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

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Program Objective

Develop sensors for cesium and 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

DOE Site Specific Problem and Research Plan

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+}

DOE Hanford Site: Cs^+ removed in columns; Sr^{2+} removed by precipitation

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

Improve fluorophore, adapt chemistry for cantilever sensors

Fiber optic sensors

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

Hanford WTP Cs and Sr inventories

Ratio of stable Cs to ^{137}Cs is variable for various waste types.

		Total Cs concentration, mol/L	
Waste type	% Cs as ^{137}Cs	Cs in feed	Cs after ion exchange
Envelope A	31%	3.3E-05	2.8E-08
Envelope B	42%	3.0E-04	6.4E-08
Envelope C	24%	3.4E-05	4.7E-08

Concentration of stable Sr to ^{90}Sr is variable for various waste types.

		Total Sr concentration, mol/L
Waste type	% Sr as ^{90}Sr	Sr in feed
Envelope A	2%	1.5E-05
Envelope B	3%	2.8E-05
Envelope C	8%	2.4E-05

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 one or more fluorophores as the reporter.

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

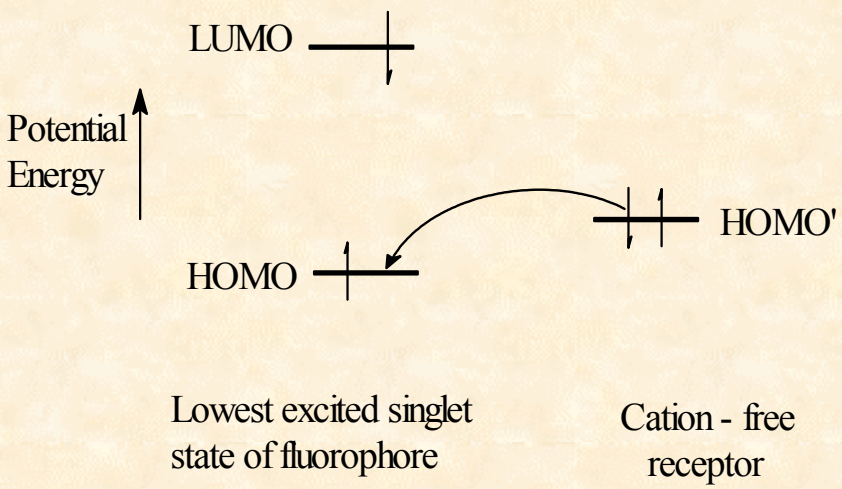
Develop an array of chemically selective sensors to correct for interference from K^+, etc. that can be coupled to fiber optics for remote analytical applications

Two methods to signal complexation:

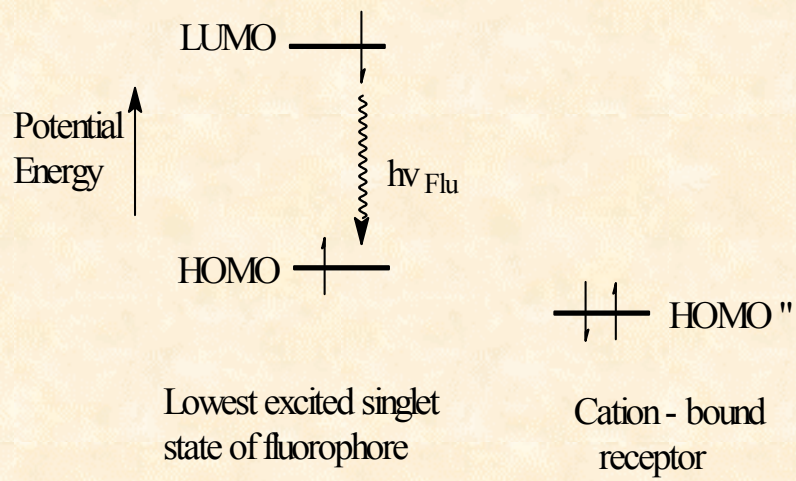
(1) PET (2) excimer formation

Fluorescence Turn-On: Photoinduced Electron Transfer (PET)

