Optical and Microcantilever-Based Sensors for Real-Time In Situ Characterization of High-Level Waste

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Program Objective

Develop sensors for strontium that can be used in real-time to characterize high-level waste (HLW) process streams - two fundamentally different approaches

Array of chemically selective sensors with sensitive fluorescent probes to signal complexation will be coupled to fiber optics for remote analysis

Sensitive microcantilever sensors where selectivity achieved by surface modification with molecular recognition agent

Different approaches share common recognition agent

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Relevance to DOE and Research Plan

DOE desires innovative methods of achieving real-time, in situ characterization of HLW and process streams

Separation methods to remove the radioisotopes are selective for an element in a particular oxidation state, not to a single isotope. Focus on sensors for Cs^+ and Sr^{2+}

Need sensors to monitor separation process for breakthrough.

Develop real time sensor element for Sr^{2+} that can be combined with existing sensor elements for Cs^+, K^+, and Na^+ in an array

Develop complexation agent for Sr(II) based on calixarene crown ether chemistry

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Fluorescent Sensors

Cs^+ and Sr^{2+} detection based on calix[4]crown-6 ethers in the 1,3-alternate (Cs^+) and cone (Sr^{2+}) conformation with a fluorophore as the reporter group.

Incorporate the molecular probe into a matrix (e.g. polymer film)

Develop an array of chemically selective sensors to correct for interference from K^+, etc. that can be coupled to fiber optics for remote analytical applications

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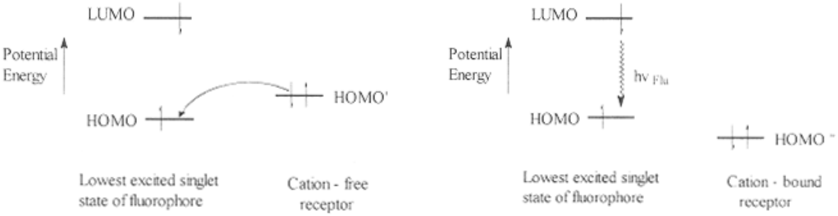
Frontier orbital energy diagram for the fluorophore -receptor pair



Cation Free **Cation Bound**

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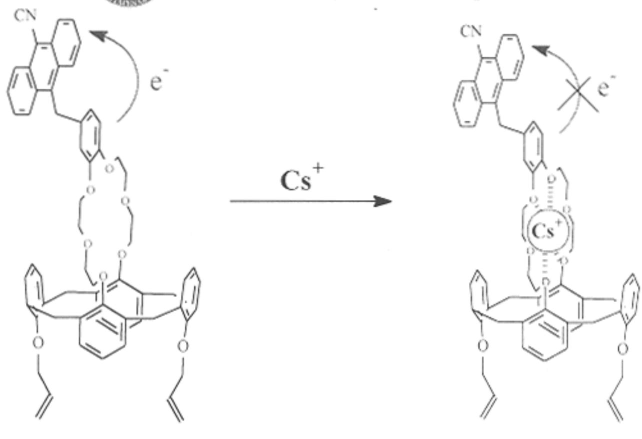
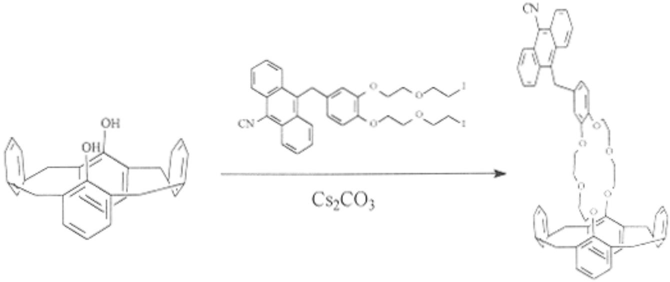


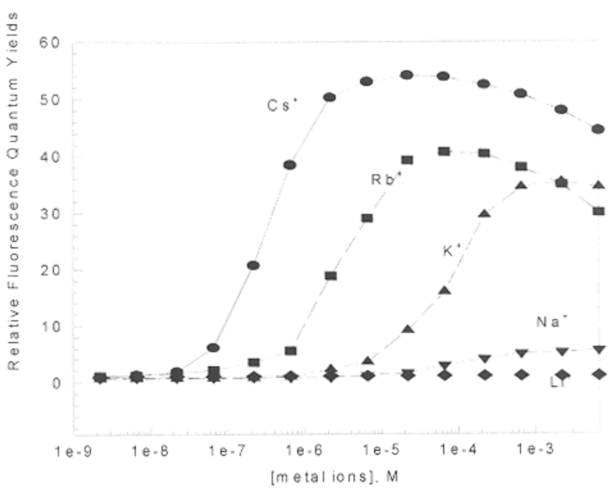
Weak Emission **Strong Emission**



Di-deoxygenated calix[4](9-cyano-10-anthrylmethyl)-benzocrown-6

Most efficient fluorescent Cs^+ selective ligand developed to date

X-ray crystallography of related systems shows shortest Cs-benzocrown-oxygen distances



Changes in the emission intensity of 1 (1×10^{-6} M) as a function of alkali metal ion concentration in aerated CH_2Cl_2:MeOH (1:1 v/v), I_{ex}= 376nm, I_{em} = 400-600 nm (integrated).

