The Synthesis of Chromophore ended Glycoles, Part IV. Bis-Coumarin Derivatives ended Polyglycols

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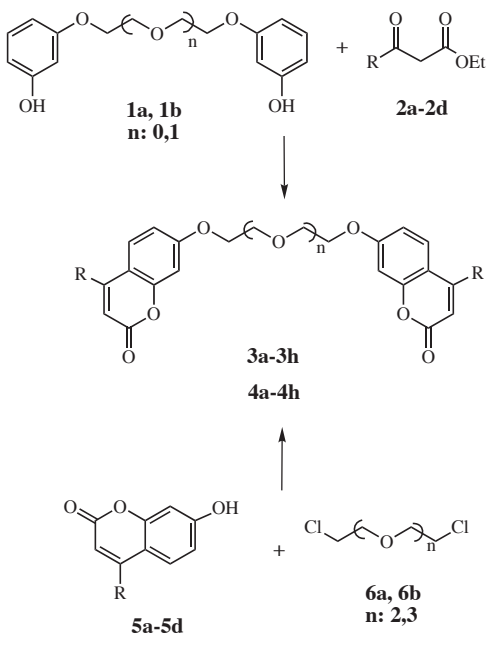

	R		R	n		R	n		R	n		R	n		R
2a	CH_3	**3a**	CH_3	0	**3e**	CH_3	1	**4a**	CH_3	2	**4e**	CH_3	3	**5a**	CH_3
2b	CF_3	**3b**	CF_3	0	**3f**	CF_3	1	**4b**	CF_3	2	**4f**	CF_3	3	**5b**	CF_3
2c	C_3H_7	**3c**	C_3H_7	0	**3g**	C_3H_7	1	**4c**	C_3H_7	2	**4g**	C_3H_7	3	**5c**	C_3H_7
2d	C_6H_5	**3d**	C_6H_5	0	**3h**	C_6H_5	1	**4d**	C_6H_5	2	**4h**	C_6H_5	3	**5d**	C_6H_5

This manuscript is dedicated to the memory of Professor Dr. Çakıl Erk who passed away August 21, 2005

The coumarin derivatives of bis-resorcin ended polyglycols were prepared in two ways: Bis-4-alkyl-7-oxycoumarin ended mono and diethyleneglycols were prepared starting from bis(3-hydroxyphenyl)glycols by coumarin condensation using relevant β-ketoesters. Accordingly, 4-methyl, 4-trifluoromethyl, 4-*n*-propyl and 4-phenyl derivatives of 7-hydroxycoumarins were prepared in good yields. They were then converted to bis-coumarin ended three and tetraethylenglycol derivatives by reacting with three and tetraethyleneglycols dichlorides in Na_2CO_3/DMF, respectively. The products were identified using IR, ^1H nmr and low resolution mass spectrometry. The Li^+, Na^+ and Rb^+ metal/Ligand selectivities of cation binding behaviour of products in acetonitrile were studied with steady state fluorescence spectroscopy.

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Introduction.

Observation of chemical molecular recognition systems involving various cation and molecule binders reveals a universal tool for understanding the roles of supramolecular interactions in chemical and biochemical systems [1-5]. Fluorescent supramolecules with strong polar groups are fast and practical for remote detection of cationic and molecular interactions [6-8]. The synthesis and the ionic recognition properties of the synthetic receptors of macrocyclic ethers and their noncyclic polyoxa initials with chromophore moieties have been our work of interest [8-14]. On the other hand, cation selectivity is the prime importance that very much depends on the analytical method [1-3]. Polyethylene glycol structures can chelate a variety of radii of the metal cations in nonpolar solutions with high yield of organic preparations as well as having significantly fast cation-ligand exchange rates for use as sensors [3-6]. Polyglycols, namely podands, with fluoroionophore recognition moieties, likewise coumarins,

