

## **Optical and Microcantilever-Based Sensors for Real-Time In Situ Characterization of High-Level Waste (81924)**

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### **Research Objective**

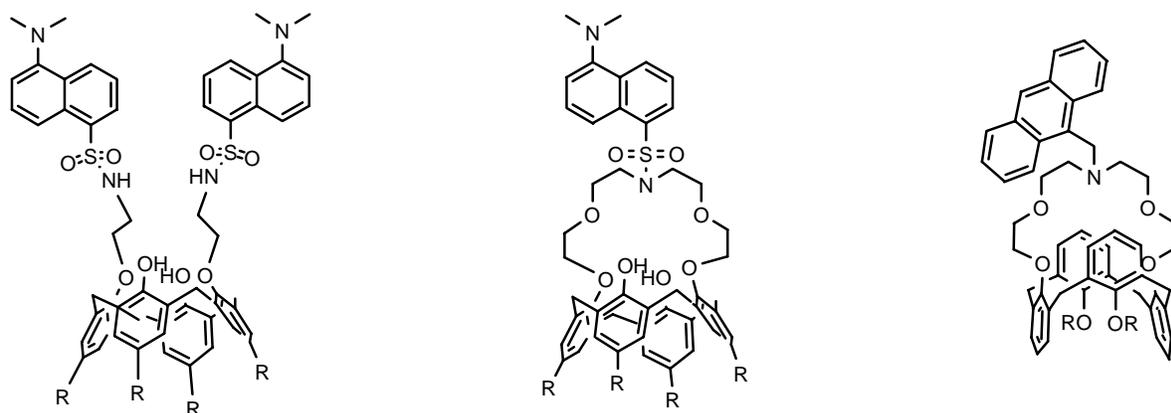
Fundamental research is being conducted to develop sensors for cesium, strontium, and pertechnetate that can be used to analyze these species in high-level waste (HLW) process streams. Sensors for these species will be combined with sensor elements for OH<sup>-</sup>, K<sup>+</sup>, and Na<sup>+</sup> in an array that will allow interferences to be corrected. Two fundamentally different approaches are being pursued, having in common the dependence on highly selective molecular recognition agents. In one approach, an array of chemically selective sensors with sensitive fluorescent probes to signal the presence of the constituent of interest will be coupled to fiber optics for remote analytical applications. The second approach employs sensitive microcantilever sensors that have been demonstrated to have unprecedented sensitivity in solution. Selectivity in microcantilever-based sensors is achieved by modifying the surface of a gold-coated cantilever with a monolayer coating of an alkanethiol derivative of the molecular recognition agent. The microcantilever-based sensors function by converting molecular complexation into surface stress. The fundamental technology for fiber optic and cantilever sensors has been developed by our collaborators David Walt and Thomas Thundat, respectively, and the goal of this project is to adapt molecular recognition chemistry to the methods already being employed. Molecular recognition with these sensors is achieved using ionophores constructed with the three-dimensional architecture provided by calix[4]arenes, a widely used platform for metal ion complexation.

### **Research Progress and Implications**

This report summarizes the research as of June, 2004, following 33 months of research in a three year project. Specific goals in this program are to develop selective complexation agents for Cs(I) and Sr(II) based on calixarene crown ether chemistry that can be adapted to fluorescence sensors and microcantilever sensors. Our approach to the design of sensors will be to immobilize agents for selective molecular recognition in a matrix that mimics the organic medium in an aqueous-nonaqueous extraction. In this manner, the matrix can enhance both the separation and the achievement of chemical selectivity. We are using previously developed Cs<sup>+</sup> selective 1,3-alt-calix[4]arene-benzocrown-6 compounds for Cs<sup>+</sup> complexation, and calix[4]arenes in the cone conformation possessing amide, ester or free carboxylic acid arms have a strong affinity to alkaline-earth cations and are being used for Sr(II) complexation. The

design of a fluorescent chemosensor based on calix[4]arene complexing agents involves attaching a fluorescent group in such a way that interactions of the metal ion will cause electronic perturbation to be transmitted to the fluorophore through electron- or charge transfer.

