

Project ID: **60217**

Project Title: **Optically-Based Array Sensors for Selective In Situ Analysis of Tank Waste**

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## RESEARCH OBJECTIVE

The objective of this research program is to conduct the fundamental research necessary to develop an array of chemically selective sensors, based on highly selective molecular recognition agents and highly sensitive fluorescence and/or phosphorescence techniques, that can be coupled to fiber optics for remote analytical applications. These sensors will be of great value to DOE for the safe and cost-effective in situ characterization of high level waste tanks. Characterization of high level tank waste currently entails obtaining and analyzing core samples at the cost of about \$1 million per sample. The ability to detect and measure specific chemicals and radionuclides directly inside a high level waste tank using a remote sensing device could result in considerable benefits with regard to both cost savings and safety issues. This multidisciplinary approach to the design of sensors will be to immobilize agents for selective molecular recognition, chosen from solvent extraction processes, in an organic polymer matrix that mimics the organic medium in an aqueous-nonaqueous extraction. In this manner the matrix will enhance both the separation and the achievement of chemical selectivity.

## RESEARCH PROGRESS AND IMPLICATIONS

A great deal has been accomplished in the first 20 months of this project. The distance dependence of electron transfer quenching of a potential fluorescent probe was studied. Calix[4]bis-crown-6-ethers in the 1,3-alternate conformation have been shown to possess a high degree of selectivity for cesium over sodium and moderate selectivity for cesium over potassium. Several systems involving the preparation of a new class of calixarene-based ionophores having attached fluorescent probe molecules were demonstrated.

We have synthesized four derivatives of alkyl pyrene covalently bonded to aza-18-crown-6 at the nitrogen position,  $\text{Py}(\text{CH}_2)_n$ , ( $n = 1-4$ ), to study the effect of spacer length on the emission properties of pyrene fluorophore upon complexation of alkali metal ions by the crown moiety. In the absence of alkali metal ions, the parent molecule is weakly fluorescent because its emission is partially quenched by photoinduced electron transfer (PET) from nitrogen lone pairs to the excited singlet state of pyrene. Complexation of alkali metal ions (e.g.  $\text{K}^+$ ) by the crown moiety prevents nitrogen lone pair from participating in PET and results in an enhancement in the observed emission from pyrene (fluorescent turn on). Since PET effect could be exerted through bond as well as space, its magnitude may show a dependence on chain length. We have examined the fluorescence behavior of these pyrene aza crown ether derivatives in the presence of alkali metal ions to determine the magnitude of such effect and its impact on the sensitivity of the fluorescent probe for detection purposes. Our results indicate that maximum efficiency for PET between pyrene moiety and aza crown ether is achieved when  $n \leq 3$ .

1,3-calix[4]bis-(9-cyano-10-anthrylmethyl)-o-benzocrown-6, (**I**), was synthesized as the first generation of cesium selective fluorescent probe operating by Photoinduced Electron Transfer (PET) mechanism. We have examined the emission behavior of **I** in the presence of the alkali metal ions lithium, sodium, potassium, and cesium to evaluate its selectivity.

The emission of **I** in a CH<sub>2</sub>Cl<sub>2</sub>:MeOH mixture (1:1) is only slightly affected by the presence of either Li<sup>+</sup> or Na<sup>+</sup> ions at concentrations as high as 0.1 M ruling out the possibility of strong complexation of these ions by **I**. In the presence of K<sup>+</sup> ions, the emission of **I** experiences a slight enhancement. The most dramatic change in the emission of **I** is observed in the presence of Cs<sup>+</sup> ions (11.7 fold increase in the emission). The association constants K<sub>11</sub> and K<sub>12</sub> (for the first and second metal ion complexation) determined from fluorescence data suggest 1:2 stoichiometry for **I** : Cs<sup>+</sup> in good agreement with the reported values for other systems that accommodate two metal ions at the complexing sites.

Two derivatives of alkylanthracene covalently bonded to 1,3-alternate calix[4]-diazacrown-6 at the nitrogen position were synthesized as the second class of cesium selective fluorescent probes to study the effect of alkali metal ion complexation on the emission properties of reporter fluorophore anthracene. The main difference between the newly synthesized probes and the one mentioned above is in the composition of crown moiety that contains two nitrogen atom in its ring bearing the fluorophore reporters. Furthermore, the mono and diaza crown-6 probes bear only one crown ring in their core and can host only one cesium ion compared to two crown rings that could host two cesium ions in 1,3-calix[4]bis-(9-cyano-10-anthrylmethyl)-o-benzocrown-6. Besides good sensitivity (8.5 and 11.5 fold increase in the emission intensity of mono and diaza crown-6 upon cesium complexation, respectively), both probes exhibit much better tolerance for potassium ion interference without compromising their sensitivity for cesium ion detection. These attractive features of mono and diaza crown-6 fluorescent probes render them more effective for the detection of cesium ions in the presence of interfering potassium ions.

## PLANNED ACTIVITIES

Research will continue in an effort to find a more sensitive PET-based fluorescent turn-on indicators of alkali metal ion complexation. We will begin evaluation of the polymeric organic matrix that will be used to attach the ionophores to the fiber optic including the necessity of adding modifiers. The objective is to maximize both selectivity and loading as a function of matrix variation. After metal ion binding has been characterized in solution, studies will begin with the materials embedded in the optimized polymeric matrix. At this stage pattern recognition analysis of the response to complex solutions will begin using an array of selective ligands attached to an imaging fiber optic bundle. If appropriate, different modifiers/polymers will be utilized for different selectivities/loading. If the research proceeds as expected, the goal is to test an imaging fiber with an array of sensor sites selective for Cs, Na, and K.

## INFORMATION ACCESS

### Presentations:

Hai-Feng Ji, R.Dabestani, and G.M.Brown, "Fluorescence Probes for the Detection of Potassium Ions," presented at the American Chemical Society National Meeting, Boston, MA, August 1998.

Publications:

Hai-Feng Ji, Gilbert M. Brown and Reza Dabestani “Calix[4]arene-based Cs<sup>+</sup> selective optical sensor” *Chem. Comm.* 609, **1999**.

Hai-Feng Ji, Reza Dabestani, Gilbert M. Brown and Robert L. Hettich “Spacer Length Effect on the Photoinduced Electron Transfer Fluorescent Probe for Alkali Metal Ions” *Photochem. Photobiol.* 69, 513, **1999**.

Hai-Feng Ji, Reza Dabestani and Gilbert M. Brown “Optical Sensing of Cesium Ions Using 1,3-Alternate Calix[4]-mono and di(Anthrylmethyl)Aza-Crown-6” *Chem. Comm.* **1999**, submitted.