PERKIN 2

Synthesis and sensing behavior of cyanoanthracene modified 1,3-alternate calix[4]benzocrown-6: a new class of Cs^+ selective optical sensors

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1,3-Calix[4]bis(10-cyano-9-anthrylmethyl-*o*-benzocrown-6), **AnCN2**, and 1,3-calix[4]-25,27-bis(allyloxy)-26,28-(10-cyano-9-anthrylmethyl-*o*-benzocrown-6), **AnCN1**, were synthesized as the first generation of Cs^+ selective optical sensors based on calixarenes. The maximum enhancement in the emission of **AnCN2** and **AnCN1** upon Cs^+ complexation was 11.7 and 8.2 in a 1 : 1 CH_2Cl_2–MeOH mixture. Their response to various alkali metal ions follows the order $Cs^+ > Rb^+ \gg K^+ \gg Na^+ > Li^+$ indicating good selectivity towards caesium. The fluorescence and absorption profile for Cs^+ complexation suggest a 1 : 1 stoichiometry for the host **AnCN1**–Cs complex and a stability constant of 10^7 M^{-1}. **AnCN2**, on the other hand, shows two plateau regions corresponding to a 1 : 2 stoichiometry for complexation of Cs^+. The first complexation constant is much higher (10^7 M^{-1}) than the second one (10^4 M^{-1}). The NMR studies further substantiate the complexation of two metal ions by **AnCN2**. This is the first report of stepwise complexation of metal ions to a 1,3-alternate calix[4]bis(crown-6) derivative.

Introduction

The chemistry of calixarenes is now a well-established field.[1,2] Calix[4]crown compounds have been shown to be highly selective towards complexation of alkali and alkaline-earth metal ions.[3,4] The calix[4]crowns are generally composed of a calixarene and a crown ether moiety bonded together by the phenolic oxygens of the calixarene and a polyether chain. Although the crown ether ring complexes with the metal ions, the calix[4]arene can assume various conformations (*e.g.* cone, partial cone, 1,2-alternate, and 1,3-alternate) that play a crucial role on the selectivity of the probe for different metal ions.[5] Some derivatives of 1,3-alternate calix[4]crown-6 ethers have been shown to possess high selectivity towards caesium in both acidic and alkaline media,[5–8] rendering them suitable for the removal of caesium from nuclear waste. The Cs–Na and Cs–K selectivity ratios for some of these calixarenes exceed 10^4 and 10^2 as measured by solvent extraction.[7] Selective caesium carriers in supported liquid membranes (SLMs) have been prepared by Asfari and co-workers.[6,9] Reinhoudt has incorporated calixarenes in PVC membranes of chemically modified field effect transistors.[10] Calixarenes have also been anchored onto silica gel for selective separation of Cs^+.[11] In most of these studies, the focus has been on the separation of radioactive Cs^+ from the nuclear fuel waste. We have utilized these attractive features of calix[4]arenes to prepare a Cs^+ selective fluorescent molecular recognition agent for the detection of caesium ions in solution. Furthermore, in an effort to address the question regarding one *vs.* two caesium ions binding by the two cavities of calix[4]bis(crown-6),[12–16] 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.[17–19] These optical probes can signal the presence of caesium ions by showing an increase in the emission intensity upon caesium complexation, induced by a photo-induced electron transfer (PET) process. Probe molecules **AnCN2** and **AnCN1** (Scheme 1) 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 caesium 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 (Scheme 2). Similar probes based on a PET process for the detection of Na^+ and K^+ ions in solution have been reported using cyanoanthracence fluorophore covalently bonded to the benzo crown ethers.[20,21]

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. Fig. 1 shows the effect of caesium ions on the absorption spectrum of **AnCN2** (3.5×10^{-6}M) in CH_2Cl_2–MeOH (1 : 1 v/v) using 0.01 M benzyl(trimethyl)ammonium hydroxide to maintain the ionic strength. The change in the intensity of the 391 nm absorption band induced by caesium ion complexation for both **AnCN2** and **AnCN1** is shown in Fig. 2. The spectral data shown in Figs. 1 and 2 suggest that: (a) the complexation of Cs^+ 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** (Fig. 2) indicating a different stoichiometery for the Cs^+ 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**–Cs^+ complexation. At low caesium concentrations ($<3 \times 10^{-5}$ M), the 1 : 1 complex predominates. As the concentration of Cs^+ is increased ($>2 \times 10^{-3}$ M), the formation of a 1 : 2 complex by the second crown ether ring is favored (Fig. 2). A similar behavior is also observed in the emission of **AnCN2** upon caesium ion complexation (*vide supra*).

