with Li$^+$ ion while **3d**, (m = 4) showed perfect interaction with K$^+$ due to marked chelation. However, **4b**, (m = 3) was interestingly sensitive to Na$^+$ as well as to Li$^+$ and Zn^{2+} cations showing the role of intermediate cation radii. The results are also in accordance with the length of the glycols, since the longer the glycol the better is the complex formation role for a larger radii of cation. This is shown, in particular, with **5b**/Zn^{2+} interactions of high performance. The fluorescence study is in general; depend on the measurement conditions, like the temperature, solvent and concentrations.

Some of the podands, like **4a**, **7a–7d** were, although, not responsive to cations as observed from the poor alterations of their fluorescence emission spectra, Table 2. This is in fact originated either from limited electronic interactions or because of hindered cation–podand interactions depending

Table 1. Spectral and structural data for the podands **3a–7d**

No.	Mp	Yield	IR (cm^{-1})	^{1}H NMR (400 MHz) ppm	^{13}C NMR (100 MHz) ppm	m.w.	mass (e/m)
3a	154	23	2918, 1734, 1400, 1163, 828	3.95(6H, s, 2CH$_3$O), 4.52(4H, s, C$_2$H$_4$O), 6.75(2H, d, Ar), 7.52(4H, m, Ar), 9.87(2H, s, CHO)	56.9, 68.6, 112.1, 113.3, 128.2, 131.3, 150.1, 156.5, 192.3	C$_{18}$H$_{18}$O$_6$	330, 312, 267, 179, 151, 91
3b	124	72	2916, 1684, 1462, 1130, 812	3.95(6H, t, 2CH$_3$O), 4.01(4H, t, 2CH$_2$O), 4.28(4H, t, 2CH$_2$O), 6.97(2H, d, Ar), 7.46(4H, m, Ar), 9.84(2H, s, CHO)	56.9, 69.5, 70.6, 111.9, 112.4, 127.9, 131.2, 150.2, 156.4, 192.3	C$_{20}$H$_{22}$O$_6$	374, 312, 267, 179, 151, 91
3c	103	75	2879, 1684, 1597, 1402, 1265, 1045, 866	3.75(4H, s, C$_2$H$_4$O), 3.91(4H, t, 2CH$_2$O), 3.91(6H, s, 2CH$_3$O), 4.22(4H, t, 2CH$_2$O), 6.95(2H, d, Ar), 7.43(4H, m, Ar), 9.81(2H, s, CHO)	56.1, 68.4, 63.5, 70.9, 110.7, 110.9, 126.9, 130.0, 148.8, 154.9, 190.9	C$_{22}$H$_{26}$O$_8$	418, 224, 179, 152, 151, 119
3d	94	44	2924, 1682, 1439, 1048, 814	3.67(4H, t, 2CH$_2$O), 3.69(4H, t, 2CH$_2$O), 3.88(4H, t, 2CH$_2$O), 3.90(6H, s, 2CH$_3$O), 4.20(4H, t, 2CH$_2$O), 6.93(2H, d, Ar), 7.38(4H, m, Ar), 9.79(2H, s, CHO)	56.3, 68.6, 69.6, 70.8, 71.0, 110.9, 111.1, 127.1, 130.1, 149.0, 155.1, 191.2	C$_{24}$H$_{30}$O$_9$	462, 223, 179, 151, 121, 93
