Recent Investigation of Synthesis, Photophysical and Absorption Spectral Characterization of Rb⁺ Selective optical Sensors Based on Calixarenes
Introduction:

The chemistry of calixarenes is now a well-established field.\cite{1,2} Calix[4]crown compounds have been shown to be highly selective towards complexation of alkali and alkaline-earth metal ions.\cite{3,4} We can define it by using their initial studies to include multi-carbon system comprising equimolar mixture of two, three, and four cations from NaOH, KOH, RbOH, and CsOH, Izatt and coworkers found that selective transport of Cs$^+$ occurs in all cases. As in the single ion system, the greatest selectivity for Cs$^+$ is shown by the calix[4]arenes, but the largest flux is found in the calix[8]arenes. That the cation flux depends, at least in part, on the relative concentrations of the cations in the source phase is illustrated by the fact that at low Cs$^+$: Rb$^+$ ratios $p$-tert-butylcalix[6]arene transports Rb$^+$ more rapidly than Cs$^+$. As this ratio increases, however, the transport of Cs$^+$ become favored. Also demonstrated is a synergistic effect in which the presence of Cs$^+$ in a two or three-cation mixture with Na$^+$ significantly increases the Na$^+$ flux over that when Na$^+$ present alone. The studies of the provo group point out the useful feature of the calixarenes as ion carries, \textit{viz.} their low water solubility, their ability to form neutral complexes with cations through the loss of protons, and their potential for allowing the coupling of cation transports with the reverse flux of protons. Most of the subsequent work from other laboratories has focused not on the
calixarenes themselves but on various derivatives. One of the earliest of these was the observation by Bocch *et. al.*\(^5\) that while the tetraacetale of \(p\)-tert-butylcalix[4]arene fails to form complexes with guanidinium ion or Cs\(^+\), the octa-(3,6-dioxahexyl)ether of \(p\)-tert-butylcalix[8]arene forms strong complexes with these cations. The para group later showed\(^6\) that the hexa(3-oxabutyl)ether of \(p\)-tert-butylcalix[6]arene also forms complexes with these ions. As extensive survey has been carried out by McKervey and his coworkers\(^7\) who prepared the carboalkoxymethyl ethers of \(p\)-tert-butylcalix[4]arene, \(p\)-tert-butylcalix[6]arene, \(p\)-tert-butylcalix[8]arene, calix[4]arene, calix[6]arene, and calix[8]arene, and measured their abilities to extract cations from the aqueous into phase non-aqueous phase.

Although we have utilized these attractive features of calix[4]arenes to prepare a Cs\(^+\) selective fluorescent molecular recognition agent for the detection of cesium ions in solution. Furthermore, in an effort to address the question regarding one vs. two cesium ions binding by the two cavities of calix[4]bis(crown-6).\(^8\)-\(^{12}\) We have attached the cyanoanthracence fluorophore to both 1,3- alternate calix[4] bis (o-benzocrown-6) and 1,3- alternate calix[4] bis (allyloxy)-o-benzocrown-6.\(^{13\text{-}15}\) These optical probes can signal the presence of cesium ions by showing an increase in the emission intensity upon cesium complexation, induced by a photo-induced electron transfer
(PET) process. Probe molecules AnCN2 and AnCN1 emit weakly as a result of PET from the oxygen lone pair electrons (on the benzo moiety) to the singlet excited state of 9-cyanoanthracene. Upon cesium ion complexation, the oxygen lone pair electrons, which will be involved in the complexation process, can no longer fully participate in the PET causing the emission to increase. Similar probes based on a PET process for the detection of Na+ and K+ ions in solution have been reported using cyanoanthrocence fluorophore covalently bonded to the benzo crown ethers.\textsuperscript{16,17} In our present paper we shall discuss the synthesis of calix[4]arenes to prepare a new class Rb+ selective optical sensors.

