Calix[4]arene-based Cs^+ selective optical sensor

Hai-Feng Ji, Gilbert M. Brown and Reza Dabestani*

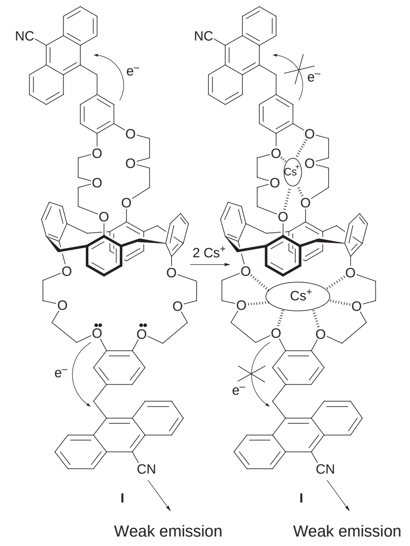
Chemical and Analytical Sciences Division, Oak Ridge National Labotatory, PO Box 2008, MS-6100, Oak Ridge, TN 37831-6100, USA.E-mail: dabestanir@ornl.gov

Received (in Columbia, MO, USA) 4th November 1998, Accepted 15th February 1999

1,3-Calix[4]bis(9-cyano-10-anthrylmethyl)-*o*-benzocrown-6 has been synthesized as a first generation caesium selective fluorescent probe, and its emission behavior in the presence of Li^+, Na^+, K^+ and Cs^+ ions has been examined.

The chemistry of calix[4]arenes, cyclic tetramers comprising phenolic and methylene moieties, has received considerable attention in recent years.[1,2] The available sites on these macrocyclic compounds that can be easily modified to tailor them for application as ionophores in catalysis,[3] and in heavy metal absorption,[4] alkali metal complexation[2] and chemical sensors[5,6] have been examined. Calix-crown compounds show high affinity for complexation of alkali and alkaline-earth metal ions.[2,7,8] Furthermore, it has been shown that derivatives of the 1,3-alternate calix[4]crown-6 ethers exhibit high selectivity towards Cs^+ ions in both acidic and alkaline media[9–12] with distribution coefficient ratios for Cs^+/Na^+ and Cs^+/K^+ exceeding 10^4 and 10^2 respectively, based on a solvent extraction technique.[12] Self-assembled ionophores with high cation selectivity for Cs^+ ions have also been reported.[13] We have taken advantage of the high selectivity of calix[4]crown ethers to synthesize a molecular recognition agent with high specificity for Cs^+ ion complexation in the presence of other alkali metal ions using the concept of fluorescence turn-on as a platform for its detection. Crown ethers have been proposed as potential extractants for the removal of Cs from nuclear waste solutions by solvent extraction.[14] ^{137}Cs produced during the nuclear era comprises a significant fraction of the radiological materials stored in the Department of Energy's (DOE) tank waste. A recent finding[15] suggests that leakage of nuclear material (^{137}Cs in particular) into the environment from the storage tanks at Hanford sites is far greater than previously estimated. Consequently, there is considerable interest within DOE to develop a caesium selective sensor that can be utilized to perform *in situ* determination of caesium in these tanks. However, to the best of our knowledge, current technologies do not provide a chemical method for *in situ* determination of Cs^+ ion concentration in nuclear waste solutions. We have undertaken this study as part of an effort to develop a technique for such determinations.

The fluorophore reporter molecule, 9-cyanoanthracene (9CA), was covalently attached to the parent molecule 1,3-alternate conformer of calix[4]bis-*o*-benzocrown-6 to prepare a molecular recognition agent that can serve as an optical sensor. The presence of caesium ions is signaled by an increase in the emission of the 9CA group upon complexation. In the absence of caesium ions, fluorescence is partially quenched by photo-induced electron transfer (PET) from the dialkoxybenzene moiety of the crown ring to the excited singlet state of 9CA.[16,17] Upon complexation, the oxygen lone pairs will no longer participlate in PET, causing the emission of 9CA to increase.