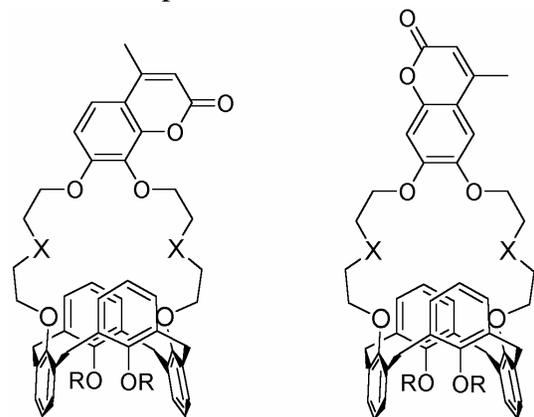
We have synthesized cyclic amidocrown calix[4]arenes and an open chain derivative having diethylamide arms for investigation as selective  $\text{Sr}^{2+}$  complexation agents, and the



R = *tert*-butyl

R = benzyl

fluorescent dansyl reporter group was utilized. The complexation and sensing properties of the dansyl crown compound was compared with unbridged calixarenes containing analogous binding moieties. The anthracene-functionalized calix[4]arene-azacrown-5 derivative senses changes by the fluorescence PET (photoinduced electron transfer) principle in which the fluorescence of the free ligand is quenched by electron transfer of the free nitrogen electron pair to the fluorophore. Upon complexation, the nitrogen lone pair no longer participates in PET causing chelation enhanced fluorescence. The results we have obtained with our optical  $\text{Cs}^+$  sensor, based on the cyanoanthracene PET effect, has been disappointing because the fluorescence enhancement is quite sensitive to the polarity of the environment, and this causes it to be difficult to translate solution results to an organic film. We chose to incorporate a coumarin derivative as the fluorophore. The coumarin plays the role of a transducer by translating the energy change due to complexation of the metal inside the cavity into a measurable quenching of the fluorescence. Use of coumarin derivatives as the fluorophores changes the sensing mechanism to cation-controlled photoinduced internal charge transfer (PCT-sensor). The azacrown derivatives proved to be poor complexing agents for strontium.