The emission behavior of probe molecules **AnCN2** and **AnCN1** was also studied in CH_2Cl_2–MeOH (1 : 1, v/v) due to low solubility of both in MeOH. Since the emission behavior of

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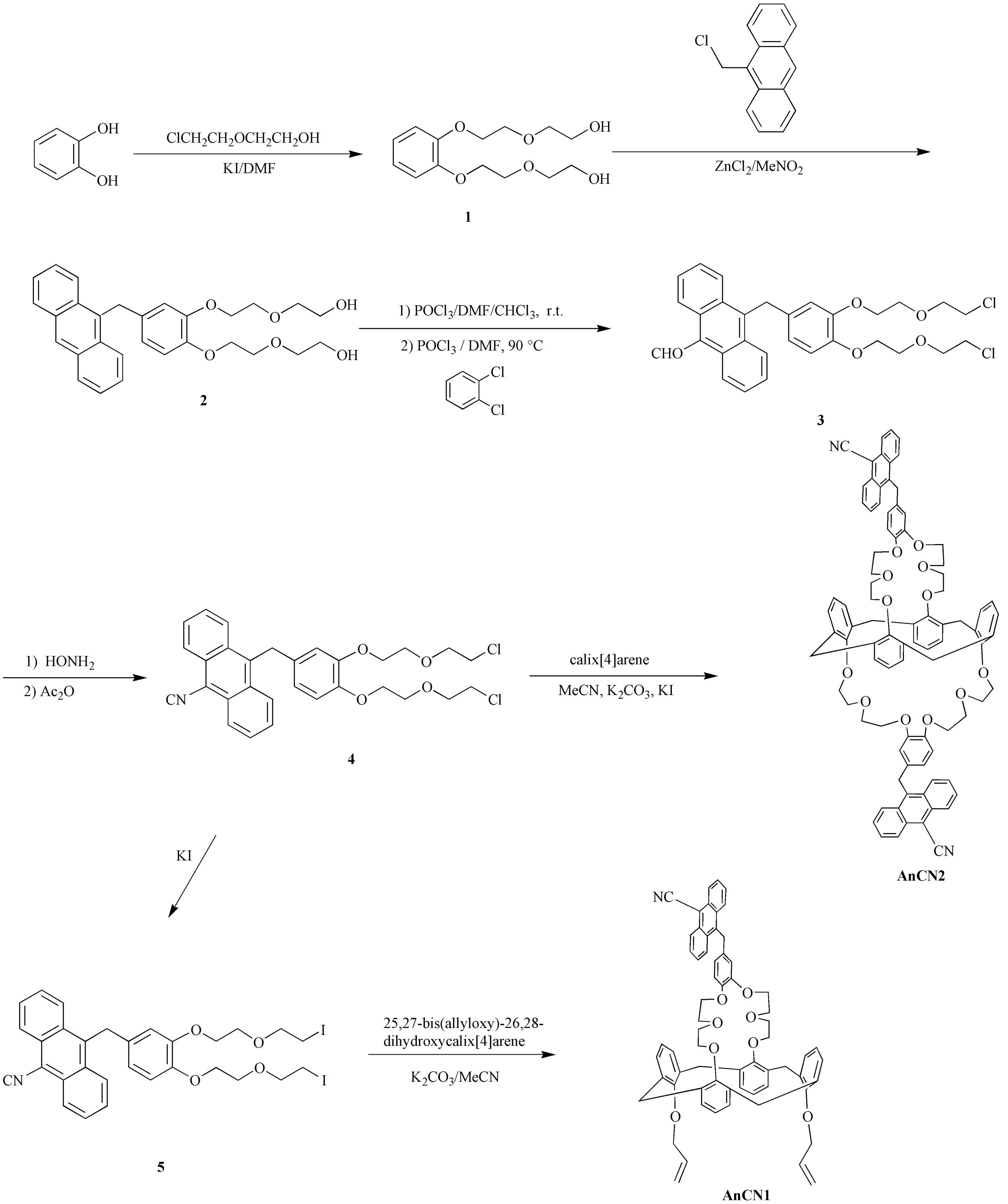


Scheme 1 The molecular structure of probes **AnCN2, AnCN1** and compounds **3**, **4**, and **5**.