Scheme 1

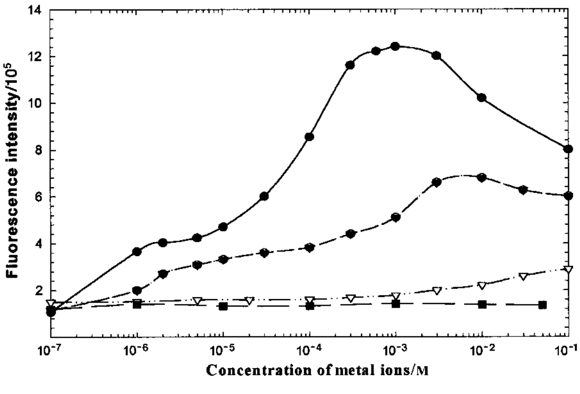


Fig. 1 Changes in the emission spectra (λ_{ex} = 320 nm) of **I** (10^{-6} M) in aerated CH_2Cl_2–MeOH (1 : 1) upon addition of alkali metal ions (acetate solution): (■) Li^+, (▽) Na^+, (▼) K^+ and (●) Cs^+.

Compound **I** 1,3-calix[4]bis(9-cyano-10-anthrylmethyl)-*o*-benzocrown-6 (Scheme 1) was synthesized[18] as the first generation of caesium selective fluorescent probes. We have examined the emission behavior of **I** in the presence of the alkali metal ions Li^+, Na^+, K^+ and Cs^+ to evaluate its selectivity. The emission of **I** in CH_2CL_2–MEOH mixture (1 : 1) is only slightly affected by the presence of either Li^+ or Na^+ ions at concentrations as high as 0.1 M (Fig. 1), ruling out the possibility of strong complexation of these ions by **I**. In the presence of K^+ ions, the emission of **I** shows a slight enhancement up to a concentration of about 0.01 M, indicating some complexation of K^+ ions by **I** (Fig. 1). At higher concentrations of K^+ ions, the emission of **I** experiences a gradual decrease. The most dramatic change in the emission of **I** is observed in the presence of Cs^+ ions. As the concentration of Cs^+ ions increases, the emission of **I** increases, reaching its maximum value at a concentration of Cs^+ ions of *ca.* 10^{-3} M (Fig. 1). The observation of two plateau regions at 10^{-6} and 2×10^{-4} M Cs^+ (Fig. 1) implies that there are two sites for complexation. To the best of our knowledge, this is the first spectroscopic observation of a stepwise complexation process showing two plateau regions. The gradual quenching of the emission from **I** observed at high concentrations of K^+ and Cs^+ (Fig. 1) may be attributable to a medium effect caused by changes in the ionic strength of the solution. The magnitude of this effect is less pronounced in the presence of Li^+ and Na^+ ions because the emission of **I** does not change significantly.

The stability constant for **I** can be estimated from the change in its fluorescence as the concentration of metal ion changes. Since **I** possesses two sites that can form a complex with Cs^+ ions (Scheme 1), eqn. (1) may be used to obtain the stability constant for complexation,[19,20] where α and χ are constants, K_{11} and K_{12} are association constants for the first and second metal ion complexation, I_o is the fluorescence intensity in the absence of metal ion, I_∞ is the intensity when no further change in fluorescence is observed upon addition of metal ion, and I is the intensity at different metal ion concentrations.

$$\frac{I - I_0}{I - I_\infty} = K_{11}[\mathrm{M}]\frac{\alpha + K_{12}\chi[\mathrm{M}]}{K_{11}[\mathrm{M}](\alpha - \chi) - \chi} \qquad (1)$$

Computational fitting of the experimental fluorescence data to eqn. (1) for both K^+ and Cs^+ allows determination of parameters α, χ, K_{11} and K_{12}. Table 1 shows the values of these parameters obtained from such fits for both K^+ and Cs^+. The association constants K_{11} and K_{12} determined by us (Table 1) suggest 1 : 2 stoichiometry for calix[4]arene: K^+ (or Cs^+) and are in good agreement with the reported values for other systems that accommodate two metal ions at the complexing sites.[21] The fact that the ratio of $(K_{11}K_{12})_{Cs^+}/(K_{11}K_{12})_{K^+} = 277$ agrees reasonably well with the reported value of ~160 (for 1,2-dichloroethane) obtained *via* solvent extraction techniques[12] suggests that fluorescence spectroscopy can be used as a method to obtain the association constants for metal ion complexation. The reported quantum yields of fluorescence for **I** in the presence of different alkali metal ions shown in Table 1 are relative to 9,10-diphenylanthracene, which has $\Phi_f = 1$.[22]

