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 Laboratory, PO Box 2008, MS-6100, Oak Ridge, TN 37831-6100, USA. E-mail: dabestaniir@ornl.gov

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

1,3-Calix[4][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. The available sites on these macrocyclic compounds that can be easily modified to tailor them for application as ionophores in catalysis, and in heavy metal sorption, alkali metal complexation and chemical sensors have been examined. Calix-crown compounds show high affinity for complexation of alkali and alkaline-earth metal ions. Furthermore, it has been shown that derivatives of the 1,3-alternate calix[4]crown ethers exhibit high selectivity towards Cs⁺ ions in both acidic and alkaline media with distribution coefficient ratios for Cs⁺/Na⁺ and Cs⁺/K⁺ exceeding 10⁴ and 10² respectively, based on a solvent extraction technique. Self-assembled ionophores with high cation selectivity for Cs⁺ ions have also been reported. We have taken advantage of the high selectivity of calix[4]crown ethers to synthesize a molecular recognition agent capable of detecting Cs⁺ ions in the presence of other alkali metal ions using the concept of fluorescence turn-on as a platform for its application. Crown ethers have been proposed as potential extractants for the removal of Cs from nuclear waste solutions by solvent extraction.

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

Compound I (Scheme 1) was synthesized as the first generation of calix[4]arene 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 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. 10⁻² 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 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. 10⁻² 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 the

![Fig. 1 Changes in the emission spectra (λex = 320 nm) of I (10⁻⁶ M) in aerated CH₂Cl₂-MeOH (1:1:1) upon addition of alkali metal ions (acetate solution): (M) Li⁺, (V) Na⁺, (V) K⁺ and (M) Cs⁺.](image-url)
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 decrease 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, \( K_{11} \) and \( K_{12} \) are association constants for the first and second metal ion complexation, \( I \), 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.

\[
\frac{I - I_0}{I} = K_{11}[\text{M}] + K_{12}[\text{M}]
\]

(1)

Computational fitting of the experimental fluorescence data to eqn. (1) for both K+ and Cs+ allows determination of parameters \( \alpha \), \( \chi \), \( K_{11} \), 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. The initial increase can be attributed to a common anion effect because the emission of CsNO3 solutions is doped with 1 \( \mu \)M NaNO3 and then allowed to separate and the fluorescence of the organic layer was measured over the range 10 \(^{-3} \) to 1 \( \mu \)M CsNO3 (Fig. 2). When the CsNO3 solutions are doped with 1 \( \mu \)M NaNO3 and then allowed to separate, the fluorescence intensity is observed over the range 10 \(^{-3} \) to 1 \( \mu \)M CsNO3 (Fig. 2). When the CsNO3 solutions are doped with 1 \( \mu \)M NaNO3 and then allowed to separate, the fluorescence intensity is observed over the range 10 \(^{-3} \) to 1 \( \mu \)M CsNO3 (Fig. 2).

![Fig. 2 Changes in the emission intensity of I in aerated CH2Cl2 as a function of Cs+ ion concentration. Aqueous solutions of CsNO3 were added to I in CH2Cl2 and after vigorous shaking the emission of the organic layer was obtained (\( \lambda_{ex} = 320 \text{ nm} \)) (7) without NaN03 and (8) with 1 \( \mu \)M NaN03.](image)

### Notes and references
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.

### 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

<table>
<thead>
<tr>
<th>Metal ion</th>
<th>( \Phi_{\text{max}} )</th>
<th>( K_{11} \cdot \text{m}^{-1} )</th>
<th>( K_{12} \cdot \text{m}^{-1} )</th>
<th>( \alpha )</th>
<th>( \chi )</th>
</tr>
</thead>
<tbody>
<tr>
<td>None</td>
<td>0.0082</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Li+</td>
<td>0.012</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Na+</td>
<td>0.016</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>K+</td>
<td>0.049</td>
<td>( 6.0 \times 10^{3} )</td>
<td>( 5.0 \times 10^{3} )</td>
<td>1.0</td>
<td>2.9</td>
</tr>
<tr>
<td>Cs+</td>
<td>0.0966</td>
<td>( 8.3 \times 10^{3} )</td>
<td>( 1.0 \times 10^{3} )</td>
<td>1.0</td>
<td>4.5</td>
</tr>
</tbody>
</table>

* Metal ion concentration range was 10\(^{-7} \) to 2 \( \times 10^{-3} \) m for K+ and 10\(^{-7} \) to 1 \( \times 10^{-3} \) m for Cs+, respectively.