AnCN1 and **AnCN2** could be influenced by the solvent polarity, we studied the effect of solvent composition on the emission profile of both probes. Fig. 3 shows the change in fluorescence intensity (450 nm) of **AnCN1** and **AnCN2** as a function of solvent composition. The maximum emission intensity for **AnCN1** and **AnCN2** is obtained in the solvent mixture containing 10% methanol in dichloromethane (Fig. 3). The observed increase in the emission intensity upon addition of a small amount of methanol to dichloromethane may suggest an interaction between methanol and the crown ether. The complexation of methanol with the crown ether through hydrogen bonding can suppress the photoinduced electron transfer process (PET), enhancing the fluorescence intensity of **AnCN1** and **AnCN2**. As the ratio of MeOH to CH_2Cl_2 is increased, the polarity effect on the electron transfer process begins to dominate causing a weakening of the complexation process that results in a decrease in fluorescence intensity. Since the fluorescence intensity does not change significantly for the solvent mixture in the range 0.5–1.0, we chose a 1 : 1 ratio of CH_2Cl_2–MeOH (v/v) for our fluorescence and absorption studies.

The fluorescence of **AnCN1** is weak ($\Phi = 0.008$) in the CH_2Cl_2–MeOH mixture due to electron transfer from the oxygen atoms of the benzo moiety to the excited singlet state of cyanoanthracence. When Cs^+ is added to a 1×10^{-6} M solution of **AnCN1** in CH_2Cl_2–MeOH, the fluorescence intensity increases (Fig. 4). The maximum enhancement (8.2 fold) in the emission is reached at $[Cs^+] = 2 \times 10^{-6}$ M (Fig. 4). The fluorescence intensity of **AnCN2** also increases upon addition of

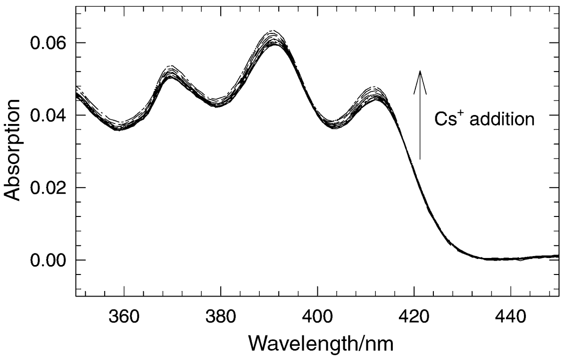


Fig. 1 The change in the absorption spectrum of **AnCN2** (3.5×10^{-6} M) in CH_2Cl_2–MeOH (1 : 1, v/v) *vs.* concentration of caesium acetate using 1×10^{-2} M benzyl(trimethyl)ammonium hydroxide to maintain a constant ionic strength.

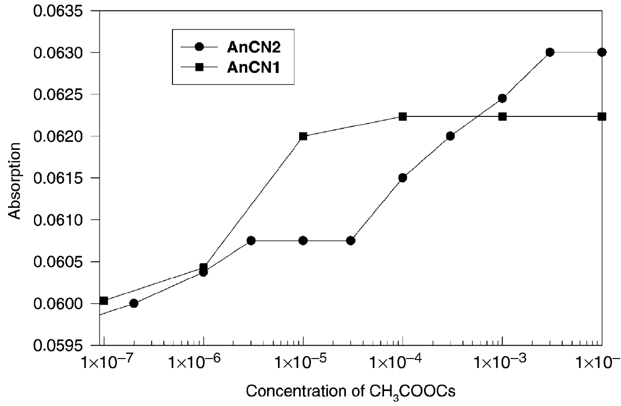
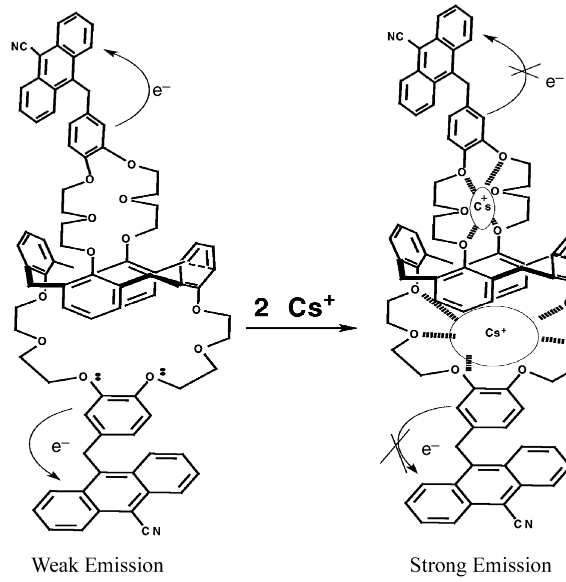


Fig. 2 The absorption *vs.* [Cs^+] profile of **AnCN2** (3.5×10^{-6} M) and **AnCN1** (6.3×10^{-6} M) in CH_2Cl_2–MeOH (1 : 1, v/v) using 1×10^{-2} M benzyl(trimethyl)ammonium hydroxide to maintain a constant ionic strength.