have been synthesized and utilized as optical cation sensors in our laboratory [14-18]. The fluorescence spectroscopy for the cationic recognition with fluoroionophoric moieties has been recently reviewed from the point of photophysical effects [6,7]. Coumarins isolated from plants could be synthesized. Using the coumarin substituted crown ethers studied with steady state fluorescence spectroscopy significant results have been obtained [9-11]. Hydroxy coumarins were condensed with ketoesters in $HClO_4$, H_2SO_4 or different methods [19]. The synthesis and ion binding roles of crown ethers bearing coumarin in general [14,18] have also been reported. However, bis-(3-hydroxyphenoxy) ended mono- and diglycols **(1a**,**1b)** synthesized previously [12] were also converted to new bis-coumarin ended polyglycols using common methods of coumarin formation in this work [9,10,14,18]. The results of both methods of coumarin derivatives are reported in Scheme 1. Different substituted coumarins with bis-ended polyglycols were prepared to investigate the electronic properties of this group on the coumarin ring [14-18]. The electron donating or withdrawing roles of the substituents, CH_3, CF_3, C_3H_7 and C_6H_5 on the fluorescence intensity of the fluoroionophore and its cationic complexes were investigated.

Results and Discussion.

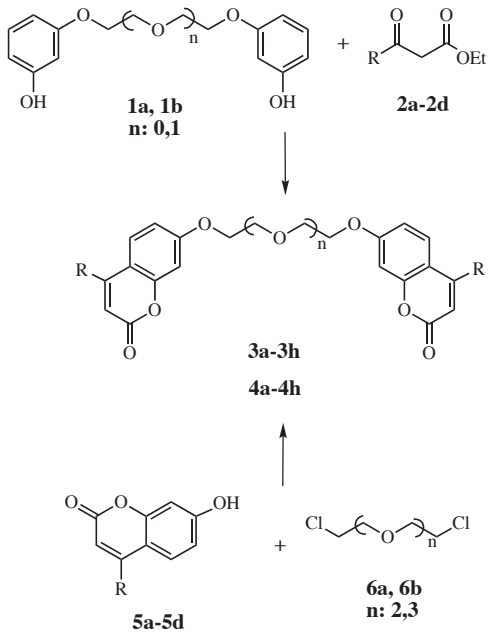
Organic Synthesis.

The reaction of 1,4-bis(3-hydroxyphenyl)-1,4-dioxabutane, **1a**, and 1,7-bis(3-hydroxyphenyl)-1,4,7-trioxaheptane, **1b**, with *β*-ketoesters; ethyl acetoacetate, ethyl trifluoromethylacetate, ethyl propionylacetate, ethyl benzoylacetate, **2a-2d**, in trifluoroacetic acid or in $HClO_4$ gave readily coumarin podands, **3a-3h**. Initial coumarins, 7-hydroxy-4-methylcoumarin, 7-hydroxy-4-trifluoromethylcoumarin, 7-hydroxy-4-propylcoumarin and 7-hydroxy-4-phenylcoumarin, **5a-5d**, were prepared *via* Pechmann reactions with resorcin and *β*-ketoesters, **2a-2d**, in good yield [19]. The reaction of initial coumarins, **5a-5d**, with tri- or tetraethyhlene glycol dichlorides, **6a** and **6b**, gave podands, **4a-4h**, in the presence of Na_2CO_3 and DMF at 80-85 °C, Scheme 1. Quantum yields of photophysical effects of some products observed with reference to quinine hydrosulphate dihydrate at 25 °C in H_2SO_4, were represented in Table 1.

Cation Complexing with Steady State Fluorescence Spectroscopy.