**Experimental Section:**

**Material and synthesis:**

All solvent and chemicals are used of AR grade and are used as such. The chemicals 2-(2-chloromethoxy) methanol, 9 (chloroethy) anthracene, phosphorus oxychloride [trichloro-(oxo)-\(\lambda^5\)-phosphorane], benzyl(triethyl)ammonium hydroxide, rubidium acetate (99.9%), cesium acetate, potassium carbonate, catechol (99%), and potassium acetate (99.9%) were used as received (Aldrich). 25, 27-Bis (allyloxy) -26,28-dihydroxy calix[4]arene was synthesized using the same procedure reported in literature.\textsuperscript{18} Ethylene chloride (Merck, 99.98%), DMF (EM science, 99.9%), ethanol (Merck, HPLC grade), benzene
(Merck, GR grade), hexane (Merck, GR grade), Sodium acetate (Fisher, 100%), and lithium acetate (Alfa, GR grade) were used as received.

**Synthesis of Complexes:**

(I). 1,2 Bis(5-hydroxy-3-oxa-1-pentyloxy) benzene(1):

Compound 1 was synthesized using a modified procedure described in the literature. A solution of 2-(2-chloromethoxy) methanol(18.0g, 145 mmol) in 60 mL dry DMF was added over 30 min to a stirred suspension of catechol (4.0g, 36.4 mmol), K$_2$CO$_3$ (40g, 290 mmol) and KI (8.3g, 50 mmol), and temperature was raised to 75°C. The mixture was stirred at 75°C for 3 days. After cooling to room temperature, the reaction mixture was filtered and the residue was washed with DMF (20ml). The solvent was removed under reduced pressure and the residue was extracted with CH$_2$Cl$_2$ and washed using 2M HCl, NaCl solution, and water, respectively. After drying over anhydrous Na$_2$SO$_4$, the solvent was removed under reduced pressure. The residue was distilled at 0.1 Torr to give 9.2g diol as colorless oil (88.4% yield, bp 185-187°C at 0.1 Torr). $^1$H NMR (CDCl$_3$): $\delta$6.92(4H, d, aromatic), 4.16 (2H, t, alcohol), 3.90 (2H, t, ether), 3.74-3.68 (4H, m, ether), 2.58 (2H, s, hydroxyl).
(II). 1,2-Bis(5-hydroxy-3-oxa-1-pentyloxy)-4-(9-anthrylethyl) benzene(2):

9-chloroethylanthracene (2.3g, 10 mmol) was added to a stirred solution of 1,2 bis (5-hydroxy-3-oxa-1-pentyloxy) benzene (7.15g, 25 mmol) and ZnCl₂ (1.3g, 10 mmol) in 100ml CH₃NO₂. The solution was stirred at 60°C for 2h. The mixture was then allowed to cool down to room temperature and the solvent was removed under reduced pressure. The residue was extracted with CH₂Cl₂ and the organic layer was washed with NaCl solution and water, and then dried over Na₂SO₄. The solvent was removed under reduced pressure and the residue was purified by flash chromatography using CH₂Cl₂-acetone (1:1) as eluent to give 3.2g of 2 (66% yield, mp 59-60°C). ¹H NMR (CDCl₃): δ 8.44 (1H, s), 8.20 (2H, d), 8.04 (2H, d), 7.46 (4H, m, benzene), 6.70 (2H, d, benzene), 6.58 (1H, d, benzene), 4.94 (2H, s, An-CH₂-benzene), 4.17-3.62 (16H, m). The molecular mass determined by MALDI-FTMS was 476 Da, verifying an empirical formula of C₂₉H₁₅O₆. Both M⁺ and (M+Na)⁺ was observed in the MS.

(III). 1,2-Bis(5-chloro-3-oxa-1-pentyloxy)-4-(10-formyl-9-anthrylethyl) benzene(3):

A solution of 2 (3.0g, 6.3 mmol) in 20 ml dry chloroform was added over 10 min to a stirred solution of phosphorus oxychloride (2.2g, 14.4 mmol) and the dry DMF (1.05g, 14.4 mmol) in dry
chloroform (30ml) and the stirring was continued for 24 h at room temperature. The chloroform was removed under reduced pressure and to the residue was added 1,2-dichlorobenzene (40ml), dry DMF (0.52g, 7.2mmol) and phosphorus oxychloride (1.1g, 7.2 mmol). The temperature of the mixture was raised to 90°C and heating was continued overnight. After cooling to room temperature, the solvent was removed under reduced pressure and the residue was extracted with CH₂Cl₂ and washed with 50 ml. of 2M HCl, NaCl solution, and water respectively. After drying over anhydrous Na₂SO₄, the solvent was removed under reduced pressure. The residue was purified by flash chromatography using ethyl ether-hexane (1:2) as eluent to give 2.0g of 3 (60% yield) as a yellow solid (mp 101-102°C). ¹H NMR (CDCl₃): δ 8.92 (2H, d, An), 8.27 (2H, d, An), 7.65-7.50 (4H, m, An) 6.71 (2H, d, benzene), 6.57 (1H, d, benzene), 5.00 (2H, s, An-CH₂-benzene), 4.10-3.60 (16H, m). The molecular mass determined by MALDI-FTMS was 540-544 Da, verifying an empirical formula of C₃₀H₃₀O₅Cl₂ Both M⁺ and (M+Na)⁺ were observed in the MS.