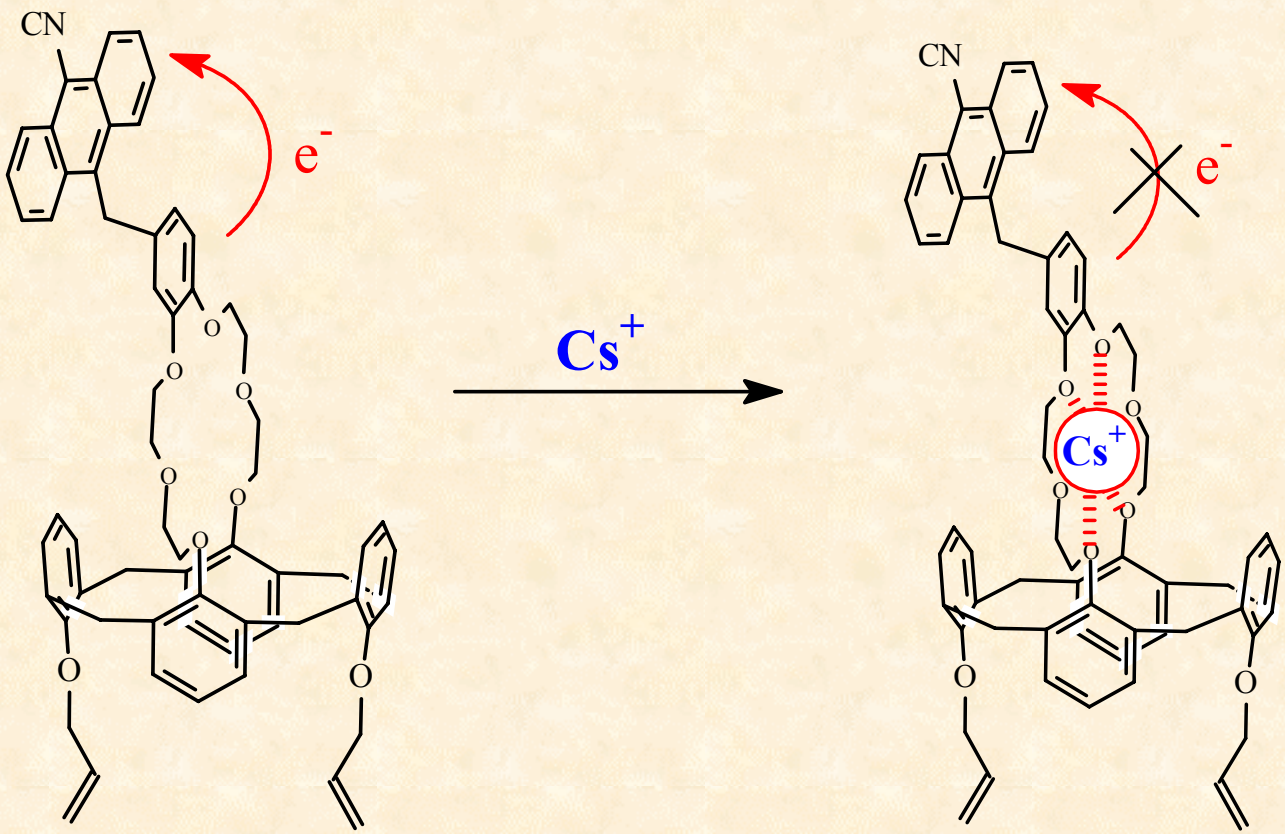
Frontier orbital energy diagram for the fluorophore -receptor pair



