Optical Sensing of Cesium Using 1,3-Alternate Calix[4]-mono- and Di(anthrylmethyl)aza-crown-6

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ABSTRACT

We have synthesized two derivatives of alkylanthracene covalently bonded to 1,3-alternate calix[4]aza-crown-6 at the nitrogen position to study the effect of alkali metal ion complexation on the emission properties of anthracene fluorophore. The mono- and dianthryl-substituted probes are weakly fluorescent because their emission is partially quenched by photoinduced electron transfer (PET) from the nitrogen lone pair to the excited singlet state of anthracene. Upon complexation of alkali metal ions (e.g. K^+ , Cs^+) by the crown moiety, the nitrogen lone pair can no longer participate in the PET process causing an enhancement in the emission of anthracene fluorophore (fluorescent turn on). The maximum fluorescence enhancement observed upon complexation of cesium ions by mono- and dianthryl-substituted calix[4]aza-crown-6 relative to the uncomplexed form was 8.5- and 11.6-fold, respectively.

INTRODUCTION

The derivatives of 1,3-alternate calix[4]crown-6 have been shown to exhibit high selectivity toward cesium ions in both acidic and alkaline media (1–7). According to solvent-extraction experiments (8), the Cs/Na and Cs/K selectivity ratios for these compounds can exceed 10^4 and 10^2 , respectively. Crown ethers have been proposed as potential extractants for the removal of radioactive cesium that comprises a significant fraction of the radiological materials stored in the Department of Energy's (DOE)† tank wastes, from nuclear waste solutions by solvent extraction (9–12). A recent report in the Chemical and Engineering News (13) suggests that leakage of nuclear material (137 Cs in particular) into the environment from the storage tanks at Hanford sites is far greater than the previous estimates. Therefore, there is considerable interest within the DOE to develop a cesium-selective sensor that can be utilized to perform in situ determination of this metal ion in these tanks. We have taken advantage of the high selectivity of calix[4]crown ethers to synthesize molecular recognition agents with high specificity for cesium ion complexation in the presence of other alkali metal ions based on fluorescence turn-on technique as a platform for its detection. Recently, we reported (14) the synthesis of 1,3-calix[4]bis-(9-cyano-10-anthrylmethyl)-o-benzocrown-6, an optical sensor for the detection of cesium in both acidic and basic media that operates by a photoinduced electron transfer (PET) mechanism. The maximum fluorescence increase observed upon binding of two cesium ions by this molecule was found to be 11.7-fold. Fluorescence sensing by PET using aza-crown ethers has also gained much popularity in recent years (15-18). In this case, the fluorescence of the fluorophore directly attached to the nitrogen atom of aza-crown ether is quenched by the lone pair electrons present on nitrogen. Complexation of alkali metal ions by the crown moiety prevents the nitrogen lone pair electrons from participating in PET and results in an enhancement in the observed emission from the fluorophore.

Utilizing this approach, we have synthesized the probe molecules I and II (Scheme 1) by covalently binding one and two anthracene fluorophores to the nitrogen atoms of a 1,3-alternate calix[4]aza-crown-6. We report here the effect of alkali metal ions on the emission properties of probe molecules I and II.

MATERIALS AND METHODS

Benzyltrimethylammonium hydroxide, cesium acetate (99.9%), rubidium acetate (99.9%), potassium acetate (99.9%), calix[4]arenes were purchased from Aldrich (Milwaukee) and used without further purification. Methylene chloride (Merck, 99.98%), methanol (Merck, HPLC grade), benzene (Merck, GR grade), hexane (Merck, GR grade), sodium acetate (Fisher, 100%), lithium acetate (Alfa, GR grade), anhydrous magnesium sulfate (Aldrich), sodium sulfate (Aldrich), borane in tetrahydrofuran (THF, 1 *M*, Aldrich), 9-chloromethylanthracene (98%, Aldrich) and 1,2-bis-(2-iodoethoxy)ethane (96%, Aldrich) were all used as received.

