Dyes and Pigments 79 (2008) 270–272

Contents lists available at ScienceDirect

Dyes and Pigments

journal homepage: www.elsevier.com/locate/dyepig

Short communication

Synthesis and fluorescence of crown ethers containing coumarin

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ARTICLE INFO

Article history:
Received 10 December 2007
Received in revised form 14 March 2008
Accepted 15 March 2008
Available online 10 April 2008

Keywords:
Crown ethers
Coumarin
Fluorescence
Synthesis
Fluorescence quenching
Ion selectivity

ABSTRACT

The syntheses and fluorescence properties of a series of novel crown ethers containing coumarin group are presented. 2-(Benzocourmarin-3-acyloxymethyl) crown ethers were synthesized by reacting the acyl chloride of benzocourmarin-3-carboxylic acid with 2-hydroxymethyl crown ethers, while 4′-(benzocourmarin-3-carboxamido) benzo crown ethers were secured by reacting the acyl chloride of benzocourmarin-3-carboxylic acid with 4′-aminobenzo crown ethers. Only the ester-type crown ethers were fluorescent. As the polarity of the solvent increased, the emission maximum λ_{em} showed a slight red shift. DMSO was used as the fluorescence quenching solvent. Increased fluorescence was observed upon the addition of alkali and alkaline earth metal ions.

1. Introduction

Macrocycle that possesses ionophore ability has been a subject for extensive investigation not only for the synthetic protocol but also for its potential applications since its discovery by Pedersen [1]. There is a growing interest in synthesizing crown ether derivatives with fluorescence properties showing marked changes upon metal complexation, aiming to develop metal ion-selective and sensitive material [2].

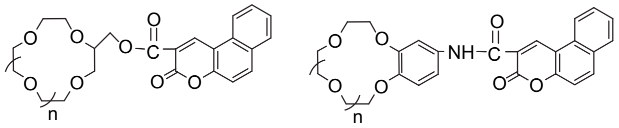
Coumarins are used in the fields of biology, medicine, perfumes, cosmetics, and laser dyes [3]. Coumarins are relatively photo-stable and their excitation and emission maxima, in many cases, are long enough to minimize the so-called "background" fluorescence of cellular components, tissues, and biological fluids. They exhibit Stokes shifts large enough to avoid significant overlap of the excitation and emission spectra, and the fluorescence quantum yields allow for ion detection at low indicator concentrations [4]. By integration of the coumarin chromophore in crown ethers, coumarin and its analogues have been extensively used in metal ion detection such as Na^+ [5], K^+ [5–8], Ca^{2+} [5,9–12], Mg^{2+} [11,13], Ba^{2+} [8], Sr^{2+} [14], Pb^{2+} [10,14], Ni^{2+} [10], Cu^{2+} [10], Al^{3+} [15], Hg^{2+} [16], and Tb^{3+} [17].

In order to develop new fluorescent probes for metal ions, six novel crown ethers containing coumarin were designed and synthesized. The coumarin moiety, benzocourmarin-3-carboxylic acid, was a fluorescent compound and easily prepared. The structures of compounds **1a**–**c** and **2a**–**c** are showed in Fig. 1.

2. Experimental

2 1. General synthesis of 2-(benzocourmarin-3-acyloxymethyl) crown ethers (1a–c)

The mixture of the acyl chloride of benzocourmarin-3-carboxylic acid (1.3 mmol), 2-hydroxymethyl crown ethers (1.3 mmol), benzene (30 mL), and triethyl amine (0.2 mL) was stirred under reflux for 24 h protected by nitrogen. The solvent was removed under reduced pressure. Purification by silica-gel column chromatography using dichlorimethane/2-propanol (10:1) as the eluent afforded the desired compound.



1a, n = 1
1b, n = 2
1c, n = 3

2a, n = 1
2b, n = 2
2c, n = 3

Fig. 1. The structure of compounds **1a**–**c** and **2a**–**c**.

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doi:10.1016/j.dyepig.2008.03.007

Table 1
Fluorescence emission data of compounds **1a**–**c**

Compound	Solvent									
	$CHCl_3$	$CH_3CO_2C_2H_5$	THF	CH_2Cl_2	CH_2ClCH_2Cl	C_2H_5OH	CH_3OH	CH_3CN	DMF	DMSO
1a										
λ_{em} (nm)	438	435	437	440	440	442	445	439	444	447
Φ_F	0.48	0.32	0.37	0.44	0.39	0.43	0.48	0.37	0.40	0.04
1b										
λ_{em} (nm)	438	434	435	438	443	440	444	442	447	447
Φ_F	0.52	0.33	0.43	0.58	0.58	0.40	0.52	0.45	0.47	0.05
1c										
λ_{em} (nm)	438	434	437	438	442	443	442	443	447	450
Φ_F	0.42	0.37	0.41	0.54	0.56	0.48	0.51	0.44	0.46	0.05