Fig. 2 shows the change in fluorescence intensity profile for **I** as a function of the concentration of Cs^+ ions. The experiment was carried out *in situ* by combining equal volumes of an aqueous solution of $CsNO_3$ and a fixed concentration of **I** in CH_2Cl_2 in a quartz cell. After vigorous shaking, the two layers were allowed to separate and the fluorescence of the organic layers was obtained. The most dramatic increase in fluorescence intensity is observed over the range 10^{-3}–10^{-1} M $CsNO_3$ (Fig. 2). When the $CsNO_3$ solutions are doped with 1 M $NaNO_3$ and then added to **I** in CH_2Cl_2, the fluorescence intensity increases rapidly and then plateaus at $[Cs^+] > 1 \times 10^{-2}$ M. This rapid initial increase can be attributed to a common anion effect exerted by the presence of excess NO_3^- ions that enhances the complexation of caesium ions at low concentrations.

In conclusion, we have synthesized the first generation of caesium selective fluorescent turn-on probes based on calix[4]arene that can host two such ions upon complexation. Although the sensitivity of our probe is not as dramatic as we had hoped for practical application, we are currently exploring various ways to improve it by manipulating the parameters that have a pronounced effect on sensitivity. Along these lines, we are also examining other potential fluorophores that may induce a much stronger response upon complexation of Cs^+ ions.

This research was funded by the Environmental Management Science Program, Office of Environmental Management, U.S. Department of Energy. Oak Ridge National Laboratory is operated by Lockheed Martin Energy Research Corporation for the U.S. Department of Energy under contract number DE-AC05-96OR22464.

Table 1 Fluorescence quantum yields and association constants K_{11} and K_{12} values calculated for **I** in the presence of different alkali metal ions

Metal ion	Φ_{max}	$K_{11}{}^a/\mathrm{M}^{-1}$	$K_{12}{}^a/\mathrm{M}^{-1}$	α	χ
None	0.0082	—	—	—	—
Li^+	0.012	—	—	—	—
Na^+	0.016	—	—	—	—
K^+	0.049	6.0×10^5	5.0×10^2	1.0	2.9
Cs^+	0.096	8.3×10^6	1.0×10^4	1.0	4.5

[a] Metal ion concentration range was 10^{-7} to 2×10^{-3} M for K^+ and 10^{-7} to 1×10^{-3} M for Cs^+, respectively.

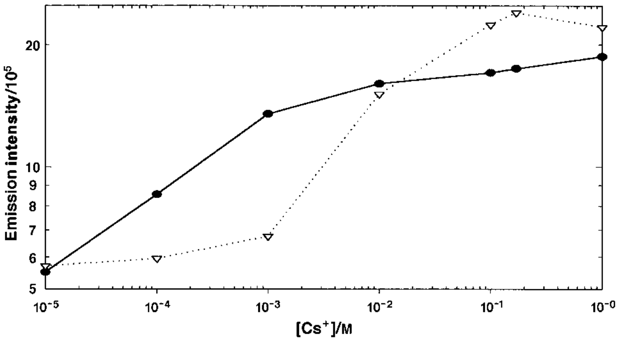


Fig. 2 Changes in the emission intensity of **I** in aerated CH_2Cl_2 as a function of Cs^+ ion concentration. Aqueous solutions of $CsNO_3$ were added to **I** in CH_2Cl_2 and after vigorous shaking the emission of the organic layer was obtained ($\lambda_{ex} = 320$ nm): (▽) without $NaNO_3$ and (●) with 1 M $NaNO_3$.

Notes and references

1 V. Bohmer, *Angew Chem., Int. Ed. Engl.*, 1995, **34**, 713.

2 C. D. Gutsche, *Calixarenes*, RSC Monographs in Supramolecular Chemistry No. 1, Royal Society of Chemistry, Cambridge, UK, 1989.

3 S. Shinkai, S. Mori, H. Koreishi, T. Tsubaki and O. Manabe, *J. Am. Chem,. Soc.*, 1986, **108**, 2409.

4 S. Shinkai, H. Koreishi, K. Ueda, T. Arimura and O. Manabe, *J. Am. Chem. Soc.*, 1987, **109**, 6371.

5 R. J. Foster, A. Cadogan, M. T. Diaz and D. Diamond, *Sens. Actuators, B*, 1991, **4**, 325.

6 J. S. Kim, I. Y. Yu, J. H. Pang, J. K. Kim, Y-Ill. Lee, K. W. Lee and Y. Z. Oh, *Microchem. J.*, 1998, **58**, 225; J. S. Kim, I. H. Suh, J. K. Kim and M. H. Cho, *J. Chem. Soc., Perkin Trans. 1*, 1998, 2307.