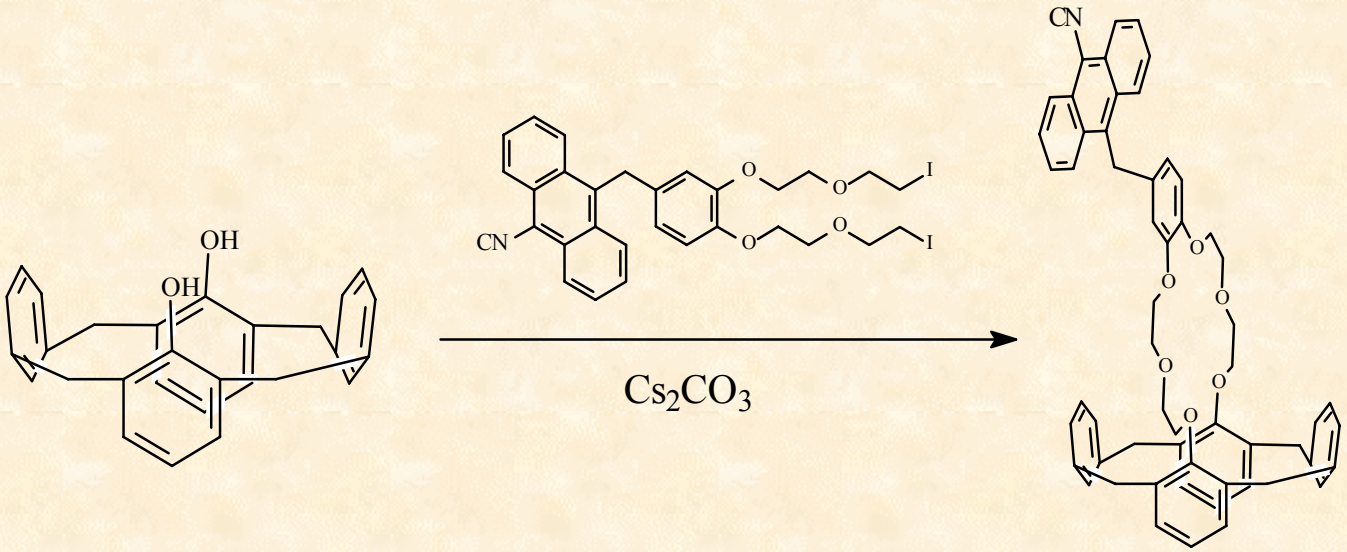
Cation Free



Cation Bound



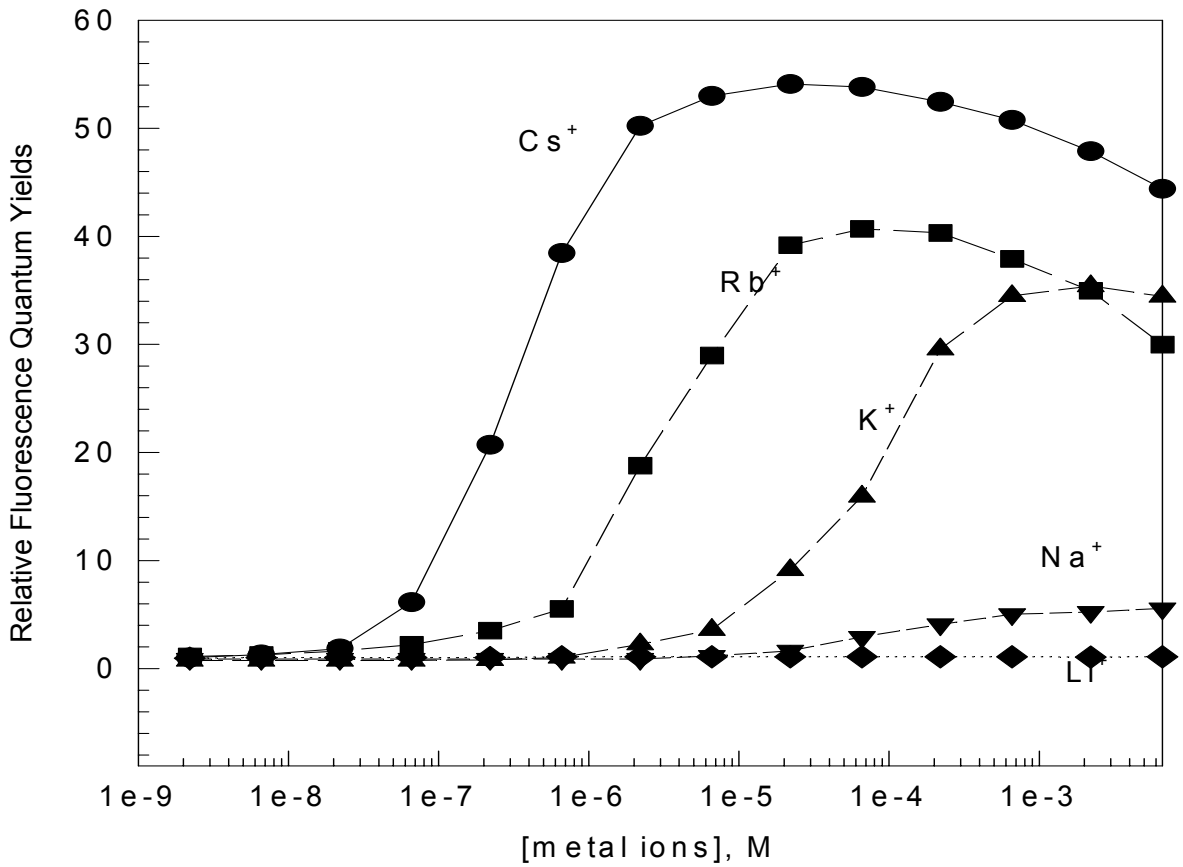
Weak Emission **Strong Emission**



