A new highly selective calix[4]crown-6 fluorescent caesium probe

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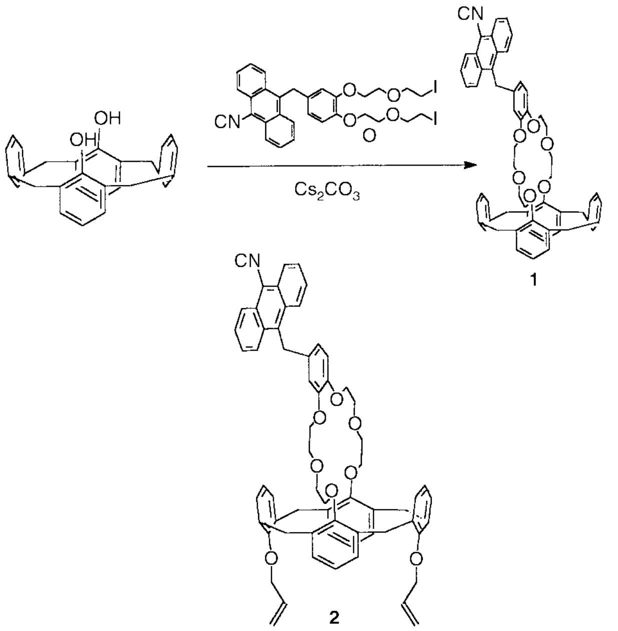
We have synthesized 1,3-alternate di-deoxygenated calix[4](9-cyano-10-anthrylmethyl)benzocrown-6, 1 and 1,3-alternate calix[4](9-cyano-10-anthrylmethyl)benzocrown-6, 2 as the second generation of caesium selective fluorescent probes; probe 1 shows 54-fold fluorescence enhancement upon caesium complexation while 2 exhibits only 8-fold enhancement; the selectivity ratios for 1 to complex caesium ion over potassium and rubidium (K_{Cs}/K_K and K_{Cs}/K_{Rb}) are *ca.* 10 fold higher than those of 2 for the same ions; the observed selectivity ratios are consistent with data reported for other 1,3-alternate calix[4]crown-6 derivatives.

Calix[4]crown-6 ethers in the 1,3-alternate conformation bind caesium with remarkable strength and selectivity.[1] Consequently, significant effort has been directed towards their use in the sensing, monitoring and remediation of ^{137}Cs, a fission product present in the wastes generated during the reprocessing of irradiated nuclear fuels.[2] The need for sensitive caesium sensors has led to the study of calix[4]crown-6 ethers as fluorescent caesium probes, and we have shown that 1,3-alternate calix[4]-bis-*o*-benzocrown-6[3a] ethers bearing cyanoanthracene fluorophores exhibit 8–12 fold fluorescence enhancement in the presence of caesium ion. The K_{Cs}/K_K and K_{Cs}/K_{Rb} ratios of 13[3b] and 1.3,[3b] respectively, indicate that the observed selectivities are consistent with data reported for other 1,3-alternate calix[4]crown-6 derivatives using UV absorption and potentiometric measurements.[4]

Recently, it was reported[5] that 1,3-alternate di-deoxygenated calix[4]crown-6 ethers exhibit enhanced selectivity for caesium over potassium and rubidium compared with their 1,3-alternate dialkoxy calix[4]crown-6 derivatives. Here, we have taken advantage of this higher caesium to potassium selectivity to synthesize a new caesium selective probe **1**. Our results suggest that **1** exhibits not only enhanced selectivity towards caesium, but also shows a fluorescence turn-on response significantly higher than any previously reported caesium sensor.

The 1,3-alternate di-deoxygenated calix[4](9-cyano-10-anthrylmethyl)-benzocrown-6, **1** was synthesized from di-dehydroxylated calix[4]arene and 1,2-bis(5-iodo-3-oxa-1-pentyloxy)-4-(10-cyano-9-anthrylmethyl)benzene[3b] by a standard procedure reported earlier.[6] The fluorescence of the 9-cyanoanthracene is quenched by the benzo moiety owing to a photoinduced electron transfer (PET) process.[7] It has been shown that binding the oxygen lone pair electrons (on the benzo moiety) by metal ion complexation partially suppresses the PET process, causing the fluorescence of the cyanoanthracene to increase.[3a,7]

The emission behavior of **1** (1×10^{-6} M) in CH_2Cl_2–MeOH (1 : 1) in the presence of five different alkali metal cations is shown in Fig. 1. The data indicates that probe **1** exhibits a significant emission enhancement upon caesium complexation (*ca.* 20-fold increase compared to uncomplexed probe) at a concentration as low as 2×10^{-7} M where no other alkali metal ion shows any response (except for Rb^+ that shows *ca.* 2-fold emission enhancement at the same concentration, Fig. 1). The fluorescence quantum yields of **1** for various alkali metal cations shown in Table 1 were determined relative to 9,10-diphenylanthracene in MeOH, $\Phi_f = 0.94$.[8] The fluorescence quantum yield of **1** is enhanced 54 times (relative to free ligand, Table 1) when fully complexed with caesium at *ca.* 2×10^{-5} M concentration of caesium ion. This is the most dramatic emission response upon caesium ion complexation of any caesium optical sensors reported to date. In comparison, the fluorescence of **2**, 1,3-alternate calix[4](9-cyano-10-anthrylme-



Scheme 1 The structures of **1** and **2**.