(IV).1,2-Bis(5-chloro-3-oxa-1-pentyloxy)-4-(10cyano-9-anthryl-ethyl) benzene(4):

A mixture of 3 (1.7g, 3.14mmol), hydroxylamine hydrochloride (0.25g, 3.6 mmol), sodium acetate (0.3g, 3.6 mmol), methanol (40ml), and water (12ml) was refluxed under stirring for 1h. After cooling to
room temperature, 100 ml of water was poured into the mixture. An orange solid precipitated out and was collected using a funnel. The solid was dried in an oven and then dissolved in 30 ml acetic anhydride and refluxed with stirring for 1h. After cooling down to room temperature, the solvent was removed under reduced pressure, and the residue was extracted with CH$_2$Cl$_2$ and washed with 2M HCl, NaCl solution, and water, respectively. After drying over anhydrous Na$_2$SO$_4$, the solvent was removed under reduced pressure. The residue was purified by flash chromatography to give 1.6g of 4 (90% yield) as a pale yellow powder (mp 112.5-114°c). $^1$H NMR (CDCl$_3$): $\delta$ 8.50 (2H, d, An), 8.30 (2H, d, An), 7.72 (2H, t, An), 7.59 (2H, t, An), 6.72 (2H, d, benzene), 6.54 (1H, d, benzene), 5.00 (2H, s, An-CH$_2$-benzene), 4.08 (2H, t, CH$_2$Cl), 4.01(2H, t, CH$_2$Cl), 3.85-3.58(12H, m, ether) The molecular mass determined by MALDI-FTMS was 537-541 Da, verifying an empirical formula of C$_{30}$H$_{29}$O$_4$NCl$_2$. Both M$^+$ and (M+Na)$^+$ were observed in the MS.


Using a procedure described earlier,$^{24a}$ a mixture of calix[4]-arene (0.17g, 0.4 mmol), 4 (0.22g, 0.4 mmol), K$_2$CO$_3$ (0.7g, 5 mmol), and KI (0.33g, 2 mmol) in 50 ml acetonitrile was refluxed under stirring for 4 days. The same quantities of K$_2$CO$_3$, KI and 4 were
added to the mixture and the refluxing was continued for another 4
days. After cooling to room temperature, the solvents were removed
under reduced pressure. The residue was extracted with CH₂Cl₂ and
washed with 2M HCl, NaCl solution, and water, respectively. After
drying over anhydrous Na₂SO₄, the solvent was removed under
reduced pressure. The residue was purified by flash chromatography to
give 0.34g of AnCN2 (52% yield) as a yellow powder (mp 153-
154.5°C). ¹H NMR (CDCl₃): δ 8.51 (d, 4H, An), 8.37 (d, 4H, An),
7.72 (t, 4H, An), 7.60 (t, 4H, An), 7.00-6.53 (m, 18H, benzene), 5.04
(s, 4H, An-CH₂-benzene), 4.06 (t, 4H, calix CH₂), 3.94 (t, 4H, calix
CH₂), 3.75-3.22(m, 32H, ether). The molecular mass determined by
MALDI-FTMS was 1354.6 Da, verifying an empirical formula of
C₈₈H₇₈O₁₂N₂. Only M⁺ and (M+K)⁺ were observed in the MS.

