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Selective Fluorimetric Recognition of Cesium Ion by 15-Crown-5-Anthracene

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Abstract A selective fluorescent cesium optode on a chromoionophore consisting of anthracene covalently linked through an imine bond to a 15-crown-5 derivative has been reported. In the present system, 15-crown-5 derivative including anthracene was used a fluoroionophore. The fluorescence response mechanism is based on the photo-induced electron transfer (PET) from the lone pair of electrons of the nitrogen to the anthracene group and inhibition of PET system by cesium binding while increasing the fluorescence intensity. Emission intensity 15-crown-5 anthracene was measured at 500 nm with absorbance at 400 nm in CH_3CN–H_2O (1:1) media. The method shows a very good selectivity and sensitivity for cesium with respect to other cations such as K^+, Na^+ and Li^+ with linear range and detection limit of 5.0×10^{-5} to 5.0×10^{-1} M and 3.0×10^{-6} M respectively.

Keywords Fluorescence · Crown ether · Cesium · PET

Introduction

New methodologies and reagents for selective determination of hazardous ionic species deteriorating the environment as a result of human activities have appeared of great scientific aims. The use of Chemo-sensors can be found in many disciplines such as clinical and medical sciences, cell biology, analytical chemistry, and environmental sciences due to the almost-infinite number of possible target ions and a large number of different techniques suitable for their study. There is a significant need for the development of chemo-sensors capable of selective recognition of cesium ions. The major source of cesium is nuclear waste materials and its toxicity is due to its ability to replace potassium in muscles and red cells. In nuclear waste, cesium must be detected in a medium where sodium and potassium are present in a large excess [1]. Various methods were reported for the determination of cesium, including atomic absorption spectroscopy [2], radio-analysis [3, 4] and ion-selective electrodes (ISEs) [5, 6]. Recent developments using ISEs were aimed at obtaining very low detection limits [7]. Although those analytical methods are sensitive and accurate, they have different disadvantages of expensive instruments and controlled experimental conditions. In contrast, fluorimetry is a simple and highly sensitive method for the assay of a large number of drugs and metals [8–11] and fluorimetric-based chemo-sensor is a very interesting category for future practical applications, thanks to the sensitivity, specificity, and low costs of fluorescence measurements [12].

Fluoroionophore chemosensors are gaining interest due to their easy use in solution as well as their high sensitivity to and selectivity for trace metal ions. Many efficient fluoroionophores have been developed for the specific recognition of metal ions including alkali metals, alkaline earth metals and zinc ions [13–15].

Anthracene and its derivatives constitute a very famous class of fluorophores with very interesting photo-physical properties. They are extensively used in designing luminescent chemosensors and switches and, recently, the possibility of these aromatic units to give π–π stacking and π–cation or π–H$^+$ interactions has been successfully investigated [16–23].

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Fig. 1 Structure of *N*-(4-benzo-15-crown-5)-anthracene-9-imine
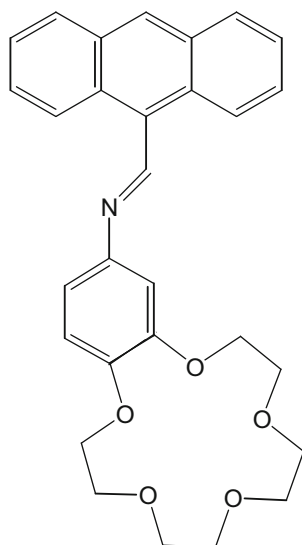
In a fluorescent molecular sensor system, crown ether derivatives have been commonly used as ionophores for cations and crown ether-based ionophores have been widely studied due to their structural and electronic features. They show a high efficiency and good selectivity for alkali metal ions [24, 25]. So many studies on the use of crown ether-based ionophores for determining lithium [26–28], sodium [29–31], potassium [32, 33], rubidium and cesium [34, 35] have been successfully carried out. A number of 1, 3-alternate calix[4]arenecrown-6 and -bis(crown-6) derivatives containing coumarin, anthracene, and some other types of fluorophores were utilized in determination of Cs^+ [36–42].