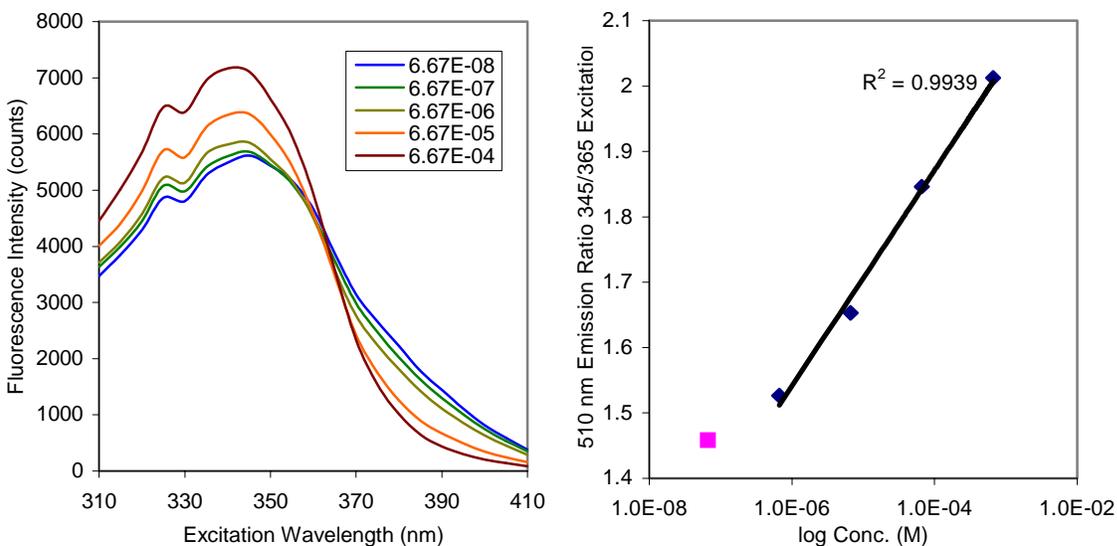
R = benzyl, propyl

R = benzyl, propyl

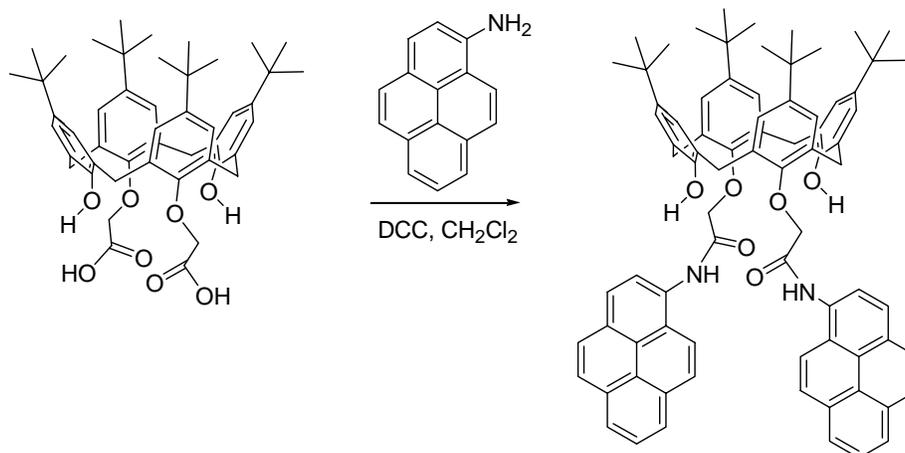
X=N,O

The determination of  $\text{Sr}^{2+}$  in the presence of  $\text{Ca}^{2+}$  and at high pH was studied using Fura-2, a  $\text{Ca}^{2+}$  sensitive ratiometric fluorescent dye produced by Molecular Probes (Eugene, OR).  $\text{Sr}^{2+}$  may be detected in the presence of  $\text{Ca}^{2+}$  and other divalent metals by performing excitation at the isosbestic point for Fura-2 upon binding with the other metal. A plot of the log of the  $\text{Sr}^{2+}$  concentration versus the ratio of fluorescence

emission at 510 nm for 345/365 excitation is linear across four orders of magnitude for aqueous  $\text{Sr}^{2+}$

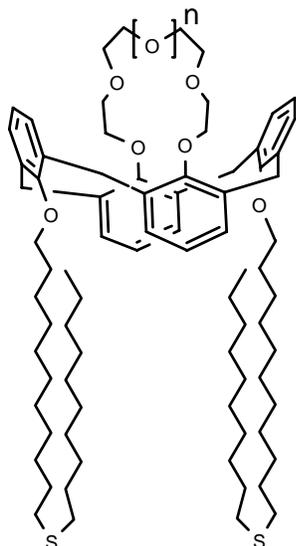


Excimer and exciplex formation and breaking is a potentially attractive signaling mechanism for metal complex formation, and we are investigating several new combinations involving pyrene, naphthalene-dimethylamine, and anthracene. Among the first we prepared is a pyrene-pyrene combination held by a calix[4]arene in the cone conformation and shown in the reaction scheme below.



In this molecule there is an exceedingly strong pyrene-pyrene interaction, and it may not be possible to weaken it in any significant way to utilize it for sensing of complexation reactions. The emission spectrum and time dependence of the emission indicate the presence of both ground state associated pyrenes and excimer formation. Other pyrene derivatives of calix[4]arene in the cone conformation were synthesized and their fluorescence spectra have

been investigated in solution. Longer hydrocarbon chains and substitution of an ether linkage for the amide linkage between the calixarene and the pyrene groups leads to weaker interactions, and these and related open chain compounds are being investigated for  $\text{Sr}^{2+}$  complexation.