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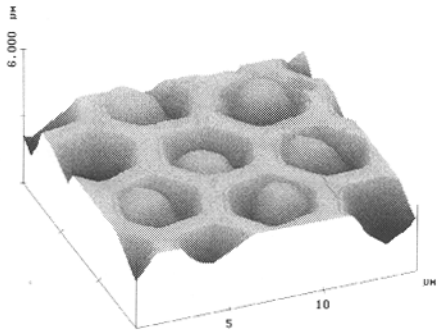

Array sensors based on microwells etched on the tip of an imaging fiber optic. Latex or silica beads can be loaded into the wells. The beads contain the molecular recognition agent

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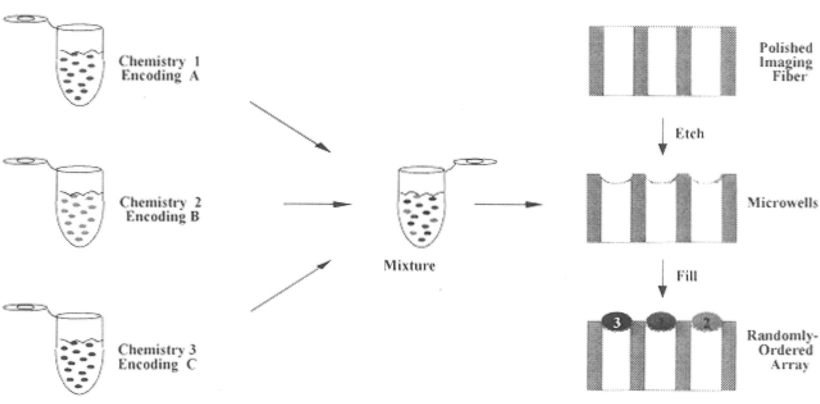

Changing the fluorescent groups allows molecular recognition agents with different selectivities to be encoded separately.

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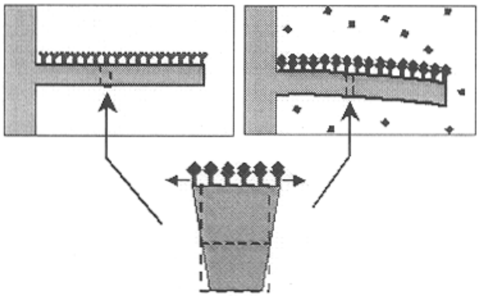
Sensors based on surface stress at a micromechanical device



Schematic diagram showing the bending response of the microcantilever following sorption of analyte molecules

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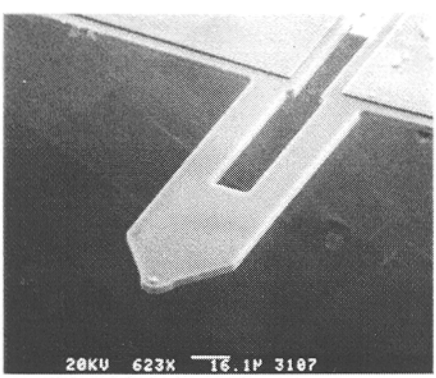
Electron Micrograph of a 200 μm Long Cantilever



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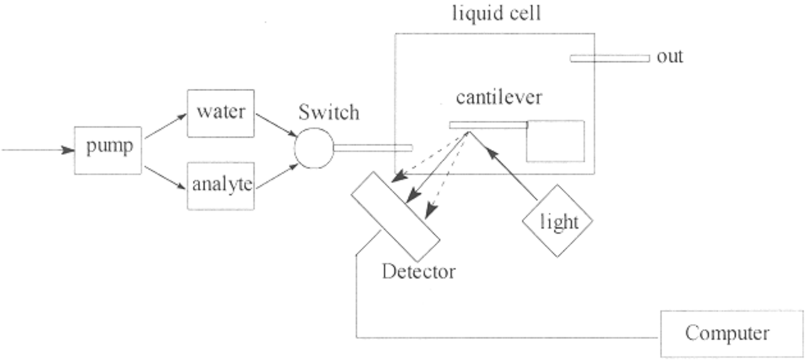
Schematic of Microcantilever Sensor Experimental Arrangement