The importance of such acyclic compounds modeling to biological systems of arrays which may function as diverse

Scheme 1



	R		R	n		R	n		R	n		R	n		R
2a	CH_3	**3a**	CH_3	0	**3e**	CH_3	1	**4a**	CH_3	2	**4e**	CH_3	3	**5a**	CH_3
2b	CF_3	**3b**	CF_3	0	**3f**	CF_3	1	**4b**	CF_3	2	**4f**	CF_3	3	**5b**	CF_3
2c	C_3H_7	**3c**	C_3H_7	0	**3g**	C_3H_7	1	**4c**	C_3H_7	2	**4g**	C_3H_7	3	**5c**	C_3H_7
2d	C_6H_5	**3d**	C_6H_5	0	**3h**	C_6H_5	1	**4d**	C_6H_5	2	**4h**	C_6H_5	3	**5d**	C_6H_5

The synthetic and structural data of coumarin podands.

Table 1

The quantum yields, $(1-I_f/I_q)$ of some products in conc. H_2SO_4, ref quinine hydrosulfate dihydrate.

	Ex. λ_{max}	Em.λ_{max}	I_f (int.)	$(1-I_f/I_q)$
5a	283	407	802	-1.140
5b	283	466	718	-0.915
5c	283	407	999	-1.664
5d	283	433	207	0.448
3a	283	484	398	-0.061
3b	283	463	63	0.832
3e	283	412	999	-1.664
3f	283	458	430	-0.147
4a	283	409	509	-0.357
4b	283	458	827	-1.205
Quin.h.s.	282	482	375 (I_q)	

molecular structures, are entitled to ionic and molecular recognition as well as the self-assembly and template directed three dimensional molecular architectures [20]. This may be reorganized by the polar side groups if available to contribute to cation chelation that are also capable to lyophilize the entire glycol and diminishing the effect of hydroxylic solvents [16-17]. This is, although, another task for the extended number of the polyethylene groups for a sufficient chelating or encapsulation [20]. We have just studied the 1/1 ratio of cation/ligand podand mixtures and observed the cationic fluorescence affectivities in acetonitrile (AN), Table 2. The chromophore effect of bis-located coumarin end groups of glymes is very strong, although, such groups may display remarkable steric effect, Table 2. The cationic selectivity of fluorescence, E_{eff}, of podands could be estimated from the assigment of the quantum yields, φ_o and φ_{max}. The fluorescence intensities of free, I_{max}, ($I_{max}=\xi_{max}\ C_{max}\ \varphi_{max}$), and complexed lumophore, I_o ($I_o=\xi_o\ C_o\ l_o\ \varphi_o$), used in Eq 1 gives E_{eff}. provided that the molar extinction coefficients of free and complexed ligands are approximately equal in experimental error limits, ($\xi_f \approx \xi_o$), in equivalent concentrations, ($C_o=C_{max}$) for 1/1 ratio gives Eq 2.

$$E_{eff} = I_o - I_{max} / I_{max} \quad (1)$$

$$E_{eff} = \varphi_o - \varphi_{max} / \varphi_{max} \quad (2)$$

The results are displaying the electron releasing roles of the substituents, CH_3, CF_3, C_3H_7 and C_6H_5 on the fluorescence intensity of the fluoroionophore and its cationic complexes were investigated. The CF_3 group has the effect to enhance the fluorescence intensities of the podands which is an important factor for the sensor roles. Contrarily C_6H_5 group has the minimum chromophore effect and the increasing length of polyethylene chain caused extensive quenching. The most interesting point is that the increasing length of polyethylene chain gave reducing cation binding selectivity for most of the chromophores podands. However, we especially studied cations and observed that Na^+ is usually sensitive for all ligands up to certain degree of selectivity. The **3b** as a dioxapodand with CF_3 group is excellent for Li^+ as well as Na^+. The **3e** is also good for all cations including Rb^+ since it is a trioxapodand but selectivity is poor. Such results indicate that the conformational adaptations influence the cation podand interactions. It was found that they even have high emission intensities that are sensitive to the type of cation, Table 2.