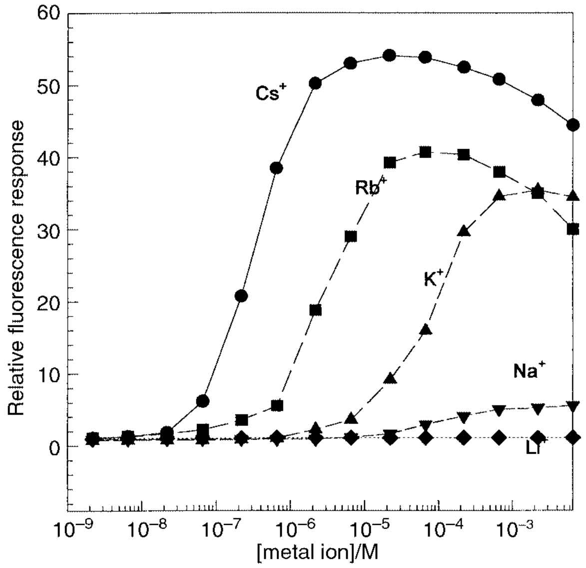


Fig. 1 Changes in the emission intensity of **1** (1×10^{-6} M) in CH_2Cl_2–MeOH (1 : 1) upon addition of alkali metal ions (as acetate salts), λ_{ex} = 376 nm. Each data point represents the integrated total area under the emission curve (λ_{em} = 400–600 nm).

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Table 1 Maximum fluorescence quantum yields and the complexation constants for both **1** and **2** in the presence of different alkali metal ions[a]

	Free	Li^+	Na^+	K^+	Rb^+	Cs^+
Φ_{em-max} of **1**	0.012	0.014	0.068	0.405	0.491	0.625
Φ_{em-max} of **2**	0.010	0.010	0.036	0.044	0.061	0.082
log (*K*) of **1**	—	—	—	4.06	5.48	6.60
log (*K*) of **2**	—	—	2.60	5.50	6.96	7.08

[a] [**1**], [**2**] = 1×10^{-6} M in CH_2Cl_2–MeOH (1:1, v/v). Metal ion concentrations: [Cs^+] = 2×10^{-5} M, [Rb^+] = 4×10^{-5} M, [K^+] = 1×10^{-3} M, [Na^+] = 1×10^{-2} M, [Li^+] = 0.1 M.

thyl)benzocrown-6, with the same fluorophore but based on a slightly different calix[4]arene platform, showed only 8.2-fold enhancement when fully complexed with caesium (Table 1). The dramatic fluorescence increase of **1** compared to **2** could be attributed to changes in the binding cavity of **1** (*vida supra*). Although Rb^+ and K^+ complexation cause the fluorescence of **1** to increase (42.6- and 35.2-fold, respectively), their maximum responses occur at higher concentrations (6×10^{-5} M and 2×10^{-3} M, respectively), indicating that their association constants with **1** are much weaker than that of caesium. Na^+ and Li^+ ions show little effect on the fluorescence of **1**, suggesting a weak interaction (complexation) between these ions and **1**.

The 1:1 complexation constant can be calculated from the emission intensity and concentration of metal ion, [M], profile shown in Fig. 1 according to eqn. (1)[7]

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

where I is the emission response of the probe at certain metal ion concentration, I_0 is the emission response of the probe in the absence of metal ions, I_∞ is the emission response when no further changes occur upon addition of the metal ion, $[\mathrm{L}]_t$ is the total concentration of probe molecule (**1** or **2**) and $[\mathrm{M}]_t$ represents the total metal ion concentration. The complexation constants K reported in Table 1 were calculated using a non-linear curve-fitting method[9] to fit the observed experimental emission data.

The complexation constant of **1** with caesium (4.0×10^6 M^{-1}) is about one-third of the value obtained for **2** (1.2×10^7 M^{-1}). On the other hand, the emission enhancement for **1** is about 7 times higher than that of **2**. The more sensitive response of **1** to caesium complexation suggests a stronger interaction between the caesium cation and the ether oxygens of the benzo group in **1**. This in turn results in a greater charge dispersion onto the oxygen of the crowns and subsequently stronger interaction between caesium and the benzo moiety. Experimental support substantiating the above argument has been provided by X-ray crystallography data.[10] Crystallographic results for a closely related series of compounds show that the average Cs–O (benzo oxygen) distance of an analog to **1** is 0.15 Å shorter than the average bond length in an analog to **2**.[10]

The complexation constants of **1** with Rb^+ (3.0×10^5 M^{-1}) and K^+ (1.2×10^4 M^{-1}) are significantly lower than those of **2** (Rb^+: 9.1×10^6 M^{-1}, K^+: 3.2×10^5 M^{-1}), resulting in the selectivity ratios of K_{Cs}/K_{Rb} = 13.2 and K_{Cs}/K_K = 347. These selectivities are *ca.* 10-fold higher than those calculated for **2** (K_{Cs}/K_{Rb} = 1.3 and K_{Cs}/K_K = 38) and other 1,3-alternate calix[4]benzocrown-6 derivatives reported previously.[3,4] Such observation clearly highlights the remarkable sensitivity of **1** as a caesium selective sensor for low Cs^+ concentrations.

We also measured the change in emission behavior of **1** with caesium in MeOH and observed only a 6.5-fold enhancement. In addition, the complexation constants of **1** with caesium and potassium were much smaller in MeOH than in CH_2Cl_2–MeOH (1:1) (8.6×10^5 M^{-1} and 3.0×10^3 M^{-1}, respectively). This could indicate that PET quenching is more efficient in the more polar MeOH environment because polarity can affect the energetics of the receptor (crown moiety) relative to that of fluorophore (to enhance PET effect) and/or MeOH can complex with the receptor competing with caesium for binding.[11] The effect of solvent polarity on the emission hehavior of **1** and previously reported probes will be published later.[3b]

In conclusion, the new di-deoxygenated calix[4]arene derived fluorescence sensor **1** shows a significantly greater emission response (fluorescence turn on) to caesium compared to **2** and the other previously reported probes and holds promise for the development of a highly selective caesium detection and monitoring system.

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