(VI).1,2-Bis(5-iodo-3-oxa-1-pentyloxy)-4-(10-cyano-9-anthryl-
ethyl) benzene(5):

A mixture of 4 (0.7g, 1.30 mmol), KI (2.0g, 12 mmol), and
acetonitrile (50ml) was purged with N₂ and refluxed with stirring for 3
days. After cooling to room temperature, the solvent was removed
under reduced pressure and the residue was extracted with CH₂Cl₂ and
washed with 2M HCl, NaCl solution, and water respectively. After
drying over anhydrous Na₂SO₄, the solvent was removed under
reduced pressure to afford 0.93g (99%) pure 5 to be used in the next
step (mp-141-142°C). The molecular mass determined by MALDI-FTMS was 721 Da, verifying an empirical formula of C_{30}H_{29}O_{4}N_{2}. Both M^+ and (M+Na)^+ were observed in the MS.

(VII).1,3-Alternate25,27-bis(allyloxy)-26,28-[4-(10cyano-9-anthrylethyl)-1,2-phenylenebis(5-dioxy-3-oxa-1-pentyloxy)]

A mixture of 25, 27-bis (allyloxy)-26,28-dihydroxycalix[4]arene (0.20g, 0.4 mmol), 5 (0.29g, 0.4 mmol), and Rb_{2}CO_{3}(1.63g, 5 mmol) in 100ml acetonitrile were refluxed with stirring for 5 days. After cooling to room temperature, the solvents were removed under reduced pressure. The residue was extracted with CH_{2}Cl_{2} and washed with 2M HCl, NaCl solution, and water respectively. After drying over anhydrous Na_{2}SO_{4}, the solvent was removed under reduced pressure. The residue was purified by flash chromatography to give 0.26 g AnCN1 (67.3% yield) as a yellow powder (mp 120-121°C). ^1H NMR (CDCl_3): δ 8.48 (d, 2H, An), 8.37 (d, 2H, An), 7.71 (t, 2H, benzene), 6.56 (d, 1H, benzene), 5.75 (m, 2H, benzene), 5.05 (s, 2H, An-CH_{2}-benzene), 4.15-3.30 (m, 24H, ether). The molecular mass determined by MALDI-FTMS was 969.4 Da, verifying an empirical formula of C_{68}H_{59}O_{8}N. Both M^+, (M+Na)^+, and (M+K)^+ were observed in the MS.
Instrumentation:

$^1$H NMR spectra were obtained on a Bruker 400 MHz using chloroform-d. UV-absorption spectra were obtained on a Cary 4 spectrophotometer, Fluorescence spectra were obtained on a spex Fluorolog-2 spectrometer equipped with double monochromators on both excitation and emission sides.

Matrix assisted laser desorption / ionization-Fourier transform ion cyclotron resonance is represented by the acronym MALDI-FTICR. All mass spectra were acquired on a Finnigan FT/MS 2001 Fourier transform ion cyclotron resonance mass spectrometer equipped with a nitrogen laser (337 nm, Laser photonics). Samples were dissolved in ethanol, mixed with a molar excess of the matrix compound (2,5-dihydroxybenzoic acid), and dried onto a stainless steel sample probe tip. Laser desorption/ ionization of samples inside the mass spectrometer resulted in the production of positively charged protonated, Na$^+$-and/or K$^+$-linked molecular ions that were detected under medium resolution conditions. Mass calibration was accomplished with external calibration of characteristic ions from oligonucleotidies (d(ACGT)).
Result and Discussion:

Absorption and emission studies:

The absorption spectra of AnCN2 and AnCN1 are similar in appearance to the spectra of cyanoanthracene. Upon complexation of metal ions, however, a slight increase in the extinction coefficients is observed as the concentration of metal ion is increased, Figure 1 shows the effect of rubidium ions on the absorption spectrum of AnCN2 (3.5×10^{-6} M) in CH₂Cl₂-EtOH (1:1 v/v) using 0.01 M benzyl (triethyl) ammonium hydroxide to maintain the ionic strength.

![Absorption spectrum](image)

**Figure 1:** The change in the absorption spectrum of AnCN2 (3.5×10^{-6} M) in CH₂Cl₂-EtOH (1:1, v/v) vs. concentration of rubidium acetate using 1×10^{-2} M benzyl (triethyl) ammonium hydroxide to maintain a constant ionic strength.