As far to our knowledge, the fluorimetric determination of cesium ion using the *N*-(4-benzo-15-crown-5) fluoroionophore has not yet been reported. It (Fig. 1) has crown ether recognition site and the anthracene moiety as fluorescent

signal transducer which are connected through an imine linkage. The fluoroionophore shows remarkably high Cs^+ sensitivity and selectivity with respect to K^+, Li^+ and Na^+ ions. The interaction of a metal ion with an organic ligand (crown-ether-based ionophores) may result in a fluorescent enhancement of fluorophore. The enhancement in the fluorescence intensity of 15-crown-5 derivative can be explained by a photoinduced electron transfer (PET) mechanism [43–47].

Experimental

Apparatus

Absorption measurements were carried out by a Shimadzu UV/VIS spectrometer (model UV-1601PC). All the spectro-fluorimetric measurements were conducted with a SPEX Fluorolog-2 spectrofluorometer. The spectrometer used a 450-W xenon lamp as the excitation light source and an R 928 photomultiplier tube powered at 950V (Hamamatsu Co.) as the detector. Absorbance and fluorescence measurements were carried out in quartz cell of 1-cm path length. Excitation and emission monochromator slit, increment, and integration time were set at 1mm, 1nm and 1s, respectively. All spectral data were obtained by SPEX DM 3000F spectroscopy computer.

Reagents

All chemicals used were of analytical grade. Acetonitrile (CH_3CN) and metal nitrate salts ($LiNO_3$, $NaNO_3$, KNO_3, $CsNO_3$) were obtained from Aldrich. 15-crown-5-anthracene was kindly gifted by Prof. Jang (Dae-Gu University, Korea).

Fig. 2 Absorption spectrum of 15-crown-5-anthracene (5.0×10^{-5} M) in CH_3CN–H_2O (1:1, *v/v*)
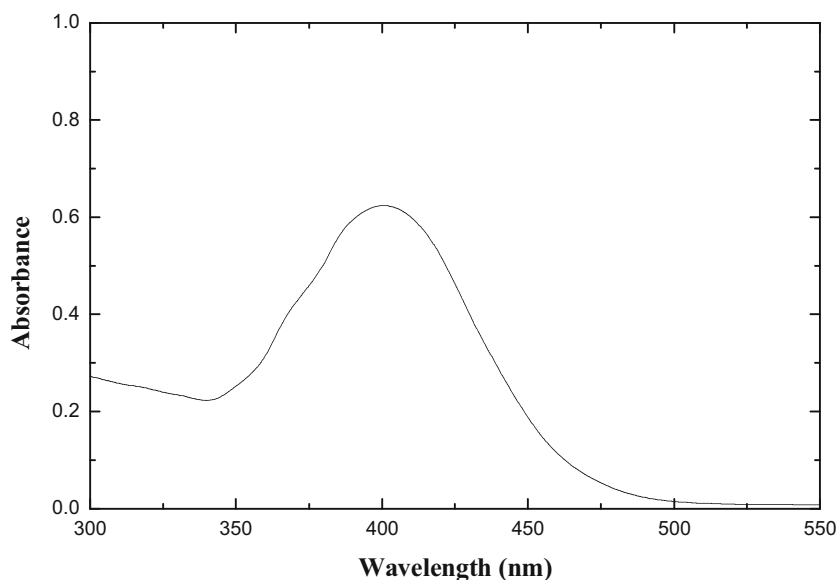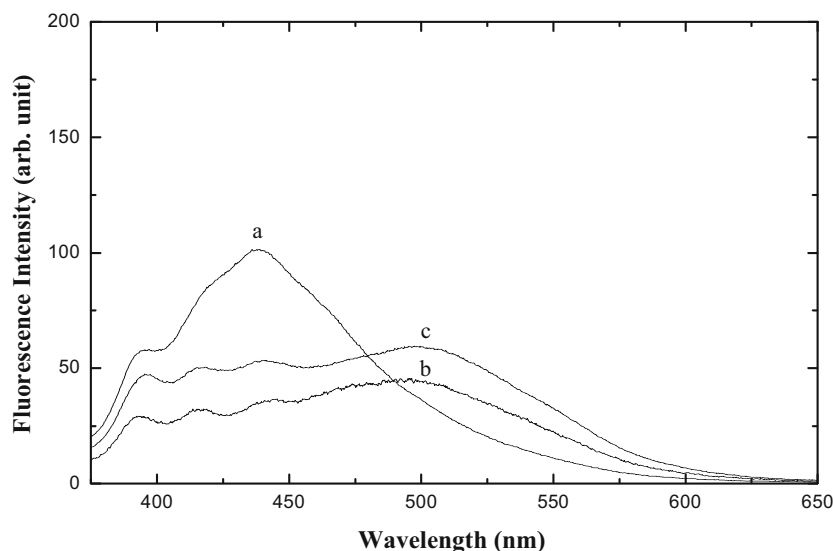
Fig. 3 Fluorescence spectra of 15-crown-5-anthracene (5.0× 10^{-5} M) in different composition solvents; λ_{ex}=400 nm, CH$_3$CN–H$_2$O (v/v) of (a) 2:1, (b) 1:1, (c) 1:2