EXPERIMENTAL

The starting chemicals, resorcin, β-ketoesters, **2a-2d**, acetonitrile (AN) and other solvents, and also alkali salts were from MERCK or FLUKA unless otherwise cited. Salts were used as is without further purification but dried at 90-95 °C for few hours and dissolved in dry AN. Bis-(3-hydroxyphenoxy) ended glycols, **1a** and **1b**, were prepared according to ref. [12].

Table 2

The 1/1 ratio of cationic fluorescence effectivities, E_{eff} of the products in AN at 20 °C.

	Ex. λ_{max}	Em. λ_{max}	I_{max}	I_o [Li^+]	I_o [Na^+]	I_o [Rb^+]	E_{eff} [Li^+]	E_{eff} [Na^+]	E_{eff} [Rb^+]
3a	284	388	211	240	165	239	0.137	-0.218	0.133
3b	284	408	778	999	999	941	0.284	0.284	0.210
3c	284	382	376	395	342	363	0.051	-0.090	-0.035
3d	284	379	21	28	29	24	0.333	0.381	0.143
3e	283	384	371	427	441	430	0.151	0.189	0.159
3f	284	410	596	601	603	589	0.008	0.012	-0.012
3g	281	344	593	576	567	542	-0.029	-0.044	-0.086
4a	284	385	541	583	575	554	0.078	0.063	0.024
4b	284	410	760	757	714	727	-0.004	-0.061	-0.043
4c	285	383	631	616	606	630	-0.024	-0.040	-0.002
4e	295	381	301	319	318	316	0.060	0.056	0.050
4f	290	495	913	914	919	930	0.001	0.007	0.019
4g	280	356	665	650	658	676	-0.023	-0.011	0.017

The tri- and tetraethylene glycol dichlorides, **6a** and **6b**, were available from our earlier studies [9,10,14,15]. IR spectra were taken as KBr pellets with a Mathson FT-IR spectrometer. ^{1}H nmr spectra were obtained with a 250 MHz BRUKER nmr spectrometer, model AVANCE-250CPX, in $CDCI_3$ or in DMSO-d_6 and TMS was the internal standard. The melting points reported are uncorrected, Table 1.

The cationic fluorescence emission and excitation spectra of free and equimolare amounts of ligand and Li^+, Na^+ and Rb^+ alkali perchlorates containing podand solutions in AN were recorded with the spectrofluorometer, from JEOL, model FP-750. Samples in a 10 mm quartz cell placed in a thermostad block were measured using the standard spectrometer software with 5 nm emission and excitation bandwidths at 20 °C. The maximum excitation and emission intensities of free and complexed products, (3.3×10^{-4} mol/L) at maximum wavelengths, λ_{em} and λ_{ex} are represented on Table 2 along with cation binding fluorescence effectivities, E_{eff} of cations, Li^+, Na^+ and Rb^+ with the products in AN at 20 °C which were estimated according to Eq 2.

Table 3

Structural and Spectral data for the coumarin podands, **3a-3h** and **4a-4h**.