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

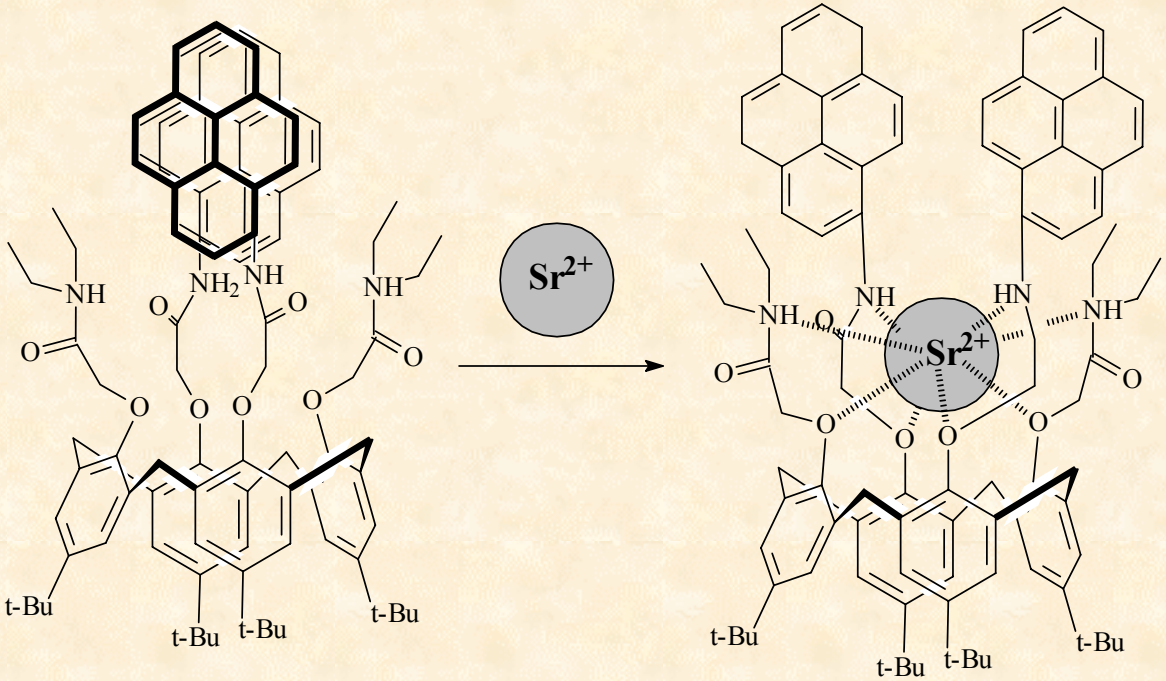
Most efficient fluorescent Cs^+ selective ligand developed to date