7 C. Asfieri, E. Dradi, A. Pochina, R. Ungaro and G. D. Andreetti, *J. Chem. Soc., Chem. Commun.*, 1983, 1075.

8 D. N. Reinhoudt, J. F. Engbersen, Z. Brozozka, H. H. Van den Viekkert, G. W. Honig, A. J. Holterman and U. H. Verkerk, *Anal. Chem.*, 1994, **66**, 3618.

9 Z. Asfari, C. Bressot, J. Vicens, C. Hill, J.-F. Rozol, H. Rouquette, S. Eymard, V. Lamare and B. Tourmois, *Anal. Chem.*, 1995, **67**, 3133; F. Arnaud-Neu, Z. Asfari, B. Souley and J. Vicens, *New. J. Chem.*, 1996, **20**, 453.

10 R. Ungaro, A. Casnati, F. Ugozzoli, A. Pochini, J.-F. Dozol, C. Hill and H. Rouquette, *Angew. Chem., Int. Ed. Engl.*, 1994, **33**, 1506; A. Casnati, A. Pochini, R. Ungaro, F. Ugozzoli, F. Arnaud-neu, S. Fanni, M.-J. Schwing, R. J. M. Egberink, F. deJong and D. N. Reinhoudt, *J. Am. Chem. Soc.*, 1995, **117**, 2767; I. M. Rudkevich, J. D. Mercer-Chalmers, W. Verboom, R. Ungaro, F. deJong and D. N. Reinhoudt, *J. Am. Chem. Soc.*, 1995, **117**, 6124.

11 W. J. McDowell, G. N. Case, J. A. McDonough and R. A. Bartsh, *Anal. Chem.*, 1992, **64**, 3013.

12 T. J. Haverlock, P. V. Bonnesen, R. A. Sachleben and B. A. Moyer, *Radiochim. Acta*, 1997, **76**, 103.

13 J. T. Davis, S. K. Tirumala and A. L. Marlow, *J. Am. Chem. Soc.*, 1997, 119, 5271.

14 I. H. Gerow and M. V. Davis, *Sep. Sci. Technol.*, 1979, **14**, 395; I. H., Gerow, J. E. Smith and M. V. Davis, *Sep. Sci. Technol.*, 1981, **16**, 519; E. Blasius and K.-H. Nilles, *Radiochim. Acta*, 1984, **35**, 173; W. W. Schultz and L. A. Bray, *Sep. Sci. Technol.*, 1987, *22*, 191; J.-F. Dozol, in *New Separation Chemistry Techniques for Radioactive Waste and Other Applications*, ed. L. Cecille, M. Casarci and L. Pietrelli, Elsevier, Amsterdam, 1991, pp. 163–172.

15 *Chem. Eng. News*, 1998, **76**, No. 37, 25.

16 R. A. Bissell, A. P. de Silva, H. Q. N. Guanratne, P. L. M. Lynch, G. E. M. Maguire, C. McCoy and K. R. A. S. Sandanayake, *Top. Curr. Chem.*, Springer-Verlag, Berlin, Heidelberg, 1993, vol. 168, pp. 223–264.

17 A. P. de Silva and K. R. A. S. Sandanayake, *J. Chem. Soc., Chem. Commun.* 1989, 1183.

18 Compound **I** was prepared according to a procedure described earlier (ref. 9) with slight modifications in reagents and reaction time. A full account of this procedure will be published later.

19 D. Marquis and J.-P. Desvergne, *Chem. Phys. Lett.*, 1994, **230**, 131.

20 D. Marquis, J.-P. Desvergne and H. Bouas-Laurent, *J. Org. Chem.*, 1995, **60**, 7984.

21 A. D'Aprano, J. Vicens, Z. Asfari, M. Salomon and M. Iammarino, *J. Solution Chem.*, 1996, **25**, 955.

22 A. Maciejewski and R. P. Steer, *J. Photochem.*, 1986, **35**, 59.

Communication 8/08636B