Comp. No.	Mp	Y (%)	IR (cm^{-1})	^{1}H-NMR (δppm)	Mass (CI)
3a	259	75	3462, 2909, 1707, 1609, 1395, 1156	2.40 (6H, s, $2CH_3$), 4.41 (4H, s, $2CH_2$), 6.15 (2H, s, cumH), 6.87 (2H, d, J=2.5 Hz, ArH), 6.91 (2H, dd, J=2.5 Hz, ArH), 7.51 (2H, d, J=8.7 Hz, ArH)	$C_{22}H_{18}O_6$ 378.382
3b	179	65	3461, 2871, 1743, 1612, 1373, 1191	4.44 (4H, s, $2CH_2$), 6.64 (2H, s, cumH), 6.93 (2H, d, J=2.5 Hz, ArH), 6.97 (2H, dd, J=2.5 Hz, ArH), 7.65 (2H, d, J=7.0 Hz, ArH)	$C_{22}H_{12}F_3O_6$ 486.318
3c	140	55	3470, 2861, 1620, 1607, 1428, 1146	1.01 (6H, t, J=7.5 Hz, $2CH_3$), 1.63-1.74 (4H, m, $2CH_2$), 2.65 (4H, t, J=7.5 Hz, $2CH_2$), 4.40 (4H, s, $2CH_2$), 6.08 (2H, s, cumH), 6.82 (2H, d, J=2.5 Hz, ArH), 6.85 (2H, dd, J=2.5 Hz, ArH), 7.49 (2H, d, J=8.8 Hz, ArH)	$C_{26}H_{26}0_6$ 434.481
3d	143	74	3470, 2908, 1724, 1611, 1375, 1152	4.32 (4H, s, $2CH_2$), 6.22 (2H, s, cumH), 6.76 (2H, d, J=2.5 Hz, ArH), 6.85 (2H, dd, J=2.5 Hz, ArH), 7.35 (2H, d, J=8.7 Hz, ArH), 7.40-7.52 (10H, m, PhH)	$C_{32}H_{22}O_6$ 502.513
3e	186	70	3468, 2900, 1720, 1619, 1370, 1129	2.38 (6H, s, $2CH_3$), 3.95 (4H, t, J=4.8 Hz, $2CH_2$), 4.20 (4H, t, J=4.8 Hz, $2CH_2$), 6.11 (2H, s, cumH), 6.79 (2H, d, J=2.5 Hz, ArH), 6.87 (2H, dd, J=2.5 Hz, ArH), 7.47 (2H, d, J=8.8 Hz, ArH)	$C_{24}H_{22}O_7$ 422.427
3f	120	39	3449, 2897, 1739, 1613, 1280, 1191	3.97 (4H, t, J=4.5 Hz, $2CH_2$), 4.23 (4H, t, J=4.5 Hz, $2CH_2$), 6.60 (2H, s, cumH), 6.90 (2H, d, J=2.5 Hz, ArH), 6.92 (2H, dd, J=2. 5 Hz, ArH), 7.61 (2H, d, J=8.0 Hz, ArH)	$C_{24}H_{16}F_6O_7$ 530.370
3g	123	60	3462, 2958, 1727, 1608, 1290, 1106	1.03 (6H, t, J=7.5 Hz, $2CH_3$), 1.65-1.76 (4H, m, $2CH_2$), 2.69 (4H, t, J=7.5 Hz, $2CH_2$), 3.95 (4H, t, J=4.5 Hz, $2CH_2$), 4.20 (4H, t, J=4,5 Hz, $2CH_2$), 6.11(2H, s, cumH), 6.80 (2H, d, J= 2.5 Hz, ArH), 6.86 (2H, dd, J=2.5 Hz, ArH), 7.50 (2H, d, J=8.8 Hz, ArH)	$C_{28}H_{30}O_7$ 476.534
3h	149	60	3443, 2925, 1726, 1607, 1266, 1154	3.96 (4H, t, J=4.8 Hz, $2CH_2$), 4.22 (4H, t, J=4.8 Hz, $2CH_2$), 6.20 (2H, s, cumH), 6.77 (2H, d, J= 2.5 Hz, ArH), 6.88 (2H, dd, J= 2.5 Hz, ArH), 7.36 (2H, d, J= 8.0 Hz, ArH), 7.40-7.52 (10H, m, PhH)	$C_{34}H_{26}O_7$ 546.566
4a	195	75	3459, 2858, 1736, 1613, 1387, 1123	2.38 (6H, s, $2CH_3$), 3.76 (4H, s, $2CH_2$), 3.89 (4H, t, J=4.5 Hz, $2CH_2$), 4.16 (4H, t, J=4.5 Hz, $2CH_2$), 6.11 (2H, s, cumH), 6,77 (2H, d, J= 2.5 Hz, ArH), 6.86 (2H, dd, J=2.5 Hz, ArH), 7.47 (2H, d, J= 8.8 Hz, ArH)	$C_{26}H_{26}O_8$ 466.480