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

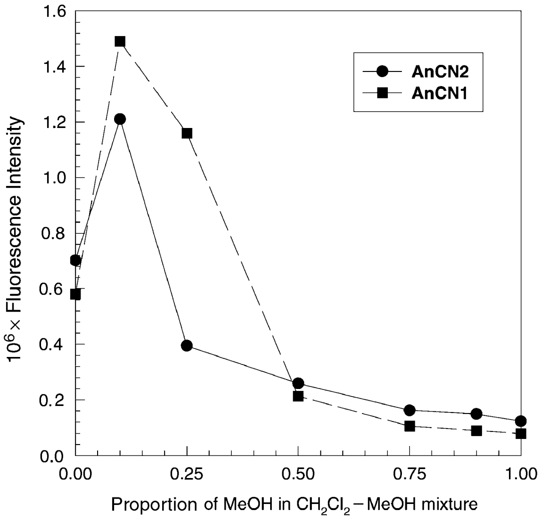


Fig. 3 The solvent polarity effect on the fluorescence spectra of **AnCN2** and **AnCN1** (1×10^{-6} M) in CH_2Cl_2–MeOH (1 : 1, v/v).

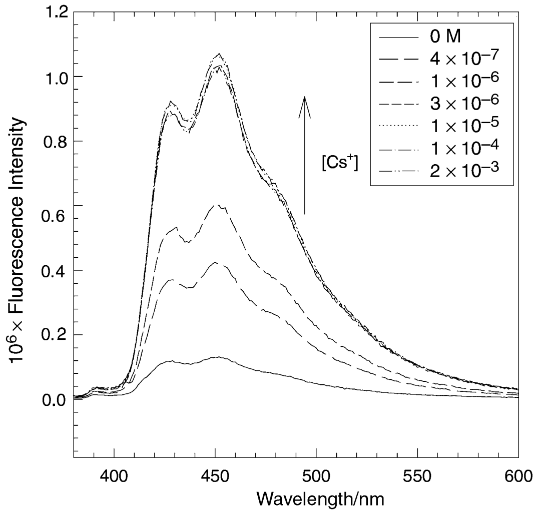


Fig. 4 Changes in the emission profile of 1×10^{-6} M **AnCN1** in CH_2Cl_2–MeOH (1 : 1, v/v) as a function of caesium ion concentration (excitation was at the isosbestic point).

Cs^+ ions with a maximum enhancement of 11.7 fold at [Cs^+] = 4×10^{-3} M. Similar to the absorption behavior, the emission response of the host **AnCN2** as a function of [Cs^+] shows a different profile compared to **AnCN1** (Fig. 5). The emission profile shows a single plateau for the complexation of caesium with **AnCN1** suggesting a 1 : 1 complexation stoichiometry while two plateau regions are observed for the complexation of **AnCN2** with Cs^+ (Fig. 5). The first plateau occurs at [Cs^+] = 2×10^{-6} M and the second one at [Cs^+] = 3×10^{-4} M. These results clearly indicate a stepwise 1 : 2 complexation stoichiometry for **AnCN2**. The first complexation is complete at [Cs^+] = 1×10^{-6} M while the second complexation process begins at [Cs^+] = 1×10^{-5} M and is complete at [Cs^+] = 3×10^{-4} M. In essence, at low concentration of **AnCN2** (1×10^{-6} M), the probe prefers to bind with only one caesium ion. The second caesium binding takes place only after the caesium concentration reaches 10^{-5} M. This feature of **AnCN2** allow us to obtain a 1 : 1 or 1 : 2 stoichiometery for **AnCN2**–Cs^+ complexation by controlling the concentration of caesium. It should be mentioned that at higher concentrations of **AnCN2** (*e.g.* 1×10^{-4} M) the two plateau regions cannot be resolved and are indistinguishable. The emission intensities of both **AnCN2** and **AnCN1** decrease after the concentration of caesium ions reaches 3×10^{-2} 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.

Figs. 6 and 7 compare the change in fluorescence intensity of both probes **AnCN1** (1×10^{-6} M) and **AnCN2** (1×10^{-6} M) in CH_2Cl_2–MeOH 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

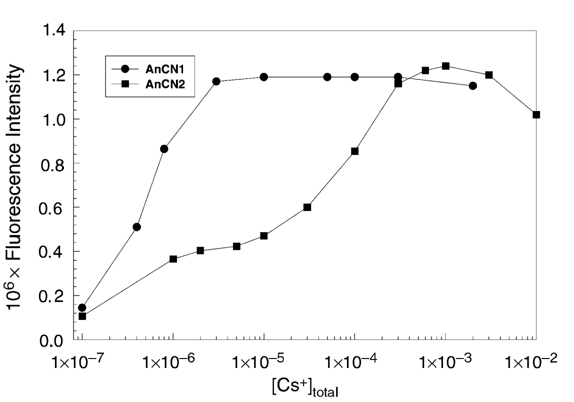


Fig. 5 Changes in the emission intensity ($\lambda = 450$ nm) of **AnCN2** (1×10^{-6} M) and **AnCN1** (1×10^{-6} M) in CH_2Cl_2–MeOH (1 : 1, v/v) as a function of caesium ion concentration (excitation was at the isosbestic point).

