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We have synthesized 1,3-alternate di-deoxygenated calix[4](9-cyano-10-anthryl)methylbenzocrown-6, 1 and 1,3-alternate calix[4](9-cyano-10-anthryl)methylbenzocrown-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\textsubscript{Cs}/K\textsubscript{K} and K\textsubscript{Cs}/K\textsubscript{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 137Cs, 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 ethers bearing cyanoanthracene fluorophores exhibit 8–12 fold fluorescence enhancement in the presence of caesium ion. The K\textsubscript{Cs}/K\textsubscript{K} and K\textsubscript{Cs}/K\textsubscript{Rb} ratios of 13 and 1.3, 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 reported5 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-anthryl)methylbenzocrown-6, 1 was synthesized from di-dehydroxylated calix[4]arene and 1,2-bis(5-iodo-3-oxa-1-pentyl-oxy)-4-(10-cyano-9-anthryl)methylbenzene 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.5,7

The emission behavior of 1 (1 × 10\textsuperscript{-6} M) in CH\textsubscript{2}Cl\textsubscript{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\textsuperscript{−7} M where no other alkali metal ion shows any response (except for Rb\textsuperscript{+} 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-diphenylnanthracene in MeOH, \(\Phi_t = 0.94\).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\textsuperscript{−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-anthryl)-
The dramatic fluorescence increase of I compared to 2 could be attributed to changes in the binding cavity of I (vida supra). Although Rb+ and K+ complexation cause the fluorescence of I to increase (42.6- and 35.2-fold, respectively), their maximum selectivities are 3,4 such calix[4]benzocrown-6 derivatives reported previously. 3,4 Such observation clearly highlights the remarkable sensitivity of I as a caesium selective sensor for low Cs+ concentrations.

We also measured the change in emission behavior of I with caesium in MeOH and observed only a 6.5-fold enhancement. In addition, the complexation constants of I with potassium and potassium were much smaller in MeOH than in CH2Cl2–MeOH (1:1) (8.6 \times 10^3 M\(^{-1}\) and 3.0 \times 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. The effect of solvent polarity on the emission behavior of I and previously reported probes will be published later. 10

In conclusion, the new di-deoxygenated calix[4]arene derived fluorescence sensor I 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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Notes and references
10 J. C. Bryan, unpublished results.
11 We thank the reviewers for bringing this point to our attention.