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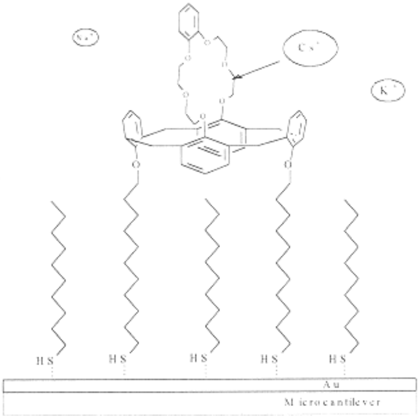
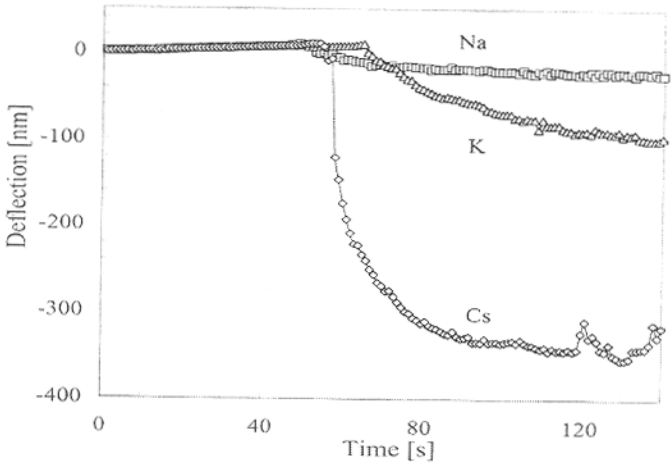


Alkanethiol derivatized ligand, mixed monolayer



Bending deflection response of the SAM coated microcantilever towards different alkali metal ions (10^{-5} M concentration of Cs+, K+, and Na+).

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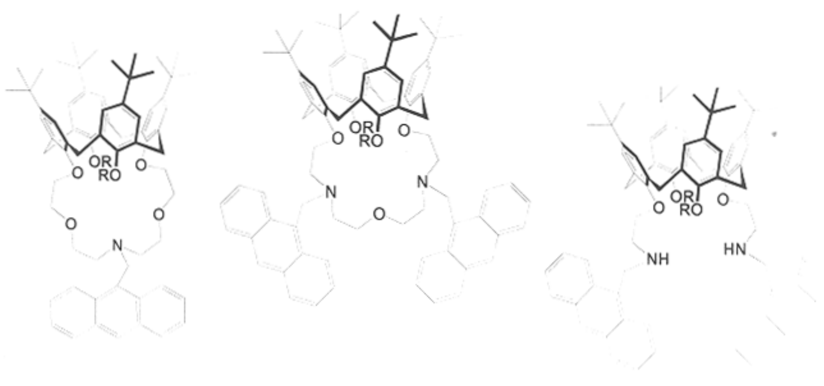

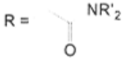

Structures of several ligands with fluorophores expected to be selective for Sr^{2+}; variations with thiol groups will be prepared for attachment to microcantilever

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Concentrations of Total Cesium and Strontium within Hanford Underground Tanks

Best Basis Inventory; Kupfur 1999; Hanlon 2000; Kirkbride 1999

	Concentration of All Isotopes of Cesium and Strontium	
Tank Type	Cs, M	Sr, M
Double Shell (28 tanks)	9.0E-5	1.5E-4
Single Shell (149 tanks)	4.6E-5	3.7E-3

	Ratio total/radionuclide inventory, Cesium and Strontium	
Tank Type	$Cs_T/^{137}Cs$	$Sr_T/^{90}Sr$
Double Shell (28 tanks)	2.5	7
Single Shell (149 tanks)	2.9	150

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Tank Wastes Currently Available in RPL for Sensor Tests

SSTs	S-101	non-complexed waste
	S-111	
	T-110	
DSTs	AN-102	complex concentrate
	AZ-101	aging waste
	AZ-102	

Problems and Challenges

Microcantilever sensor elements have been shown to have better sensitivity than fluorescent sensor elements

Fiber optic platform for sensor arrays is better developed

Fiber optic array sensor can withstand the harsh environment of HLW better than microcantilever

Improve sensitivity of fiber optic sensor; translate solution results to polymer beads

Make microcantilever more robust to strong alkali, SiC instead of Si, protect with silane reagents