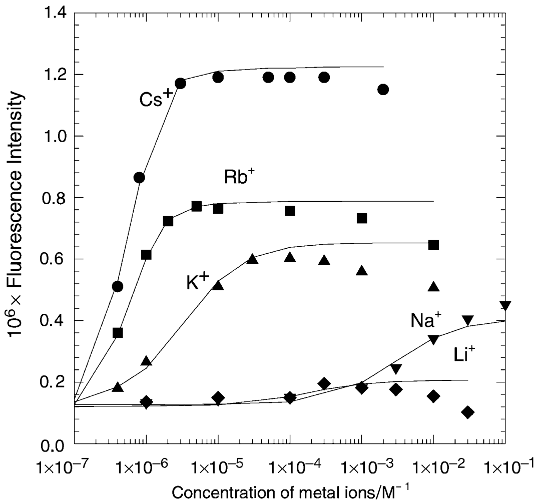


Fig. 6 Changes in the emission intensity of **AnCN1** (1×10^{-6} M) in CH_2Cl_2–MeOH (1 : 1, v/v) as a function of various alkali metal ions (M = Li, Na, K, Rb, Cs). The lines were obtained using a non-linear curve fitting method [22] (excitation was at the isosbestic point).

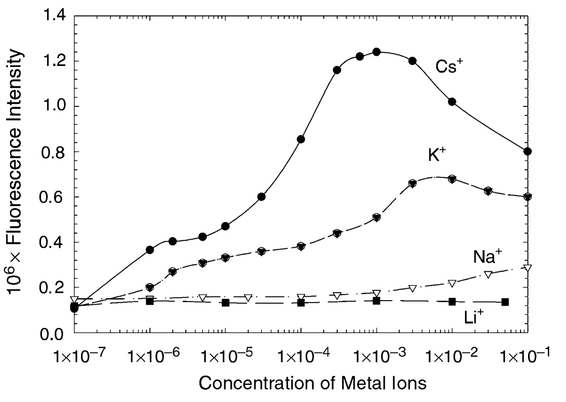


Fig. 7 Changes in the emission intensity of **AnCN2** (1×10^{-6} M) in CH_2Cl_2–MeOH (1 : 1, v/v) as a function of concentration of various alkali metal ions (M = Li, Na, K, Rb, Cs). The lines were obtained using a non-linear curve fitting method [22] (excitation was at the isobestic point).

$\log K_{11} = 3.1$ and $\log K_{12} = 1.6$ for **AnCN2**, Tables 1 and 2). 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 Cs^+ suggesting a strong complexation compared with other alkali metal ions. The fluorescence quantum yields (Φ) for complexed **AnCN2** and **AnCN1** are listed in Tables 1 and 2.

Table 1 The maximum fluorescence quantum yield (Φ) and stability constants, K, for the complexation of various alkali metal ions by **AnCN1** (1×10^{-6} M) in CH_2Cl_2–MeOH (1 : 1, v/v)

	Metal ion, M^+				
	Free	Na^+	K^+	Rb^+	Cs^+
Φ_{max}	0.0085	0.031	0.037	0.052	0.070
$\log K$	—	2.6	5.5	6.96	7.08 (6.90)^a

^{a} Calculated from UV-absorption measurement.

Table 2 The maximum fluorescence quantum yield (Φ), a, χ, and stability constants K_{11}, K_{12} for the complexation of various alkali metal ions by **AnCN2** (1×10^{-6} M) in CH_2Cl_2–MeOH (1 : 1, v/v)

	Metal ion, M^+				
	Free	Na^+	K^+	Rb^+	Cs^+
Φ_{max}	0.0082	0.016	0.049	0.091	0.096
$\log K_{11}$	—	3.1	5.7	6.3	6.9 (6.7^a)^c
$\log K_{12}$	—	1.6	2.7	3.9	4.0 (3.7^1)^c
a	—	—	1.0	—^{b}	1.0
χ	—	—	2.9	—^{b}	4.5

^{a} Calculated from UV-absorption measurement. ^{b} Not determined. ^{c} The calculated values for $\log K_{11}$ and $\log K_{12}$ for the complexation of caesium by calix[4]bis(naphthocrown-6), **6**, are 5.47 and 3.47 respectively.