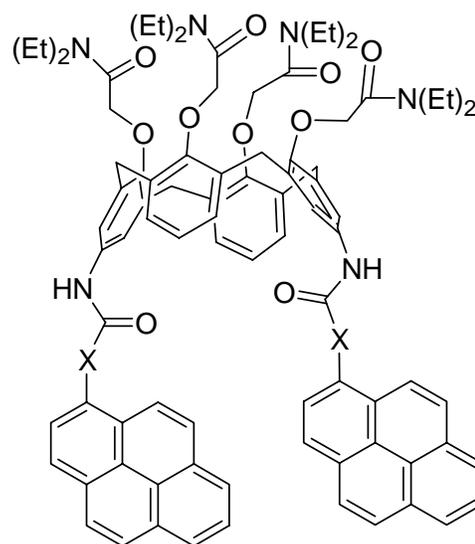
Our previous work on the development of a microcantilever sensor for cesium required the codeposition of decanethiol to function, and this codeposition of SAMs appears to be irreproducible. Thus we synthesized the dialkane thiol derivatives shown in the figure to the left and a SAM of this ligand on Au is stable for months. This ligand with  $n = 2$  is selective for  $\text{Cs}^+$ , and the cantilever shows a deflection with  $\text{Cs}^+$  concentrations as low as  $1 \times 10^{-11} \text{M}$  in pure water alone. In either 0.1 M NaCl or 0.1 M  $\text{NaNO}_3$  the cantilever is nearly reversible in a matter of less than 10 minutes. The deflection of the cantilever, due to the addition of  $10^{-5} \text{M}$   $\text{Cs}^+$ , was investigated as a function of the  $\text{NaNO}_3$  background electrolyte concentration. The magnitude of the response at 1 M  $\text{NaNO}_3$  suggests a useful sensor may be constructed using this technology.

## Planned Activities

Work in progress on some of the systems mentioned above will be completed and manuscripts will be submitted for publication in the remaining months of this project. A renewal proposal was submitted, and if it is approved one of the systems we plan to investigate is the molecules below for strontium selectivity

In our efforts to design ligand that will be signaled by excimer or exciplex formation, it seems that the free ligand (metal free) is initially in a pinched cone conformation ( $C_{2v}$ ) and it rearranges to a symmetrical cone conformation ( $C_{4v}$ ) on complexation. The amide group attached to the benzene assures that the benzene ring, nitrogen, and carbonyl group will all be in the same plane. Molecular mechanics calculations will be used to design the spacer group X, shown in the figure, to determine how far apart the pyrene groups can be for effective signaling. The change from a pinched cone to a symmetrical cone confirmation is expected to make a significant change in the degree of interaction between the pyrenes.

Work is in progress to develop coatings to make microcantilever sensors that are selective for  $\text{Sr}(\text{II})$  using compounds with an amide-ether combination that can impart selectivity. Our success with dialkanethiol derivatives will lead us to continue to make these derivatives for stable SAM coatings. Microcantilever sensors for pertechnetate should follow the same rules as ion exchange processes, and we have had previous success in designing sensors for chromate anion. We



X = different spacer

propose to investigate a series of potential monolayer forming dialkanethiol compounds having quarternary ammonium and alkylpyridinium head groups.

### **Information Access**

Gudrun Goretzki, Peter V. Bonnesen, Reza Dabestani, and Gilbert M. Brown, "Fluorophores as Chemosensors Based on Calix[4]arenes and Three Different Fluorescence Reporters," submitted for publication, Proceedings of the EMSP Symposium on Nuclear Waste Management, 226th ACS National Meeting, New York City, 2003.

Gudrun Goretzki, Gilbert M. Brown, Peter V. Bonnesen, "Fluorescent chemosensors based on calix[4]arene-crown ethers," presented at Calix 2003, 7th International Conference on Calixarenes (ICC), Vancouver, BC, Canada, August 13 – 16, 2003

Gudrun Goretzki, Peter V. Bonnesen, Gilbert M. Brown, "Fluorophores as Chemosensors for  $\text{Sr}^{2+}$  and  $\text{Cs}^+$  Based on Calix[4]arenes and Coumarin Reporter Groups," 226th ACS National Meeting, New York City, NY, September 7 – 11, 2003..

Gilbert M. Brown, Gudrun Goretzki, Peter V. Bonnesen, Reza Dabestani, Vassil Boiadjev, and Thomas Thundat, "Fluorescent and Microcantilever Sensors for Cesium and Strontium," 227<sup>th</sup> ACS National Meeting, Anaheim, CA, March 28-April 1, 2004