2 2. *General synthesis of 4′-(benzocourmarin-3-carboxamido)benzo crown ethers (**2a**–**c**)*

The mixture of the acyl chloride of benzocourmarin-3-carboxylic acid (1.3 mmol), 4′-aminobenzo crown ethers (1.5 mmol), 1,4-dioxane (30 mL), and pyridine (0.5 mL) was stirred under reflux for 24 h protected by nitrogen. The solvent was removed under reduced pressure, and water (20 mL) was added to the resulting solid and stirred. The solid was collected and purified by silica-gel column chromatography using dichlorimethane/2-propanol (10:1) as the eluent to afford the solid product.

3. Results and discussion

Only compounds **1a**–**c** of ester-type crown ethers were fluorescent. The fluorescence emission spectra of compounds **1a**–**c** were recorded at the concentration of 1×10^{-6} M. The λ_{em} data are presented in Table 1. The fluorescence quantum yields (Φ_F) of compounds **1a**–**c** were determined via comparison methods, using coumarin 120 as a standard sample with $\Phi_F = 0.77$ in methanol.

The wavelengths of fluorescence emission maxima of compounds **1a**–**c** are very similar in the same solvent. In dichloromethane, the λ_{em} is 440 nm, 438 nm, and 438 nm, respectively. So the size of the crown ether ring has little influence on its fluorescence property.

The results in Table 1 show that the fluorescence properties of crown ethers **1a**–**c** are affected by the solvent polarity. As the solvent polarity increases, the emission maximum λ_{em} shows a red shift. In chloroform, dichloromethane, 1,2-dichloroethane, and methanol, compounds **1a**–**c** exhibit stronger fluorescence emission. For instance, in dichloromethane, the values of Φ_F for compounds **1a**–**c** are 0.44, 0.58, and 0.54, respectively. It is interesting to note that DMSO is a fluorescence quenching solvent for compounds **1a**–**c**. In DMSO, the Φ_F values for compounds **1a**–**c** are only 0.04–0.05.

Table 2
Fluorescence emission data of compounds **1a**–**c** complexed with alkali and alkaline earth metal cations in acetonitrile

Compound	Cation					
		Li^+	Na^+	K^+	Mg^{2+}	Ba^{2+}
1a						
λ_{em} (nm)	443	440	442	440	440	447
Int_c/Int_l[a]		1.07	1.06	1.06	1.05	1.22
1b						
λ_{em} (nm)	441	441	442	441	447	450
Int_c/Int_l[a]		1.06	1.09	1.02	1.08	1.22
1c						
λ_{em} (nm)	441	442	441	443	441	449
Int_c/Int_l[a]		1.12	1.16	1.18	1.13	1.41

[a] Int_c: intensity of emission band of ligand containing cation; Int_l: intensity of emission band of the ligand.

The changes of the fluorescence spectra of compounds **1a**–**c** after the addition of metal cations are shown in Table 2. The fluorescence emission spectra of compounds **1a**–**c** were recorded at the concentration of 1×10^{-5} M, alkali and alkaline earth metal perchlorates at the concentration of 1×10^{-4} M in acetonitrile.

Among Li^+, Na^+, K^+, Mg^{2+}, and Ba^{2+}, only Ba^{2+} generates relatively large shifts of λ_{em} for compounds **1a**–**c**. For compound **1a**, λ_{em} shifts from 443 nm to 447 nm. For compound **1b**, λ_{em} shifts from 441 nm to 450 nm. For compound **1c**, λ_{em} shifts from 441 nm to 449 nm.

A slight or moderate increase of fluorescence was observed upon the addition of guest cations. When the guest cations were added, the relative emission intensity ratio, used as an indication of the molecular recognition sensing, changed from 1.22 to 1.05 for **1a**, from 1.22 to 1.02 for **1b**, and from 1.41 to 1.12 for **1c**. Ba^{2+} causes moderate increase of fluorescence emission of crown ethers **1a**–**c**. Especially for **1c**, the relative emission intensity ratio is up to 1.41.

4. Conclusions

Six novel crown ethers containing coumarin group have been synthesized and only compounds **1a**–**c** were fluorescent. As the polarity of the solvent increases, the emission maximum λ_{em} shows a slight red shift. DMSO is the fluorescence quenching solvent. A slight or moderate increase of fluorescence was observed upon the addition of guest cations. Compound **1c** exhibited relatively higher Ba^{2+} fluorescence selectivity than the others.

Acknowledgment

We thank the financial support of the 985 project from Sun Yat-Sen University.

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