Complexation constants

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

$$\frac{I - I_0}{I_\infty - I} = K\{[M]_t - [L]_t\left(\frac{I - I_0}{I_\infty - I_0}\right)\} \qquad (1)$$

different concentrations of metal ions, I_0 is the emission response of the probe with no metal ion present, I_∞ 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 [22] 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 [23]).

$$\frac{I - I_0}{I - I} = K_{11}[M]\frac{a + K_{12}\chi[M]}{K_{11}[M](a - \chi) - \chi} \qquad (2)$$

In eqn. (2), parameters a and χ 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_∞ 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, χ, 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 stoichiometery and are in good agreement with the reported values for other systems that accommodate two metal ions at the complexing sites.[13] The fact that the ratio of $(K_{11} \times K_{12})_{Cs^+}/(K_{11} \times K_{12})_{K^+} = 277$ agrees reasonably well with the reported value of ~160 (for 1,2-dichloroethane) by a solvent extraction technique,[8] suggests 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 shown in Table 2, are relative to 9,10-diphenylanthracene which has $\Phi_f = 1$.[24]

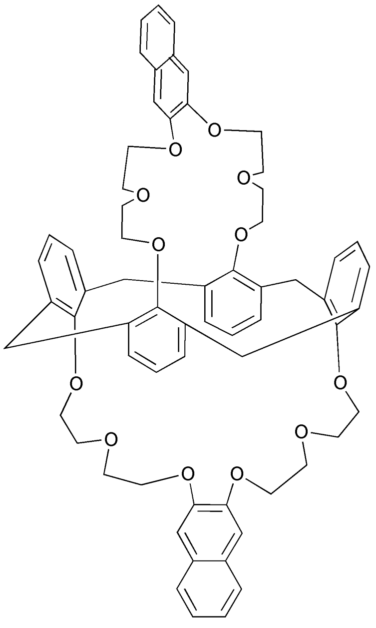
The first binding constant K_{11} (1×10^7 M^{-1}) of **AnCN2** is very similar to that of **AnCN1** (9.6×10^6 M^{-1}), and both are higher than the value reported for other compounds with similar structure.[6b] It should be mentioned that the second complexation constant K_{12} (1×10^4 for Cs^+) is much lower than the first complexation constant, K_{11} (1×10^7 for Cs^+). This behavior can be attributed to the stepwise complexation of alkali metal ions by **AnCN2**. When the concentration of alkali metal ion is very low, the second metal ion cannot compete 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 ($[M^+] = 1 \times 10^{-6}$ to 8×10^{-6} M range). In order to distinguish the two stepwise complexation processes, the host concentration, $[L]_t$, must be $<1 \times 10^{-5}$ M. We have used $[L]_t = 1 \times 10^{-6}$ M in our studies to resolve this two step complexation process.

Considering the symmetrical structure of the molecule **AnCN2**, the first binding of caesium appears to affect the complexation behavior of the second Cs^+. 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 caesium ion induces a conformational change in the second polyether loop that results in reduced affinity for the second caesium ion. The fact that the maximum enhancement in the emission of **AnCN2** upon complexation of caesium 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 caesium ions in the cavities upon complexation. Since electron transfer is channeled through the benzo group, these observations suggest that the repulsion will move Cs^+ closer to the alkoxybenzene group to cause less fluorescence quenching of cyanoanthracene.

The complexation constants for both **AnCN1** and **AnCN2** with caesium calculated using absorption data are also listed in Tables 1 and 2. The values are very 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 caesium. 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.[14] This would argue against repulsion by the two Cs^+ ions and favors crown ether conformation as the controlling factor in the magnitude of the K values.

The coalescence effect[15] 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 caesium. However, **AnCN2**–Cs^+ 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 $CDCl_3$–CD_3OD (1 : 1) mixture, and caesium acetate was added to the mixture as in fluorescence and UV-absorption study. The ratio of ligand to caesium was determined by weight and was found to match the ratio of protons in the host **AnCN2** and protons in CH_3COOCs. The NMR results strongly support the 1 : 2 stoichiometry for the host **AnCN2**–Cs^+ complexation.