Stock solutions of alkali metal ions (1.0×10^{-1} M) were prepared by dissolving the 99.9% pure metal nitrate salts in purified water. The stock solution (1.0×10^{-4} M) of 15-crown-5-anthracene was prepared by dissolving 15-crown-5-anthracene in acetonitrile.

Results and discussion

15-crown-5-anthracene is fluorescent in CH$_3$CN–H$_2$O media. It showed characteristic emission of anthracene at round 500 nm with absorbance at 400 nm (Fig. 2). Fluorescence spectra in different composition of solvent are shown in Fig. 3. Maximum emission intensity was obtained in solvent **a** (CH$_3$CN–H$_2$O/2:1, v/v). Fluorescence intensity of 15-crown-5-anthracene in solvent **c** is higher than that in solvent **b**. These results indicate that protonation degree of 15-

crown-5-anthracene is higher in solvent **c**. To minimize interference of protonation, the subsequent experiments were performed in solvent **b** (CH$_3$CN–H$_2$O/1:1, v/v). In addition, because of low intensity in the absence of cesium ion, measurement in solvent b has advantage of the effective observation (high sensitivity) for the enhancement of fluorescence intensity by cesium ion.

The fluoroionophoric property of the 15-crown-5-anthracene was investigated by measuring the fluorescence in the presence of various concentrations of Cs$^+$ ions. The luminescence spectrum of the host free 15-crown-5-anthracene was measured in CH$_3$CN–H$_2$O (1:1, v/v, $E_x = 400$ nm) media. It showed a very poor fluorescence. The week fluorescence intensity can be explained that the emission of the anthracene group in the fluoroionophore is quenched by intramolecular photo-induced electron transfer from the lone pair of electrons of the nitrogen to the adjacent

Fig. 4 Fluorescence spectra of 15-crown-5-anthracene (5.0× 10^{-5} M) in the presence of increasing concentration of Cs$^+$ in CH$_3$CN–H$_2$O (1:1, v/v); λ_{ex}= 400 nm, CsNO$_3$ concentration of (a) 0 M, (b) 5.0×10^{-5} M, (c) 7.0×10^{-5} M, (d) 1.0×10^{-4} M, (e) 5.0×10^{-4} M, (f) 7.0×10^{-4} M, (g) 1.0×10^{-3} M, (h) 5.0×10^{-3} M, (i) 7.0×10^{-3} M, (j) 1.0×10^{-2} M, (k) 5.0×10^{-1} M in CH$_3$CN–H$_2$O solvent