Synthesis of 1,3-alternate 25,27-dibenzyloxy calix[4]bisamidecrown-6 (IV). Using a procedure described earlier (1), 0.80 g (1.32 \times 10⁻³ mol) of 25,27-dibenzyloxy-26,28-dihydroxy-p-H-calix[4]arene, prepared by a literature procedure (19), was added to a mixture of N,N'-[1,2-ethanediylbis(oxy-2,1-ethanediyl)]-bis-2-chloroacetamide (0.40 g, 1.34 \times 10⁻³ mol) and Cs₂CO₃ (3.0 g, 9.2 \times 10⁻³ mol) in 150 mL acetonitrile and refluxed under string for 5 days. After cooling to room temperature, the solvent was removed under reduced pressure. The residue was extracted with CH₂Cl₂ and the organic layer was washed with 2 N HCl, NaCl solution and water, respectively. After drying over anhydrous Na₂SO₄, the solu-

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^{*}Abbreviations: DOE, Department of Energy; MALDI-FTICR, matrix-assisted laser desorption/ionization Fourier transform ion cyclotron resonance; PET, photoinduced electron transfer; THF, tetrahydrofuran; TMS, trimethylsilane.

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Scheme 1. The synthetic route for the preparation of fluorescent probe molecules I and II.

tion was concentrated and the mixture was purified by flash chromatography to give 0.45 g of IV (a white powder 37.5% yield, Scheme 1). ¹H NMR (CDCl₃), δ 7.40–7.48 (ArH in benzyl, m, 4H), 7.28–7.35 (ArH in benzyl, m, 6H), 6.98 (ArH, d, 4H), 6.90 (ArH, t, 2H), 6.78 (ArH, d, 4H), 6.58 (ArH, t, 2H), 4.93 (PhCH₂O, s, 4H), 4.24 (COCH₂O, s, 4H), 3.82 (CH₂O, m, 8H), 3.71 (CH₂N, m, 4H), 3.48–3.61 (ArCH₂Ar, dd, 8H).

Synthesis of 1,3-alternate 25,27-dibenzyloxy-calix[4]azacrown-6 (V). A 0.50 g (0.63 mmol) sample of IV was added to 50 mL of 1 M borane in THF at 5-10°C. The resulting mixture was refluxed for 36 h and after cooling, 50 mL hydrochloric acid (18% by volume) was carefully added to the mixture and refluxed for another hour. After cooling, sodium hydroxide was added to the solution until a pH of 12 was reached. The aqueous layer was separated and extracted with methylene chloride. All the organic layers were combined and the solvent was removed under reduced pressure. The residue was dissolved in chloroform and washed with water twice, then dried over anhydrous MgSO4. Removal of the solvent by evaporation gave 0.45 g of crude V (a white solid, 91% yield, Scheme 1). For structural analysis, a small portion of this solid was chromatographed on 70-160 mesh silica gel using acetone-methanol (1: 1, vol/vol) as eluant. The remaining portion was used directly in the next reaction step. ¹H NMR (CDCl₃), & 7.40-7.52 (ArH in benzyl, m, 4H), 7.25-7.35 (ArH in benzyl, m, 6H), 7.08 (ArH, d, 4H), 6.94 (ArH, t, 2H), 6.67 (ArH, d, 4H), 6.42 (ArH, t, 2H), 4.85 (PhCH₂O, s, 4H), 3.60-4.08 (CH₂O and ArCH₂Ar, m, 20H), 3.15 (CH₂N, m, 8H).

Synthesis of 1,3-alternate 25,27-dibenzyloxy calix[4]mono(anthrylmethyl)-aza-crown-6 (I) and 1,3-alternate 25,27-dibenzyloxy calix[4]di(anthrylmethyl)-aza-crown-6 (II). A mixture of crude compound V (0.20 g, 0.25 mmol), anthrylmethyl chloride (0.2 g, 0.88 mmol) and sodium carbonate (1.0 g) in 50 mL benzene was refluxed under stirring for 24 h. After cooling, benzene was removed under reduced pressure. The residue was dissolved in chloroform and washed with Na₂CO₃ and water, respectively, and then dried over anhydrous Na₂SO₄. The solvent was evaporated off and the product was chromatographed on silica gel using methylene chloride : hexane (3:1) mixture as eluant to give 0.12 g of II as the major fraction (a yellow solid, 99% pure) and 11 mg of I as the minor fraction (Scheme 1).

The proton NMR for II (CDCl₃) shows: δ 8.60 (AnH, d, 4H),



Scheme 2. The synthetic route for the preparation of reference compound III.