In summary, 1,3-calix[4]bis[(10-cyano-9-anthrylmethyl)-*o*-benzocrown-6], **AnCN2**, and 1,3-calix[4]-25,27-bis(allyloxy)-26,28-[(10-cyano-9-anthrylmethyl)-*o*-benzocrown-6], **AnCN1**, were synthesized as the first generation of Cs^+ selective optical sensors based on calixarenes. The maximum emission increases for **AnCN2** and **AnCN1** upon Cs^+ complexation were 11.7 and 8.2 fold respectively. The sensitivity of both probes to various alkali metal ions decreases in the following order $Cs^+ > Rb^+ > K^+ > Na^+ > Li^+$ rendering them remarkable sensors for caesium detection. The fluorescence and absorption data for Cs^+ complexation by **AnCN1** suggest a 1 : 1 stoichiometry with a stability constant of 10^7 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 Cs^+ by **AnCN2** with the first complexation constant being much higher (10^7 M^{-1}) than the second (10^4 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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Experimental

^1H 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 methanol, 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 oligonucleotides (d(ACGT)).

For absorption and emission studies, a CH_2Cl_2–MeOH (1 : 1, v/v) solvent mixture was employed. For the NMR complexation studies, $CDCl_3$–CD_3OD (1 : 1, v/v) was used as the solvent mixture. The chemicals 2-(2-chloroethoxy)ethanol, 9(chloromethyl)anthracene, phosphorus oxychloride [trichloro-(oxo)-λ^5-phosphorane], benzyl(trimethyl)ammonium hydroxide, caesium acetate (99.9%), rubidium acetate, potassium carbonate, catechol (99%), and potassium acetate (99.9%) were used as received (Aldrich). 25,27-Bis(allyloxy)-26,28-dihydroxycalix[4]arene was synthesized using the same procedure reported in the literature.[25] Methylene chloride (Merck, 99.98%), DMF (EM Science, 99.9%), methanol (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.

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

Compound **1** was synthesized using a modified procedure described in the literature.[26] A solution of 2-(2-chloroethoxy)ethanol (18.0 g, 145 mmol) in 60 ml dry DMF was added over 30 min to a stirred suspension of catechol (4.0 g, 36.4 mmol), K_2CO_3 (40 g, 290 mmol) and KI (8.3 g, 50 mmol), and the 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 (20 ml). The solvent was removed under reduced pressure and the residue was extracted with CH_2Cl_2 and washed using 2 M HCl, NaCl solution, and water, respectively. After drying over anhydrous Na_2SO_4, the solvent was removed under reduced pressure. The residue was distilled at 0.1 Torr to give 9.2 g diol as a colorless oil (88.4% yield, bp 185–187 °C at 0.1 Torr). ^1H NMR ($CDCl_3$): δ 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, hydroxy).

1,2-Bis(5-hydroxy-3-oxa-1-pentyloxy)-4-(9-anthrylmethyl)benzene (2)

9-Chloromethylanthracene (2.3 g, 10 mmol) was added to a stirred solution of 1,2-bis(5-hydroxy-3-oxa-1-pentyloxy)benzene (7.15 g, 25 mmol) and $ZnCl_2$ (1.3 g, 10 mmol) in 100 ml CH_3NO_2. The solution was stirred at 60 °C for 2 h. The mixture was then allowed to cool down to room temperature and the solvent was removed under reduced pressure. The residue was extracted with CH_2Cl_2 and the organic layer was washed with NaCl solution and water, and then dried over Na_2SO_4. The solvent was removed under reduced pressure and the residue was purified by flash chromatography using CH_2Cl_2–acetone (1 : 1) as eluent to give 3.2 g of **2** (66% yield, mp 59–60 °C). ^1H NMR ($CDCl_3$): 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-CH_2-benzene), 4.17–3.62 (16H, m). The molecular mass determined by MALDI-FTMS was 476 Da, verifying an empirical formula of $C_{29}H_{32}O_6$. Both M^+ and $(M + Na)^+$ were observed in the MS.

1,2-Bis(5-chloro-3-oxa-1-pentyloxy)-4-(10-formyl-9-anthrylmethyl)benzene (3)

A solution of **2** (3.0 g, 6.3 mmol) in 20 ml dry chloroform was added over 10 min to a stirred solution of phosphorus oxychloride (2.2 g, 14.4 mmol) and dry DMF (1.05 g, 14.4 mmol) in dry chloroform (30 ml) 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 (40 ml), dry DMF (0.52 g, 7.2 mmol) and phosphorus oxychloride (1.1 g, 7.2 mmol). The temperature of the mixture was raised to 90 °C and the heating was continued overnight. After cooling to room temperature, the solvent was removed under reduced pressure and the residue was extracted with CH_2Cl_2 and washed with 50 ml of 2 M HCl, NaCl solution, and water respectively. After drying over anhydrous Na_2SO_4, the solvent was removed under reduced pressure. The residue was purified by flash chromatography using ethyl ether–hexane (1 : 2) as eluent to give 2.0 g of **3** (60% yield) as a yellow solid (mp 101–102 °C). ^1H NMR ($CDCl_3$): 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-CH_2-benzene), 4.10–3.60 (16H, m). The molecular mass determined by MALDI-FTMS was 540–544 Da, verifying an empirical formula of $C_{30}H_{30}O_5Cl_2$. Both M^+ and $(M + Na)^+$ were observed in the MS.