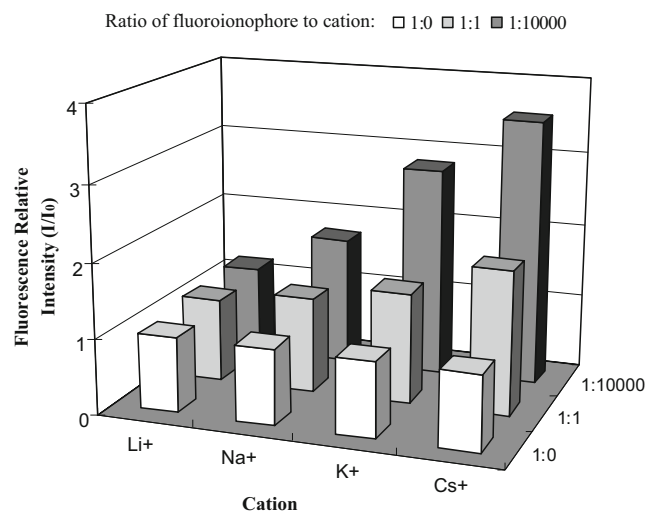Ratio of fluoroionophore to cation: ☐ 1:0 ☐ 1:1 ▨ 1:10000
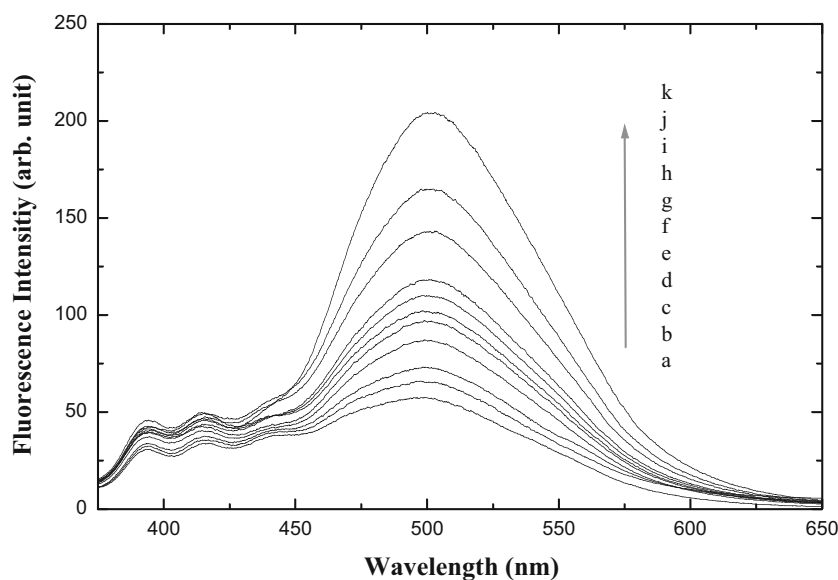
Fig. 5 Fluorescence enhancement ratios (I/I_0) at 500 nm for interaction of 15-crown-5 anthracene (5.0×10^{-5} M) with alkali metal ions in $CH_3CN–H_2O$ (1:1, v/v); λ_{ex}=400 nm

anthracene group [48]. In this medium, addition of Cs^+ induces the enhancement of emission behavior of 15-crown-5-anthracene as shown in the Fig. 4. Maximum fluorescence intensity was observed at 500 nm with excitation at 400 nm. The enhancement of fluorescence intensity upon cesium binding suggests that upon complexation the lone pair of electrons on the nitrogen of fluoroionophore is stabilized and thermodynamically it is unfavorable for them to serve intramolecular photo-induced electron transfer to the immediate anthracene group upon photoexcitation of the fluoroionophore, causing the emission intensity to enhance. A linear response of the fluorescence intensity as a function of cesium concentration was observed from 5.0×10^{-5} to 5.0×10^{-1}M. The detection limit calculated as three times the standard deviation of the blank signal was found to be 3.0×10^{-6} M with correlation coefficient of 0.9985.

Finally we examined the selectivity of 15-crown-5-anthracene for Cs^+ with respect to other cations such as Na^+, K^+, and Li^+ (Fig. 5). The emission of 15-crown-5-anthracene in $CH_3CN–H_2O$ (1:1) is not affected by the presence of Li^+ and Na^+ at the concentration as high as 0.5 M, excluding the possibility of strong complexation of these ions by the fluoroionophore. The emission of fluoroionophore shows a slight increment up to a concentration of K^+ about 0.5 M, indicating complexation of K^+ with 15-crown-5-anthracene because of some high stability constants ratio. In comparison with Na^+, K^+, and Li^+ ions, 15-crown-5-anthracene shows outstanding selectivity for Cs^+ and excellent sensitivity (up to 3.0×10^{-6} M). As the concentration of Cs^+ ions increases, the fluorescence intensity of the fluoroionophore increases, gaining its maximum value at the concentration of Cs^+ of *ca.* 0.5 M.

In conclusion these results demonstrated that the fluoroionophore is a novel ion probe that exhibits remark-

ably high sensitivity and selectivity for Cs^+ by several orders of magnitude and has a good photochemical stability compared to the other previously reported probes. We are currently examining other potential fluorophores that may induce a much intense fluorescence response upon complexation of alkaline metal ions.

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