The change in the intensity of the 391 nm absorption band induced by rubidium ion complexation for both AnCN2 and AnCN1 is shown as Figure 2. The spectral data shown in Figure 1 and 2 suggest that: (a) the complexation of Rb⁺ by the crown ether influences the absorption coefficients of cyanoanthracene in AnCN2 and (b) there are two
plateau regions in the absorption profile of AnCN2 compared to only one plateau region for AnCN1 (Figure 2) indicating a different stoichiometry for the Rb⁺ complexation by AnCN1 and AnCN2. The behavior of AnCN1 is consistent with the expected 1:1 complexation stoichiometry, while that of AnCN2 conforms to a stepwise 1:1 and 1:2 AnCN2-Rb⁺ complexation. At low rubidium concentrations (< 3 × 10⁻⁵ M), the 1:1 complex predominates.

![Graph showing absorption vs. concentration of CH₂Cl₂-EtOH (1:1, v/v) using 1×10⁻² M benzyl (triethyl)ammonium hydroxide to maintain a constant ionic strength.](image)

**Figure 2:** The absorption vs. [Rb⁺] profile of AnCN2(3.5×10⁻⁶ M) and AnCN1(6.3×10⁻⁶ M) in CH₂Cl₂-EtOH (1:1, v/v) using 1×10⁻² M benzyl (triethyl)ammonium hydroxide to maintain a constant ionic strength.

As the concentration of Rb⁺ is increased (> 2 × 10⁻³ M), the formation of a 1:2 complex by the second crown ether ring is favored (Figure 2). A similar behavior is also observed in the emission of AnCN2 upon rubidium ion complexation (*vide supra*).
Scheme 1: The molecular structure of probes AnCN2, AnCN1 and compound 3, 4, and 5.
The emission behavior of probe molecules AnCN2 and AnCN1 was also studied in CH₂Cl₂-EtOH (1:1, v/v) due to low solubility of both in EtOH. Since the emission behavior of AnCN1 and AnCN2 could be influenced by the solvent polarity, we studied the effect of solvent composition on the emission profile of both probes. Figure 3 shows the change in fluorescence intensity (450 nm) of AnCN1 and AnCN2 as a function of solvent composition.

**Scheme 2:** The PET effect on the emission of uncomplexed and complexed AnCN₂ in the absence and presence of alkali metal ion.

The maximum emission intensity for AnCN1 and AnCN2 is obtained in the solvent mixture containing 10% ethanol in dichloromethane (Figure 3).
Figure 3: The solvent polarity effect on the fluorescence spectra of AnCN2 and AnCN1 (1x10^{-5} M) in CH₂Cl₂-EtOH (1:1, v/v).

The observed increase in the emission intensity upon addition of a small amount of ethanol to dichloromethane may suggest an interaction between ethanol and the crown ether. The complexation of ethanol with the crown ether through hydrogen bonding can suppress the photo-induced electron transfer process (PEP), enhancing the fluorescence intensity of AnCN1 and AnCN2. As the ratio of EtOH to CH₂Cl₂ is increased, the polarity effect on the electron transfer process begins to dominate causing a weakening of the complexation process that result in a decrease in fluorescence intensity. Since the fluorescence intensity does not change significantly for solvent mixture in the range 0.5-1.0, we chose a 1:1 ratio of CH₂Cl₂-EtOH (v/v) for our fluorescence and absorption studies.
The fluorescence of AnCN1 is weak ($\Phi = 0.008$) in the CH$_2$Cl$_2$-EtOH mixture due to electron transfer from the oxygen atoms of the benzo moiety to the excited singlet state of cyanoanthracene. When Rb$^+$ is added to a 1×10$^{-6}$ M solution of AnCN1 in CH$_2$Cl$_2$-EtOH, the fluorescence intensity increases (Figure 4).

![Figure 4: Changes in the emission profile of 1×10$^{-6}$M AnCN1 in CH$_2$Cl$_2$-EtOH (1:1, v/v) as a function of rubidium ion concentration (excitation was at the isosbestic point).](image)

The maximum enhancement (8.2 fold) in the emission is reached at [Rb$^+$] = 2×10$^{-6}$ M (Figure 4) The fluorescence intensity of AnCN2 also increases upon addition of Rb$^+$ ions with a maximum enhancement of 11.7 fold at [Rb$^+$] = 4×10$^{-3}$ M. Similar to the absorption behavior, the emission response of the host AnCN2 as a function of [Rb$^+$] shows a different profile compared to AnCN1 (Figure 5). The emission profile shows a single plateau for the complexation of rubidium with AnCN1.
suggesting a 1:1 complexation stoichiometry while two plateau regions are observed for the complexation of **AnCN2** with Rb\(^+\) (Figure 5). The first plateau occurs at [Rb\(^+\)] = 2×10\(^{-6}\) M and the second one at [Rb\(^+\)] = 3×10\(^{-4}\) M. These results clearly indicate a stepwise 1:2 complexation stoichiometry for **AnCN2**.