4b	110	30	3460, 2825, 1747, 1612, 1351, 1142	3.78 (4H, s, $2CH_2$), 3.91 (4H, t, J= 4.7 Hz, $2CH_2$), 4.21 (4H, t, J= 4.7 Hz, $2CH_2$), 6.20 (2H, s, cumH), 6,81 (2H, dd, J= 2.5 Hz, ArH), 6.90 (2H, d, J=2.5 Hz, ArH), 7.37 (2H, d, J=8.8 Hz, ArH)	$C_{26}H_{20}F_6O_8$ 574.423
4c	119	65	3468, 2889, 1736, 1613, 1206, 1130	0.97 (6H, t, J=7.6 Hz, $2CH_3$), 1.61-1.69 (4H, m, $2CH_2$), 2.62 (4H, t, J=7.6 Hz, $2CH_2$), 3.69 (4H, s, $2CH_2$), 3.82 (4H, t, J=4.8 Hz, $2CH_2$), 4.11 (4H, t, J=4.8 Hz, $2CH_2$), 6.05 (2H, s, cumH), 6.74 (2H, d, J=2.5 Hz, ArH), 6.80 (2H, dd, J=2.5 Hz, ArH), 7.44 (2H, d, J=8.8 Hz, ArH)	$C_{30}H_{34}O_8$ 522.586
4d	203	70	3470, 2877, 1704, 1623, 1296, 1125	3.76 (4H, s, $2CH_2$), 3.88 (4H, t, J=4.6 Hz, $2CH_2$), 4.17 (4H, t, J=4.6Hz, $2CH_2$), 6.18 (2H, s, cumH), 6.76 (2H, d, J=2.5 Hz, ArH), 6.86 (2H, dd, J=2.5 Hz, ArH), 7.26 (2H, d, J=8.3 Hz, ArH), 7.42-7.50 (10H, m, PhH)	$C_{36}H_{30}O_8$ 590.619
4e	255*	55	3461, 2900, 1734, 1627, 1385, 1147	2.37 (6H, s, $2CH_3$), 3.60-3.73 (8H, m, $4CH_2$), 3.87 (4H, t, J=4.7 Hz, $2CH_2$), 4.15 (4H, t, J=4.7 Hz, $2CH_2$), 6.31 (2H, s, cumH), 6,78 (2H, d, J=2.5 Hz, ArH), 6.85 (2H, dd, J=2.5 Hz, ArH), 7.46 (2H, d, J=8.8 Hz, ArH)	$C_{28}H_{30}O_9$ 510.532
4f	297*	55	3090, 2875, 1752, 1698, 1204, 1141	3.67 (4H, s, $2CH_2$), 3.72 (4H, d, J=4.0 Hz, $2CH_2$), 3.88 (4H, t, J=4.6 Hz, $2CH_2$), 4.18 (4H, t, J=4.6 Hz, $2CH_2$), 6.51(2H, s, cumH), 6.80 (2H, d, J= 2.5 Hz, ArH), 6.84 (2H, dd, J=2.5 Hz, ArH), 7.50 (2H, d, J=8.8 Hz, ArH)	$C_{28}H_{24}F_6O_9$ 618.574
4g	243*	69	3479, 2909, 1724, 1620, 1392, 1144	0.95 (6H, t, J=7.6 Hz, $2CH_3$), 1.58-1.67 (4H, m, $2CH_2$), 2.60 (4H, t, J=7.6 Hz, $2CH_2$), 3.51-3.65 (8H, m, $4CH_2$), 3.80 (4H, t, J=4.8 Hz, $2CH_2$), 4.10 (4H, t, J=4.8 Hz, $2CH_2$), 6.03 (2H, s, cumH), 6.75 (2H, d, J=2.5 Hz, ArH), 6.80 (2H, dd, J=2.5 Hz, ArH), 7.43 (2H, d, J=8.8 Hz, ArH)	$C_{32}H_{38}O_9$ 566.639
4h	310*	41	3474, 2925, 1712, 1694, 1377, 1136	3.54-3.69 (8H, m, $4CH_2$), 3.82 (4H, t, J=4.7 Hz, $2CH_2$), 4.11 (4H, t, J=4.7 Hz, $2CH_2$), 6.12 (2H, s, cumH), 6.73 (2H, dd, J= 2.5 Hz, ArH), 6.81 (2H, d, J= 2.5 Hz, ArH), 7.29 (2H, d, J= 8.8 Hz, ArH), 7.33-7.43 (10H, m, PhH)	$C_{38}H_{34}O_9$ 634.671