4a	92	76	3076, 2885, 1697, 1429, 1024, 860	3.76(4H, s, 2CH$_2$O), 3.91(6H, s, 2CH$_3$O), 3.93(4H, t, 2CH$_2$O), 4.26(4H, t, 2CH$_2$O), 6.99(2H, d, Ar), 7.44(4H, m, Ar), 9.84(2H, s, CHO)	56.7, 69.3, 70.2, 71.7, 110.6, 113.1, 127.1, 127.7, 151.2, 155.2, 192.4	C$_{22}$H$_{26}$O$_8$	418, 223, 179, 151, 121, 95
4b	70	80	2947, 1680, 1595, 1402, 1265, 1140, 944	3.63(8H, m, 4CH$_2$O), 3.88(6H, s, 2CH$_3$O), 3.89(4H, t, 2CH$_2$O), 4.23(4H, t, 2CH$_2$O), 6.90(4H, d, Ar), 7.31(4H, m, Ar), 9.78(2H, s, CHO)	56.0, 68.5, 69.4, 70.7, 70.9, 109.3, 111.9, 126.7, 130.3, 149.9, 153.9, 191.0	C$_{24}$H$_{30}$O$_9$	462, 233, 179, 151, 121, 95
5a	54	79	2930, 1689, 1595, 1487, 1257, 1076, 910	3.61(4H, s, 2CH$_2$O), 3.73(4H, t, 2CH$_2$O), 3.89(6H, s, 2CH$_3$O), 4.32(4H, t, 2CH$_2$O), 7.11(4H, m, Ar), 7.39(2H, d, Ar), 10.46(2H, s, CHO)	56.1, 61.5, 72.0, 74.4, 118.2, 119.6, 124.0, 130.0, 151.0, 153.1, 192.2	C$_{22}$H$_{26}$O$_8$	418, 223, 179, 151, 121, 95
5b	74	54	2947, 1684, 1463, 1255, 1099, 779	3.62(8H, m, 4CH$_2$O), 3.78(4H, t, 2CH$_2$O), 3.89(6H, s, 2CH$_3$O), 4.34(4H, t, 2CH$_2$O), 7.14(4H, m, Ar), 7.20(2H, m, Ar), 10.04(2H, s, CHO)	56.1, 70.4, 70.7, 70.8, 73.3, 118.0, 118.9, 129.2, 130.3, 151.5, 153.1, 191.3	C$_{24}$H$_{30}$O$_9$	462, 233, 179, 151, 121, 95
6a	188	25	2875, 1755, 1655, 1472, 1140, 960	4.52(4H, s, C$_2$H$_4$O), 5.69(2H, s, cumH), 7.21(2H, t, Ar), 7.29(2H, t, Ar), 7.54(2H, t, Ar), 7.80(2H, d, Ar)	55.6, 69.7, 91.0, 116.5, 117.7, 123,6 124.2, 133.3, 154.3, 163.6, 166.6	C$_{20}$H$_{14}$O$_6$	350, 233, 227, 163, 162, 121
6b	175	22	2880, 1750, 1640, 1480, 1115, 955	4.06(4H, t, CH$_2$O), 4.33(4H, t, CH$_2$O), 5.70(2H, s, cumH), 7.20(2H, t, Ar), 7.28(2H, t, Ar), 7.53(2H, t, Ar), 7.80(2H, d, Ar)	69.5, 69.9, 91.4, 116.3, 117.6, 123.7, 124.1, 133.4, 154.3, 163.7, 166.5	C$_{22}$H$_{18}$O$_7$	394, 233, 163, 162, 162, 121
6c	90	17	2870, 1750, 1655, 1480, 1140, 782	3.79(4H, s, CH$_2$O), 3.97(4H, t, CH$_2$O), 4.28(4H, t, CH$_2$O), 5.68(2H, s, cumH), 7.23(2H, t, ArH), 7.29(2H, t, ArH), 7.53(2H, t, ArH), 7.08(2H, d, ArH)	70.6, 70.9, 73.1, 92.8, 117.1, 119.6, 126.7, 127.1, 134.4, 155.3, 164.4, 166.7	C$_{24}$H$_{22}$O$_8$	438, 233, 227, 161, 162, 121
6d	50	10	2876, 1753, 1651, 1421, 1114, 780	3.72(8H, m, CH$_2$O), 3.98(4H, t, CH$_2$O), 4.22(4H, t, CH$_2$O), 5.78(2H, s, cumH), 7.23(2H, t, ArH), 7.29(2H, t, ArH), 7.53(2H, t, ArH), 7.08(2H, d, ArH)	68.3, 68.6, 70.1, 70.4, 89.4, 115.2, 116.0, 122.8, 123.5, 132.0, 152.8, 161.8, 165.0	C$_{26}$H$_{26}$O$_9$	482, 233, 227, 163, 162, 121