*Figure 5*: Changes in the emission intensity (\(\lambda=450\) nm) of **AnCN2** (1×10\(^{-6}\) M) and **AnCN1** (1×10\(^{-6}\) M) in CH\(_2\)Cl\(_2\)-MeOH (1:1, v/v) as a function of rubidium ion concentration (excitation was at the isosbestic point).

The first complexation is complete at [Rb\(^+\)] = 1×10\(^{-6}\) M while the second complexation process begins at [Rb\(^+\)] = 1×10\(^{-5}\) M is complete and is complete at [Rb\(^+\)] = 3×10\(^{-4}\) M. In essence, at low concentration of **AnCN2** (1×10\(^{-6}\) M), the probe prefers to bind with only one rubidium ion. The second rubidium binding takes place only after the rubidium concentration reaches 10\(^{-5}\) M. This feature of **AnCN2-Rb\(^+\)** complexation by controlling concentration of rubidium. It should be mentioned that at higher concentration of **AnCN2**
the two plateau regions cannot be resolved and are indistinguishable. The emission intensities of both AnCN2 and AnCN1 decrease after the concentration of rubidium ions reaches $3 \times 10^{-2} \text{M}$. This is due to medium effects such as changes in the ionic strength of the solution, which will increase the polarity of the media rendering the PET process more effective.

![Graph](image)

**Figure 6:** Changes in the emission intensity of AnCN1 ($1 \times 10^{-6} \text{M}$) in CH$_2$Cl$_2$-MeOH (1:1, v/v) as a function of various alkali metal ions (M=Li, Na, K, Rb, Rb). The lines were obtained using a non-linear curve fitting method22 (excitation was at the isosbestic point).

Figure 6 and 7 compare the change in fluorescence intensity of both probes AnCN1 ($1 \times 10^{-6} \text{M}$) and AnCN2 ($1 \times 10^{-6} \text{M}$) in CH$_2$Cl$_2$-EtOH for different alkali metal ions. In both cases, Li$^+$ has no significant effect on the observed emission while, Na$^+$ shows a small enhancement at high concentrations of this ion suggesting a weak complexation ($\log K = 2.6$ for AnCN1 and $\log K_{11} = 3.1$ and $\log K_{12} = 1.6$ for AnCN2, Tables 1 and 2).
Figure 7: Changes in the emission intensity of AnCN2 (1×10^{-6} M) in CH₂Cl₂-MeOH (1:1, v/v) as a function of concentration of various alkali metal ions (M= Li, Na, K, Rb, Rb). The lines were obtained using a non-linear curve fitting method (excitation was at the isobestic point).

Both K⁺ and Rb⁺ show moderate enhancement (log $K = 5.5$ and $6.9$, respectively for AnCN1, and log $K_{11} = 5.7$ and $6.3$ and log $K_{12} = 2.7$ and $3.9$, respectively for AnCN2, Tables 1 and 2). The most dramatic effect is observed for Rb⁺ suggesting a strong complexation compared with other alkali, metal ions. The fluorescence quantum yield ($\Phi$) for complexed AnCN2 and AnCN1 are listed in Tables 1 and Table 2.

<table>
<thead>
<tr>
<th>Metal ion, M⁺</th>
<th>Free</th>
<th>Na⁺</th>
<th>K⁺</th>
<th>Rb⁺</th>
<th>Cs⁺</th>
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<tr>
<td>$\Phi_{\text{max}}$</td>
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<td>0.035</td>
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</table>

Calculated from UV-absorption measurement.