8.46 (AnH, s, 2H), 8.04 (AnH, d, 4H), 7.55 (AnH, t, 4H), 7.45 (AnH, t, 4H), 7.28–7.36 (ArH in benzyl, m, 6H), 6.84–6.95 (ArH in benzyl, m, 4H), 6.68 (ArH, t, 2H), 6.61 (ArH, t, 4H), 6.56 (ArH, d, 4H), 6.35 (ArH, t, 2H), 4.82 (PhCH₂O, s, 4H), 4.72 (AnCH₂N, s, 4H), 3.34–3.80 (CH₂O and ArCH₂Ar, m, 20H), 2.92 (CH₂N, d, 4H), 2.68 (CH₂N, d, 4H).

The proton NMR (CDCl₃) for I shows: δ 8.60 (AnH, d, 2H), 8.46 (AnH, s, 1H), 8.0 (AnH, d, 2H), 7.52 (AnH, t, 2H), 7.45 (AnH, t, 2H), 7.35–7.44 (ArH in benzyl, m, 6H), 6.06–7.20 (ArH, m, 6H), 6.54–6.76 (ArH, m, 8H), 6.36 (ArH, m, 2H), 4.78 (PhCH₂O, s, 4H), 4.71 (AnCH₂N, s, 2H), 3.28–3.86 (CH₂O and ArCH₂Ar, m, 20H), 2.80–3.12 (CH₂N, m, 8H).

Synthesis of 6,9-dioxa-3,12-di-anthrylmethyl-aza-tetradecanel,14-diol (III). A mixture of 1,2-bis-(2-iodoethoxy)ethane (0.37 g, l mmol), anthrylmethyl ethanolamine (0.5 g, 2 mmol) and potassium carbonate (1.0 g) in 50 mL acetonitrile was refluxed for 2 days. After cooling, the solvent was evaporated off and the residue was dispersed in chloroform and then filtered. The filtrate was evaporated under reduced pressure and the residue was washed with acetone twice to get 0.50 g of a pale yellow solid (80% yield, Scheme 2). ¹H NMR (CDCl₃), δ 8.46 (AnH, d, 4H), 8.39 (AnH, s, 2H), 7.96 (AnH, d, 4H), 7.50 (AnH, t, 4H), 7.42 (AnH, t, 4H), 4.66 (AnCH₂N, s, 4H), 3.48 (CH₂O, t, 4H), 3.42 (OCH₂CH₂O, s, 4H), 3.36 (CH₂O, d, 4H), 2.85 (CH₂N, t, 4H), 2.68 (CH₂N, d, 4H).

N,N'-[1,2-ethanediylbis(oxy-2,1-ethanediyl)]-bis-2-chloroacetamide was synthesized using a literature procedure (20). Anthrylmethyl ethanolamine was synthesized from anthrylmethyl chloride and ethanolamine (excess) in benzene.

Proton NMR spectra were recorded on a Bruker MSL-400 (Fremont, CA) spectrometer using chloroform-d as the solvent. Shifts reported in ppm are relative to trimethylsilane (TMS). Fluorescence spectra of aerated samples were obtained on a Spex Fluorolog-2 spectrometer (Instrument SA) equipped with double monochromators on both excitation and emission sides.

Matrix-assisted laser desorption/ionization Fourier transform ion cyclotron resonance (MALDI-FTICR). Mass spectra for compounds I, II, IV and V were obtained with a Finnigan Fourier transform mass spectrometer, FTMS-2000 (Madison, WI) equipped with a laser photonics (Orlando, FL) nitrogen laser (337 nm). A small amount of each sample dissolved in methanol was mixed with an excess of the laser matrix compound (2,5-dihydroxybenzoic acid) and then dried onto a stainless-steel solid probe. Laser desorption/ionization of this sample inside the mass spectrometer resulted in the production of positively charged protonated molecular ion that was detected under medium mass resolution conditions. Table 1 shows the mass spectral results obtained by MALDI-FTICR for compounds I, II, IV and V.

Table 1. The observed molecular ions for compounds I, II, IV and V by MALDI-FTICR

Com- pound	Empirical formula	Calculated MW, M	M + H ⁺
I	C67H66N2O6	995.500	996.509
II	$C_{82}H_{76}N_{2}O_{6}$	1185.578	1186.586
IV	C ₅₂ H ₅₂ N ₂ O ₈	833.380	834.388
V	$C_{52}H_{56}N_2O_6$	805.422	806.429
	- 52 - 50 - 2 - 0		