on the end groups. The results, in general, evidenced that the podand chelation of the cations involved in AN could be observed quantitatively using fluorescence spectroscopy. The reported work on this topic has shown the marked interest very recently [20].

Experimental

Fluorescence measurements

The fluorescence emission and excitation spectra were recorded with the spectrafluorometer, from JEOL, model FP-750, at 25 °C in a 10 mm of the thermo-stated quartz cell using the standard spectrometer software in high sensitivity mode. Spectral emission and excitation bandwidths are 10 nm. The emission intensity of quinine sulphate, $(2 \times 10^{-2}$

Table 2. The fluorescence data and cation effect on **3a–7d** in AN, cation and podand conc. 5.0×10^{-5} M/L

Podand	λ_{exmax}	λ_{emmax}	I_{max}	I_o (Li$^+$)	E_{eff} (Li$^+$)	I_o (Na$^+$)	E_{eff} (Na$^+$)	I_o (K$^+$)	E_{eff} (K$^+$)	I_o (Zn^{2+})	E_{ff} (Zn^{2+})
3a	340	405	71.7	69.9	0.03	70.7	0.01	84.0	−0.15	65.5	0.09
3b	345	410	32.6	153.6	−0.79	43.9	−0.26	39.3	−0.17	51.0	−0.36
3c	345	407	20.0	26.7	−0.25	27.3	−0.27	27.4	−0.27	27.7	−0.28
3d	344	415	41.7	56.9	−0.27	44.8	−0.07	159.0	−0.74	41.6	0.00
4a	344	405	43.3	52.7	−0.18	51.0	−0.15	47.8	−0.09	38.3	0.13
4b	345	407	17.0	10.1	0.68	35.0	−0.51	12.0	0.42	10.9	0.56
5a	345	410	49.9	62.7	−0.20	61.6	−0.19	64.0	−0.22	68.7	−0.27
5b	345	408	38.0	35.8	0.06	36.0	0.06	29.1	0.31	24.5	0.55
7a	344	410	40.0	49.0	−0.18	44.1	−0.09	38.0	0.05	41.6	−0.04
7b	345	410	43.9	47.5	−0.08	43.1	0.02	43.0	0.02	45.8	−0.04
7c	344	410	45.4	55.6	−0.18	52.6	−0.14	54.6	−0.17	46.9	−0.03
7d	345	410	87.8	94.9	−0.07	86.1	0.02	86.1	0.02	91.6	−0.04

λ_{exmax}; Wavelength maxima of fluorescence excitation spectra of the fluorophore.
λ_{emmax}; Wavelength maxima of fluorescence emission spectra of the fluorophore. I_{max}; Intensity of maxima of fluorescence emission spectra of the free fluorophore.
I_o(Me); Intensity of maxima of fluorescence excitation spectra of the complexed fluorophore.
E_{eff}; The ratio of maxima of complexed and free podands to indicate the effect of complex formation on the fluorescence, $I_o - I_{max}/I_{max} = E_{eff}$ in acetonitrile at 25 °C in 0.5×10^{-4} M/L.

M/L), I_{max} = 998, was found. The emission intensity of the free podands, I_{max} and the emission intensity of the cation-podand mixtures, I_o, of the equivalent concentrations, $(0.5 \times 10^{-4}$ mol/L), are represented in Table 2. The fluorescence emission maximum, λ_{emmax} and excitation maximum, λ_{exmax} wavelengths along with the quantum efficiency, E_{ff}, of the complex formation are given in Table 2.

Organic syntheses

The starting chemicals, vanillin derivatives, acetonitrile, AN, were from MERCK or FLUKA unless otherwise cited. The bis-dihalides of the poly glycols were available from the earlier studies [17]. IR spectra were taken as KBr pellets with a JASCO FT-IR spectrometer, model-5300. The EI Mass spectra were obtained with FISONS instrument, model VG-Zabspec. ^{1}H and ^{13}C NMR spectra were obtained with a 400 MHz BRUKER nmr spectrometer, model AVANCE-400CPX and TMS was the internal standard. The melting points reported are uncorrected.

The podands, **3a–3d** were obtained form iso-vanillin, **2a**, reacting with **1a–1d**. Accordingly, **4a** and **4b** were obtained from p-vanillin, **2b**, reacting with **1c** and **1d**. The **5a** and **5b** were obtained from *o*-vanillin, **2c**, reacting with **1c** and **1d** respectively. 4-Hydroxycoumarin, **6a** reacted with **1a–1d** to afford **7a–7d**.

General procedure of the synthesis of the podands is as follows; The phenols (vanillin derivatives), **2a-2c** (10–50 mmol), bis-polyglycol halides, **1a-1d** (5–25 mmol) and Na$_2$CO$_3$ (10–50 mmol) were added to DMF, (30–50 ml), or DMSO, (30–50 ml) and heated while stirring for three to four days at 80–85 °C. The reaction mixtures were acidified (HCl) and raw products of **3a–3c** and **7a–7d** were filtered and crystallized but, the oily raw products, **3c**, **4a**, **4b**, **5a** and **5b** were extracted from the acidified mixture with chloroform, which were dried and chromatographed on the

Alumina, (Basic), with CH$_2$Cl$_2$. Most of the final products were recrystallised from ethanol-water or methanol-water. The melting points and the yields of the products as well as the low resolution EI mass spectroscopy data, IR, ^{13}C and ^{1}H NMR spectral data are displayed in Table 1.

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