Table 1: The maximum fluorescence quantum yield ($\Phi$) and stability constants, $K$, for the complexation various alkali metal ions by AnCN1 (1×10^{-6}M) in CH₂Cl₂-EtOH (1:1,v/v)
<table>
<thead>
<tr>
<th>Metal ion, M⁺</th>
<th>Free</th>
<th>Na⁺</th>
<th>K⁺</th>
<th>Rb⁺</th>
<th>Cs⁺</th>
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<tr>
<td>Φ_{max}</td>
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<td>0.047</td>
<td>0.089</td>
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<td>logK_{11}</td>
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<tr>
<td>logK_{12}</td>
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<td>3.7</td>
<td>3.8(3.7²)⁶⁶</td>
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<tr>
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<td>-</td>
<td>0.9</td>
<td>-b</td>
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<tr>
<td>χ</td>
<td>-</td>
<td>-</td>
<td>2.7</td>
<td>-b</td>
<td>4.3</td>
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</table>

*a* Calculated from UV-absorption measurement. *b* Not determined. *c* The calculated values for $K_{11}$ and log $K_{12}$ for the complexation of cesium by calix[4]naphthocrown-6), 6, are 3.47 respectively.

**Table 2**: The maximum fluorescence quantum yield ($\Phi$), a, $\chi$, and stability constants $K_{11}$, $K_{12}$ for the complexation of various alkali metal ions by AnCN2(1×10⁻⁶ M) in CH₂Cl₂-EtOH(1:1, v/v)

**Complexation Constants:**

The complexation constant $K$ for AnCN1 with various alkali metal ions was determined from the emission data (Figure 6) using eqn. (1) where $I$ is the emission response of the probe for

$$\frac{I - I_\infty}{I_\infty - I} = K\{[M]_0 - [L]_0\left(\frac{I - I_0}{I_\infty - I_0}\right)\}$$

(1)
different concentrations of metal ions, \( I_0 \) is the emission response of the probe with no metal present, \( I_\infty \) is the emission response when no further changes occur upon addition of the metal ion, and \([M]_t\) and \([L]_t\) represent total concentration of metal ions and the probe. The complexation constant \( K \) was calculated using a non-linear curve-fitting method\(^{20}\) to fit the observed experimental emission data. Since eqn (1) only applies to a 1:1 complex formation, we invoked eqn (2) to calculate the complexation constants \( K_{11} \) and \( K_{12} \) for AnCN2 (1:2 stoichiometry\(^{21}\)).

\[
\frac{I - I_0}{I - I_\infty} = K_{11}[M] \frac{a + K_{12} \chi(M)}{K_{11}[M](a - \chi - \chi)}
\]

In eqn. (2), parameters \( a \) and \( \chi \) are constants, \( K_{11} \) and \( K_{12} \) represent association constants for the first and second metal ion complexation, \( I_0 \) is the fluorescence intensity in the absence of metal ions, \( I_\infty \) is the intensity when no further change in fluorescence is observed upon addition of metal ions, and \( I \) is the intensity at different metal ion concentrations. Non-linear least squares curve fitting of the experimental fluorescence data to eqn (2) allows determination of parameters \( a, \chi, K_{11} \) and \( K_{12} \). Table 2 shows the values of these parameters obtained from such fits for all the alkali metal ions. The measured association constants \( K_{11} \) and \( K_{12} \) suggest a 1:2 stoichiometry and are in good agreement with the reported values for
other systems that accommodate two metal ions at the complexing sites.\textsuperscript{9} The fact that the ratio of \( (K_{11}\times K_{12})_{\text{Rb}^+} / (K_{11}\times K_{12})_{\text{K}^+} \) = 277 agrees reasonably well with the reported value of ~160 (for 1,2-dichloroethane) by a solvent extraction technique,\textsuperscript{22} suggest that fluorescence spectroscopy can be used as a method to obtain the association constants for metal ion complexation. The reported quantum yields for fluorescence of AnCN2 in the presence of different alkali metal ions shows in Table 2, are relative to 9,10 - diphenylanthracene which has \( \phi_j = 1.\textsuperscript{23} \)

The first binding constant \( K_{11} (1\times10^7 \text{M}^{-1}) \) of AnCN2 is very similar to that of AnCN2 (9.6\times10^6 \text{ M}^{-1}), and both are higher than the value reported for other compounds with similar structure\textsuperscript{24b}. It should be mentioned that the second complexation constant \( K_{12} (1\times10^4 \text{ for Rb}^+) \) is much lower than the first complexation constant, \( K_{11} (1\times10^7 \text{ for Rb}^+) \). This behavior can be attributed to the stepwise complexation of alkali metal ions AnCN2. When the concentration of alkali metal ion is very low, the second metal ion cannot complete with the first due to its lower binding capability. The first and second metal ion complexation capabilities are so different that no significant second ion binding takes place even when complexation of the first ion with AnCN2 is complete ([M\textsuperscript{+}] = 1\times10\textsuperscript{6} to 8\times10\textsuperscript{6} \text{ M range}). In order to distinguish the two

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stepwise complexation processes, the host concentration, \([L]_h\), must be < 1\times10^{-5} \text{ M}. We have used \([L]_i = 1\times10^{-6} \text{ M}\) in our studies to resolve this two step complexation process.