RESULTS AND DISCUSSION

Scheme 1 shows the synthetic method used to prepare fluorescent probe molecules I and II for this study. Figure 1 compares the fluorescence spectra for compounds I, II and III (reference compound) in CH₂Cl₂: MeOH (1:1, vol/vol). The spectrum of II exhibits a red-shifted shoulder around 500 nm, similar to that reported for bis-9-anthryls in a fourmembered chain (21), which is assigned to an intramolecular excimer formed between the two anthracene moieties. Compound I shows no such red-shifted emission while III shows some residual red-shifted emission (450-550 nm) that could be attributed to an intramolecular excimer formation. When Cs^+ ions were added to II in a CH_2Cl_2 : MeOH (1:1, vol/vol) mixture, the fluorescence intensity of anthracence monomer increased concomitant with the loss of excimer emission (Fig. 2). This increase in emission arises from disabling the PET effect induced by nitrogen lone pairs that results from cesium complexation. The disappearance of excimer emission upon Cs⁺ complexation by the crown moiety suggests that intramolecular excimer formation is inhibited under these conditions. This inhibition may be caused by the geometrical constraint imposed on the molecule upon Cs⁺ binding. Under these conditions, the aza-crown ether ring will no longer be able to fold easily to achieve the geometry required for intramolecular excimer formation between the two anthracene molecules. The maximum emission enhancement observed for II at 416 nm was about 11.6-fold (relative to Cs⁺-free emission) for $[Cs^+] = 2 \times 10^{-2} M$. A similar enhancement in the emission of I upon addition of Cs+ ions (that complex the nitrogen lone pairs on the anthracene fluorophore disabling them from participating in PET) was also observed (not shown). The fluorescence intensity of III



Figure 2. Changes in the emission spectra of II $(1 \times 10^{-6} M)$ in aerated CH₂Cl₂: MeOH (1:1, vol/vol) as the concentration of cesium ion (CH₃CO₂Cs) is increased, room temperature, $\lambda_{ex} = 350$ nm.

showed no response to the addition of Cs^+ ions. This observation is in good agreement with the inability of III to complex Cs^+ ions.

Figure 3 compares the change in fluorescence intensity of probe molecule II in CH₂Cl₂: MeOH (1:1, vol/vol) for different metal ions. Although a similar change in the emission of I for different alkali metal ions was observed (not shown), the emission of reference compound III showed no response to alkali metal ion presence (not shown). It is clear that Li⁺ and Na⁺ ions have little effect (if any) on the observed emission, suggesting no complexation while K⁺ shows slight enhancement, indicating weak complexation (Fig. 3). Although the emission of II is enhanced moderately in the presence of Rb⁺, the most dramatic change in the emission behavior is observed in the presence of Cs⁺ indicative of a strong complexation. A similar trend in the emission behavior was also observed for complexation of the above alkali metal cations with compound I (not shown). The maximum fluorescence enhancement observed for I upon binding of cesium ions was 8.5-fold, which is smaller than that for II (11.6fold). This difference can be explained in terms of dissociation of intramolecular excimer to the corresponding monomers in II upon binding of Cs⁺ ions by the crown moiety. This notion is further supported by the observation that in-



Figure 1. Fluorescence spectra of **I**, **II** and **III** ($1 \times 10^{-6} M$) in aerated CH₂Cl₂: MeOH (1:1, vol/vol) at room temperature, $\lambda_{ex} = 350$ nm.



Figure 3. Changes in the emission spectra of II $(1 \times 10^{-6} M)$ in aerated CH₂Cl₂: MeOH (1:1, vol/vol) upon addition of alkali metal ions Li⁺, Na⁺, K⁺, Rb⁺ and Cs⁺ (acetate solutions) at room temperature, $\lambda_{ex} = 350$ nm.

Com- pound		M ⁺ free	Li+	Na ⁺	K⁺	Rb⁺	Cs+	H⁺
I	Ф _{тах}	0.002	0.002	0.002	0.006	0.009	0.017	0.40
	β		_	-	2.6E2	2.3E3	5.8E3	
II	Ф _{лах}	0.003	0.004	0.004	0.009	0.019	0.034	0.73
	β		_		3.0E2	2.4E3	5.4E3	—
III	Φ_{max}	0.004	0.004	0.004	0.004	0.004	0.004	0.66

Table 2. Fluorescence quantum yield (Φ) and the complexation constants (β) for I, II and III ($1 \times 10^{-6} M$) in CH₂Cl₂: MeOH (1:1, vol/ vol) in the absence and presence ($[M^+] = 2.5 \times 10^{-2} M$) of alkaline metal ions (H^+ : protonated forms of I, II and III)

tramolecular excimer emission is diminished after the addition of cesium ions to a solution of II (Fig. 2). Thus, dissociation of the intramolecular excimer to the corresponding monomers upon cesium complexation results in an increase in the monomer emission for II relative to I.