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

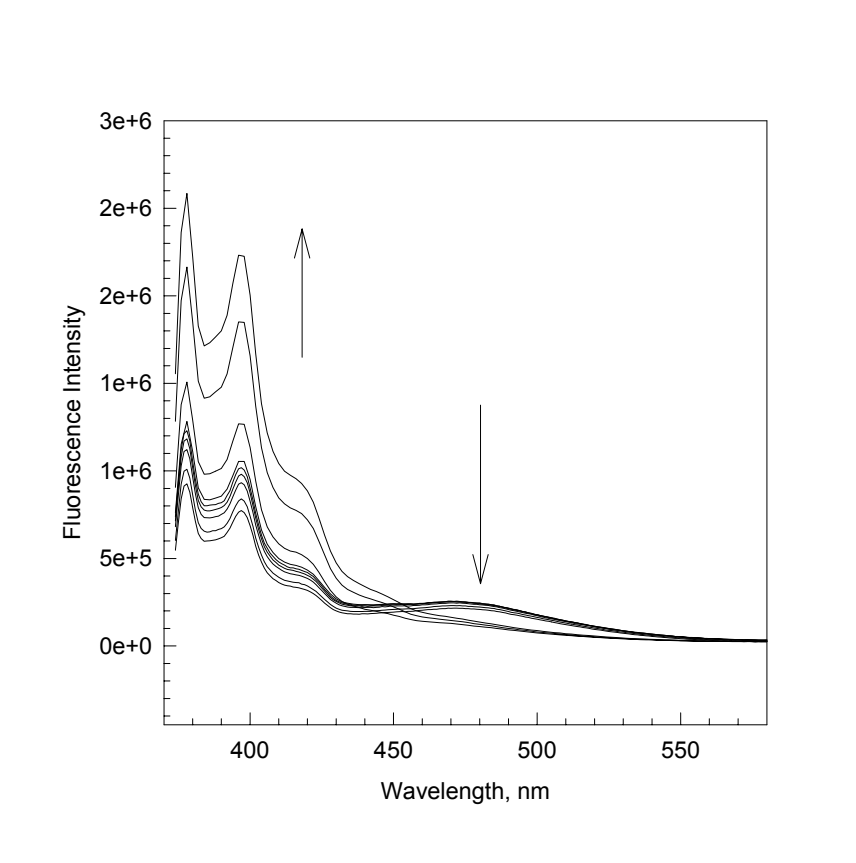


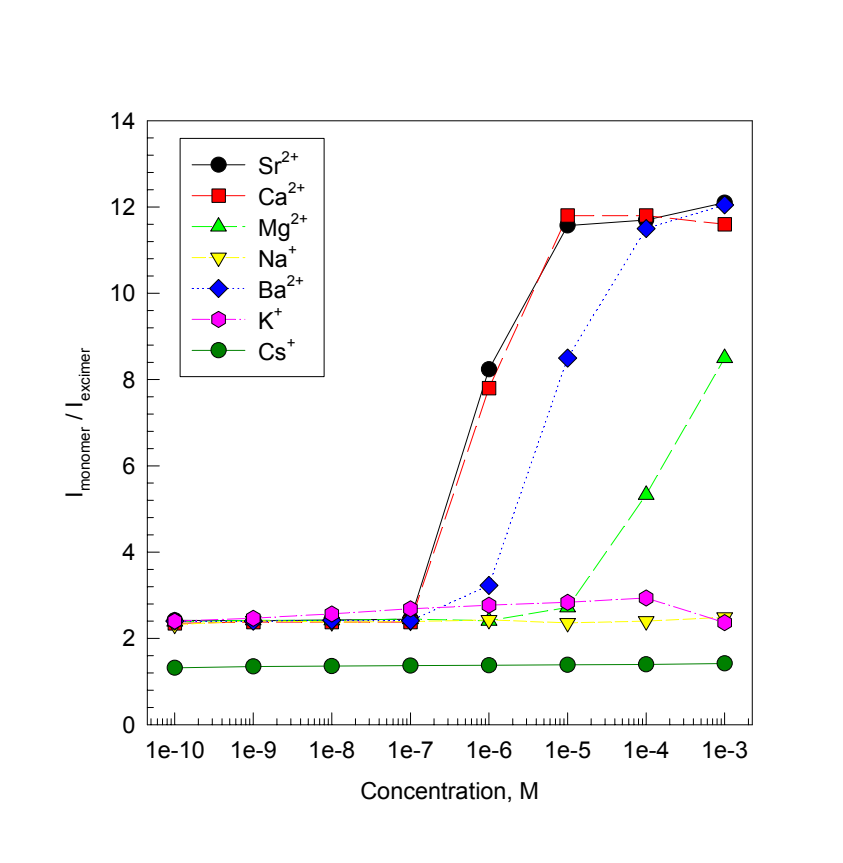
Changes in the emission intensity of 1 ($1x10^{-6}$ M) as a function of alkali metal ion concentration in aerated CH_2Cl_2:MeOH (1:1 v/v), l_{ex}= 376nm, l_{em} = 400-600 nm (integrated).