Considering the symmetrical structure of the molecule AnCN2, the first binding of rubidium appears to affect the complexation behavior of the second Rb\(^+\). The reason for the observed lower value of \(K_{12}\) compared to \(K_{11}\) may be due to the following effects. (1) Static electron-repulsion from the first metal ion in the complexed calix [4]crown and (2) binding of the first rubidium ion induces a conformational change in the second polyether loop that results in reduced affinity for the second Rb\(^+\). The fact that the maximum enhancement in the emission of AnCN2 upon complexation of rubidium is only 11.7 fold, which is higher than 8.2 fold for AnCN1
but not twice the value if both fluorophores contributed equally, provides additional evidence in support of electron-repulsion between the two rubidium ions in the cavities upon complexation. Since electron transfer is channeled through the benzo group, these observations suggest that the repulsion will move Rb\(^+\) closer to the alkoxybenzene group to cause less fluorescence quenching of cyanoanthracene.

The complexation constants for both AnCN1 and AnCN2 with rubidium calculated using absorption data also listed in Tables 1 and Table 2. The values are similar to those obtained from the emission measurements. For comparison, the complexation constant for calix[4]bis(naphthocrown-6),6, which is commercially available, was also measured using absorption data and is listed in Table 2. Two plateau regions were also observed in the absorption spectra of 6 upon complexation of rubidium. Interestingly, the first complexation constant (\(K_{11}\)) for compound 6 is much lower than that of AnCN2 although they both have similar structure. The value however, is very close to the data reported in the literature.\(^\text{10}\) This would argue against repulsion by the two Rb\(^+\) ions and favors crown ether conformation as the controlling factor in the magnitude of \(K\) values.

The coalescence effect\(^\text{11}\) and the high concentration of host molecule hamper the use of the NMR technique to observe the two
plateau regions for the stepwise complexation of AnCN2 with rubidium. However, AnCN2-Rb⁺ stoichiometry can still be determined by the change in proton ratio of the host molecule. The 400 MHz ¹H NMR spectra was obtained for a 1×10⁻³ M concentration of AnCN2 in CDCl₃-CD₃OD (1:1) mixture, and rubidium acetate was added to the mixture as in fluorescence and UV-absorption study. The ratio of ligand to rubidium was determined by weight and was found to match the ratio of protons in the host AnCN2 and protons in CH₃COORb. The NMR results strongly support the 1:2 stoichiometry for the host AnCN2-Rb⁺ complexation.

In summary, 1,3-calix[4]bis[(10-cyano-9-anthrylethyl)-o-benzocrown-6], AnCN2, and 1,3-calix[4]-25,27-bis(allyloxy)-26,28-[(10-cyano-9-anthrylethyl)-o-benzocrown-6], AnCN1, were synthesized as the first generation of Rb⁺ selective optical sensors based on calixarenes. The maximum emission increases for AnCN2 and AnCN1 upon Rb⁺ complexation were 11.7 and 8.2 fold respectively. The sensitivity of both probes to various alkali metal ions decrease in the following order Rb⁺> K⁺ > Na⁺ > Li⁺ rendering them remarkable sensors for rubidium detection. The fluorescence and absorption data for Rb⁺ complexation by AnCN1 suggest a 1:1 stoichiometry with a stability constant of 10⁷ M⁻¹. A similar study for AnCN2, on the other hand, reveals two plateau regions at low
concentration of the host suggesting a 1:2 stoichiometry for the complexation of Rb$^+$ by AnCN2 with the first complexation constant being much higher ($10^7\text{M}^{-1}$) than the second ($10^4\text{M}^{-1}$). This is the first report of a stepwise complexation process involving a 1,3 alternate calix[4] crown-6 derivative and an alkali metal ion.
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