* decompose.

Preparation of Coumarin Podands, **3a**-**3d**.

In a reaction flask, compound **1a**, (10.0 mmol) with *β*-ketoesters, **2a-2d**, (10-12 mmol) were refluxed for 6-8 h in trifluoroacetic acid (25-30 mL) or heated at 75-80 °C in $HClO_4$ (45-50 mL) for 6-8 h. The reaction mixture was cooled and kept at -10 °C for overnight. The crude product was collected by filtration, washed with water to remove acidic residues and dried at 80 °C. The crude product was dissolved in $CHCl_3$ (20 mL) and chromatographed on alumina (basic) with $CHCl_3$ (4x25 mL) to give the compounds, **3a-3d**. The mp, yields, IR spectra, and ^1H nmr spectra of compounds, **3a**-**3d**, are displayed in Table 3 [8,11,12].

Preparation of Coumarin Podands, **3e**-**3h**.

In a reaction flask, compound **1b**, (10.0 mmol) with *β*-ketoesters, **2a-2d**, (10-12 mmol) were refluxed for 6-8 h in trifluoroacetic acid (25-30 mL) or heated at 75-80 °C in $HClO_4$ (45-50 mL) for 6-8 h. The reaction mixture was cooled and kept at -10 °C for overnight. The crude product was collected by filtration, washed with water to remove acidic residues and dried at 80 °C. The crude product was dissolved in $CHCl_3$ (20 mL) and chromatographed on alumina (basic) with $CHCl_3$ (4x25 mL) to give the compounds, **3e-3h**. The mp, yields, IR spectra and ^1H nmr spectra of compounds, **3e**-**3h**, are displayed in Table 3 [8,11,12].

Preparation of Coumarin Podands, **4a-4d**.

The initial coumarins, **5a-5d**, (20 mmol), with triethyhlene glycol dichloride, **6a**, (10 mmol), Na_2CO_3 (20 mmol) and DMF (50 mL) were heated at 80-85 °C for 72-80 h while stirring, respectively, then acidified with HCl (40 mL, 0.2 *N*) and collected with filtration, washed with water to remove acidic residiues and dried at 80 °C. The crude product was dissolved in CH_2Cl_2 (20 mL) and chromatographed on alumina (neutral) with CH_2Cl_2 (4x25 mL) to give the compounds, **4a-4d** The mp, yields, IR spectra, and ^1H nmr spectra of compounds, **4a**-**4d**, are displayed in Table 3.

Preparation of Coumarin Podands, **4e-4h**.

The initial coumarins, **5a-5d**, (20 mmol), with tetraethyhlene glycol dichloride, **6b**, (10 mmol), Na_2CO_3 (20 mmol) and DMF (50 mL) were heated at 80-85 °C for 72-80 h while stirring, respectively, then acidified with HCl (40 mL, 0.2 *N*) and collected with filtration, washed with water to remove acidic residues and dried at 80 °C. The crude product was dissolved in CH_2Cl_2 (20 mL) and chromatographed on alumina (neutral) with CH_2Cl_2 (4x25 mL) to give the compounds, **4e-4h** The mp, yields, IR spectra, and ^1H nmr spectra of compounds, **4e**-**4h**, are displayed in Table 3.

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