1,2-Bis(5-chloro-3-oxa-1-pentyloxy)-4-(10-cyano-9-anthrylmethyl)benzene (4)

A mixture of **3** (1.7 g, 3.14 mmol), hydroxylamine hydrochloride (0.25 g, 3.6 mmol), sodium acetate (0.3 g, 3.6 mmol), ethanol (40 ml), and water (12 ml) was refluxed under stirring for 1 h. 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 1 h. After cooling down to room temperature, the solvent was removed under reduced pressure, and the residue was extracted with CH_2Cl_2 and washed with 2 M HCl, NaCl solution, and water, respectively. After drying over anhydrous Na_2SO_4, the solvent was removed under reduced pressure. The residue was purified by flash chromatography to give 1.6 g of **4** (90% yield) as a pale-yellow powder (mp 112.5–114 °C). ^1H NMR ($CDCl_3$): δ 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_2Cl), 4.01 (2H, t, CH_2Cl), 3.85–3.58 (12H, m, ether). The molecular mass determined by MALDI-FTMS was 537-541 Da, verifying an empirical formula of $C_{30}H_{29}O_4NCl_2$. Both M^+ and $(M + Na)^+$ were observed in the MS.

1,3 Alternate 25,27 : 26,28-bis[4-(10-cyano-9-anthrylmethyl)-1,2-phenylenebis (5-dioxy-3-oxa-1-pentyloxy)]calix[4]arene (AnCN2)

Using a procedure described earlier,[6a] a mixture of calix[4]arene (0.17 g, 0.4 mmol), **4** (0.22 g, 0.4 mmol), K_2CO_3 (0.7 g, 5 mmol), and KI (0.33 g, 2 mmol) in 50 ml acetonitrile was refluxed under stirring for 4 days. The same quantities of K_2CO_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 CH_2Cl_2 and washed with 2 M HCl, NaCl solution, and water, respectively. After drying over anhydrous Na_2SO_4, the solvent was removed under reduced pressure. The residue was purified by flash chromatography to give 0.34 g of **AnCN2** (52% yield) as a yellow powder (mp 153–154.5 °C). ^1H NMR ($CDCl_3$): 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-CH_2-benzene), 4.06 (t, 4H, calix CH_2), 3.94 (t, 4H, calix CH_2), 3.75–3.22 (m, 32H, ether). The molecular mass determined by MALDI-FTMS was 1354.6 Da, verifying an empirical formula of $C_{88}H_{78}O_{12}N_2$. Only M^+ and $(M + K)^+$ were observed in the MS.

1,2-Bis(5-iodo-3-oxa-1-pentyloxy)-4-(10-cyano-9-anthrylmethyl)benzene (5)

A mixture of **4** (0.7 g, 1.30 mmol), KI (2.0 g, 12 mmol), and acetonitrile (50 ml) was purged with N_2 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 CH_2Cl_2 and washed with 2 M HCl, NaCl solution, and water respectively. After drying over anhydrous Na_2SO_4, the solvent was removed under reduced pressure to afford 0.93 g (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 $C_{30}H_{29}O_4NI_2$. Both M^+ and $(M + Na)^+$ were observed in the MS.

1,3-Alternate 25,27-bis(allyloxy)-26,28-[4-(10-cyano-9-anthrylmethyl)-1,2-phenylenebis(5-dioxy-3-oxa-1-pentyloxy)]calix[4]arene (AnCN1)

A mixture of 25,27-bis(allyloxy)-26,28-dihydroxycalix[4]arene

(0.20 g, 0.4 mmol), **5** (0.29 g, 0.4 mmol), and Cs_2CO_3 (1.63 g, 5 mmol) in 100 ml 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_2Cl_2 and washed with 2 M HCl, NaCl solution, and water respectively. After drying over anhydrous Na_2SO_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, An), 7.59 (t, 2H, An), 7.25–6.82 (m, 12H, benzene), 6.72 (d, 2H, benzene), 6.56 (d, 1H, benzene), 5.75 (m, 2H, benzene), 5.05 (s, 2H, An-CH_2-benzene), 5.10–4.78 (m, 4H, calix CH_2), 4.34 (m, 4H, calix CH_2), 4.15–3.30 (m, 24H, ether). The molecular mass determined by MALDI-FTMS was 969.4 Da, verifying an empirical formula of $C_{64}H_{59}O_8N$. Both M^+, $(M + Na)^+$, and $(M + K)^+$ were observed in the MS.

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