Synthesis and Effect of Cation Binding on Photophysical Properties of 1,8-Anthraceno-18-Crown-5

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Abstract: A new type of anthracene crown ether 1,8-anthraceno-18-crown-5 has been synthesized and the photophysical properties upon complexation with alkali and alkaline-earth metal cations were investigated .The fluorescence quantum yield and lifetime are appreciably enhanced, and the stability constant Ks were determined by fluorometric titration. It was found that the magnitude of Ks is controlled by the size and charge density of the complexed cations.

Keywords: Crown ether, photophysical property, cation-binding.

The systems consisting of a fluorophore linked to a crown ether moiety are extensively investigated[1-3]. Since drastic changes in their photophysical properties can be observed by complexation with ion, they can be used for ionic detection[4,5]. Recent reports focus on azamacrocyclic derivatives with fluorophores[1,6], in which the fluorophore and crown ether moiety were linked *via* nitrogen atom. The presence of a basic nitrogen atom which is easy to be protonated leads to enhancement of fluorescence quantum yield[1,6,7]. We replaced the nitrogen atom of the crown by oxygen which is expected to enhance the alkali and alkali-earth cation binding.

Compound **2** was prepared from compound **1** which was in turn synthesized by the reaction of 1,8-dichloro-9,10-anthraquinone with tetraethylene glycol[8]. Compound **2** was then obtained from compound **1** by reduction.

There are several methods for reduction of anthraquinone to anthracene9,10. Klanderman11 prepared substituted anthracenes via the intermediate 9,10-dihydroxy-9,10-dihydroanthracene and anthrones by three steps. Several methods have been tried, and the procedure using sodium borohydride in 2-propanol was most promising. The mechanism of this reduction reaction presumably requires fast reduction of both carbonyl groups followed by loss of water to form the anthrone as a transient intermediate. Compound 2 is then obtained by aromatization through loss of a second water molecule[12].

1   **2**
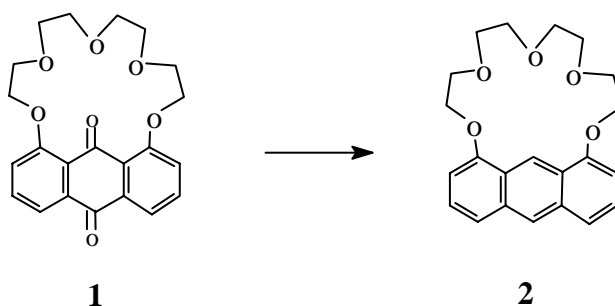
Experimental

To a suspension of 3.98g (10 mmol) of anthraquinone 1 in 150 mL of 2-propanol was added 9.0 g (237 mmol) of NaBH4. The mixture was refluxed for 12 h, then cooled and poured into ice water, and treated slowly with acetic acid at 0°C until the pH value of the mixture was 6. The mixture was extracted with CH2Cl2. The organic phase was washed with water and dried over MgSO4. The solvent was evaporated and yellow solid was obtained. Further purification by column chromatography on silica gel, using chloroform-petroleum ether (9:1) as eluant gave 2.65g (72%) of compound 2 as pale yellow solid13.

Figure 1. Emission spectra of the anthraceno crown ether and its complex with metal salts; Concentration of the ligand is 1.0×10^{-5} M; concentration of salts is 1.0×10^{-3} M in methanol. $\lambda_{ex} = 373$nm
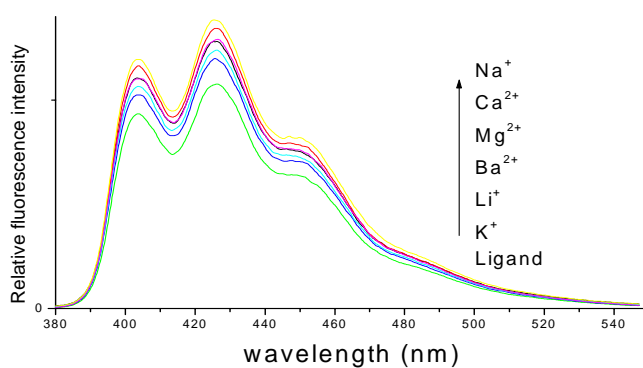
The emission spectra of compound **2** is shown in **Figure 1**. We can see that the relative fluorescence intensity of compound **2** was enhanced by complexation with alkali metal and alkaline-earth metal cations. Furthermore, both fluorescence quantum yield and lifetime are enhanced as indicated in **Table 1**. This may be attributed to the more rigid structure of the complex compared with the free ligand so that internal quenching due to conformational change is prevented.

Table 1 Fluorescence quantum yield, lifetime, and stability constant of compound **2**
and its complexes in methanol

| | Ligand [b] | complex [a] | | | | | |
		Li$^+$	Na$^+$	K$^{+\,c}$	Mg^{2+}	Ca^{2+}	Ba^{2+}
Ionic diameter Å		1.36	1.94	2.66	1.32	1.98	2.68
Φ_F [d]	0.20	0.27	0.29	0.26	0.28	0.28	0.28
τ (ns)	2.7	3.2	3.4	3.2	3.3	3.3	3.3
$\log_{10}Ks$		6.63	6.95	6..40	7.11	7.38	7.28

a. Concentration of salts is 1.0×10^{-3}M; b. Concentration of the ligand is 1.0×10^{-5} M. λ_{ex}=373nm; c. potassium acetate; d. anthracene used as standard (Φ_F=0.27 in ethanol λ_{ex}=365.5 nm).

The stability constant can be determined from the variation of fluorescence intensity at proper observation wavelength (427 nm) with the addition of cations. In our experiment, the stoichiometry of the complex is determined from fluorometric titration to be 1:1 in the investigated concentration range ($2.0 \times 10^{-6} \sim 1.0 \times 10^{-3}$). The stability constant Ks can be obtained by the following equation[14].

$$I = I_0 + \frac{I_{\lim} - I_0}{2c_0}\left[c_0 + c_m + \frac{1}{K_s} - \left[\left(c_0 + c_m + \frac{1}{K_s} \right)^2 - 4c_0 c_m \right]^{\frac{1}{2}} \right]$$

Where I_0, I corresponds to the fluorescence intensity of the free ligand and the complex, respectively. In the presence of excess of metal ion, I reaches the limiting value $I_{\lim}$, c_0 is concentration of the ligand, c_m is the metal ion concentration. Ks then can be determined by a nonlinear least-squares analysis of I. The results are included in **Table 1**.

We can see that among cations of the same charge, Na$^+$ and Ca^{2+} give the most stable complex showing that they fit best into the crown cavity. The results also show that the divalent cation binding were stronger by the crown giving larger Ks value. It is worthwhile to note that the Ks of lithium complex is higher than that of potassium complex despite the fact that the diameter of lithium ion is smaller than that of potassium ion. A possible explanation of this discrepancy is that the lithium ion is the most strongly solvated in methanol. Therefore a better fit to the slightly larger cavity should be obtained compared with potassium ion.

Reference and Notes

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