The fluorescence quantum yields (Φ) calculated for compounds I, II and III relative to that of anthracene in deaerated ethanol, $\Phi_F = 0.3$ (22), are shown in Table 2. The quantum yield values reported for II and III are relative to one anthracene moiety. As can be seen from the data in Table 2, the II/I quantum yield ratio for metal-free compounds (0.003/0.002 = 1.5) is less than the ratio for III/I (0.004/0.002 = 2). This is in good agreement with the observation that II forms an intramolecular excimer (at the expense of a decrease in monomer emission) while III does not. It is important to note that the quantum yields of cesium-complexed forms for both I and II are considerably lower than their corresponding protonated form (where the nitrogen lone pair has been protonated diminishing its role in the PET process). Such behavior clearly suggests that cesium complexation does not completely disable the nitrogen lone pair from participation in the PET process. This is most likely due to the nature of the nitrogen heteroatom, which is not as good a complexing agent as oxygen (present in the crown ring) for alkali metal ions.

Table 2 also lists the complexation constants (β) calculated according to Eq. 1 (23) where I_F is the emission intensity of the probe (L) at different concentrations of metal ion (M⁺), I_{Fmin} is the emission intensity of probe in the absence of any metal ion, and I_{Fmax} is the maximum emission intensity for the probe observed at the highest metal ion concentration employed.

$$\frac{\mathbf{I}_{F} - \mathbf{I}_{F_{min}}}{\mathbf{I}_{F_{max}} - \mathbf{I}_{F}} = \beta \left[[\mathbf{M}^{+}] - [\mathbf{L}] \left(\frac{\mathbf{I}_{F} - \mathbf{I}_{F_{min}}}{\mathbf{I}_{F_{max}} - \mathbf{I}_{F_{min}}} \right) \right]$$
(1)

For $I_F \gg I_{Fmin}$, Eq. 1 reduces to 2.

$$\frac{I_F}{I_{F_{max}} - I_F} = \beta \left[[M^+] - [L] \left(\frac{I_F}{I_{F_{max}}} \right) \right]$$
(2)

Using an iteration procedure, the emission data for all the alkali metal ions studied were fitted to Eq. 1 in order to obtain the value of β from the best fit (Table 2). The selectivity ratios for Cs⁺/K⁺ obtained for I and II from the calculated β values are 22.3 and 18, respectively. These values are considerably lower than the value of Cs⁺/K⁺ ~160 reported for calix[4]crown-6 by a solvent extraction technique (8). We attribute the lower selectivity ratios for I and II to the presence of nitrogen atoms in the crown ring that reduce its complexation ability for alkali metal ions. This notion is

further supported by our previous results where we calculated a value of 277 for Cs⁺/K⁺ ratio from the β values obtained for calix[4]bis(9-cyano-10-anthrylmethyl)-o-ben-zocrown-6 as the complexing agent (14).

In conclusion, we have synthesized cesium-selective fluorescent turn-on probes molecules I and II based on calix[4]arene that contain one and two anthracene fluorophores covalently bonded to the nitrogen atom of the crown moiety. The main difference between the newly synthesized probes and the one we reported earlier (14) is in the composition of the crown moiety that contains two nitrogen atoms in its ring bearing the fluorophore reporters. Both I and II are weakly emitting as a result of PET from the nitrogen lone pairs to the excited singlet state of anthracene fluorophore. The emission of I and II is enhanced significantly (8.5- and 11.6-fold, respectively) upon addition of cesium ions, suggesting that the complexation of the nitrogen atom lone pair by cesium reduces their ability to participate in the PET process. Although both I and II show much better tolerance for potassium ion interference compared to our previously reported probe (14), they exhibit poor selectivity for Cs^+/K^+ ratio. The selectivity ratio is a crucial parameter and must be maximized for the development of an efficient cesium optical sensor capable of detecting small amounts of this metal ion in the presence of high concentration of potassium ions. To this end, we are currently investigating other derivatives of calix[4] arenes that exhibit a very high selectivity ratio for Cs⁺/K⁺ as potential candidates for application to optical sensing of cesium.

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