Excimer Formation: strontium binding changes distance between pyrene rings – detect change in fluorescence spectrum

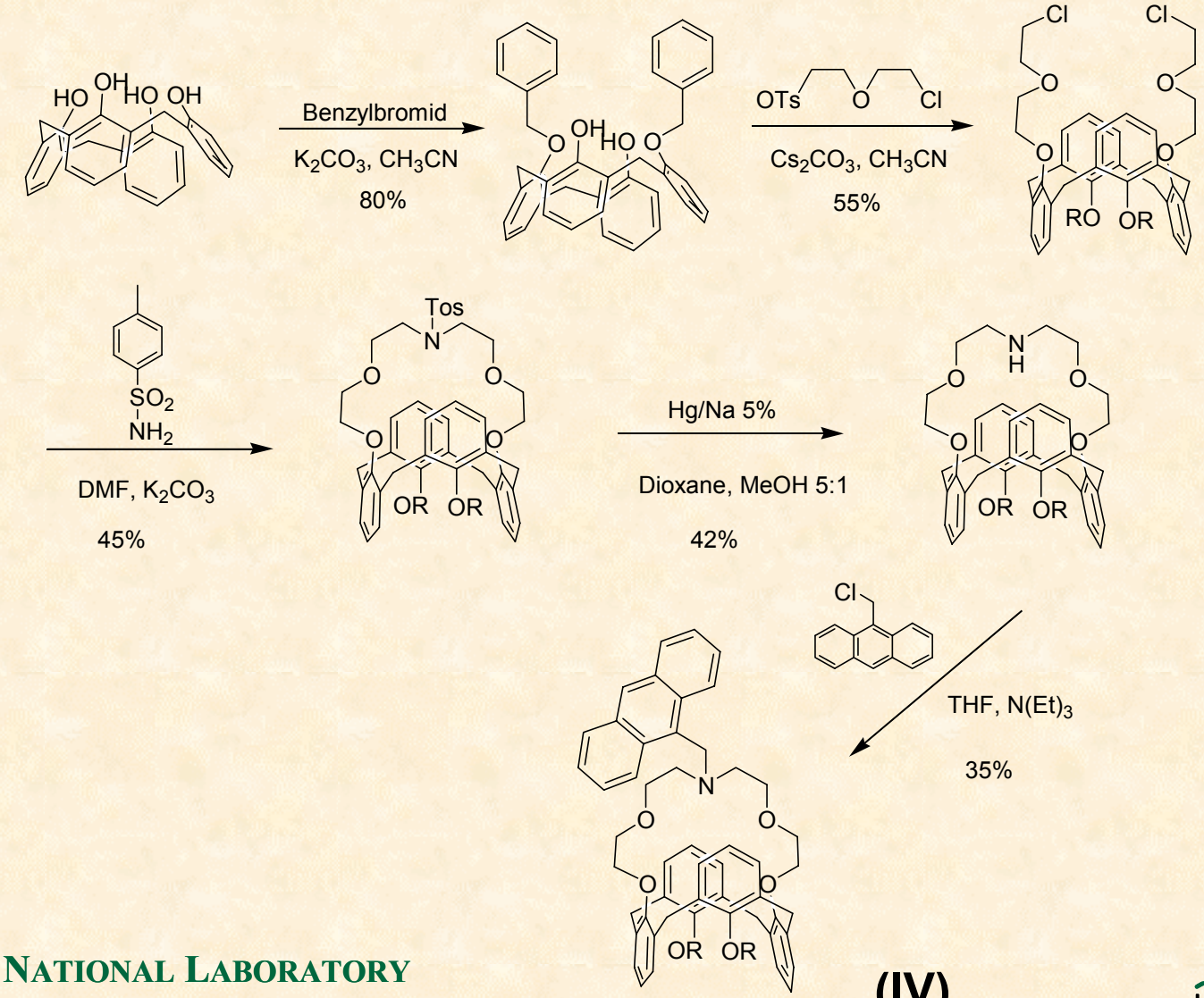


Addition of Sr^{2+} causes excimer peak to disappear and monomer peak to increase – very selective over alkali metal ions – modest selectivity other divalent



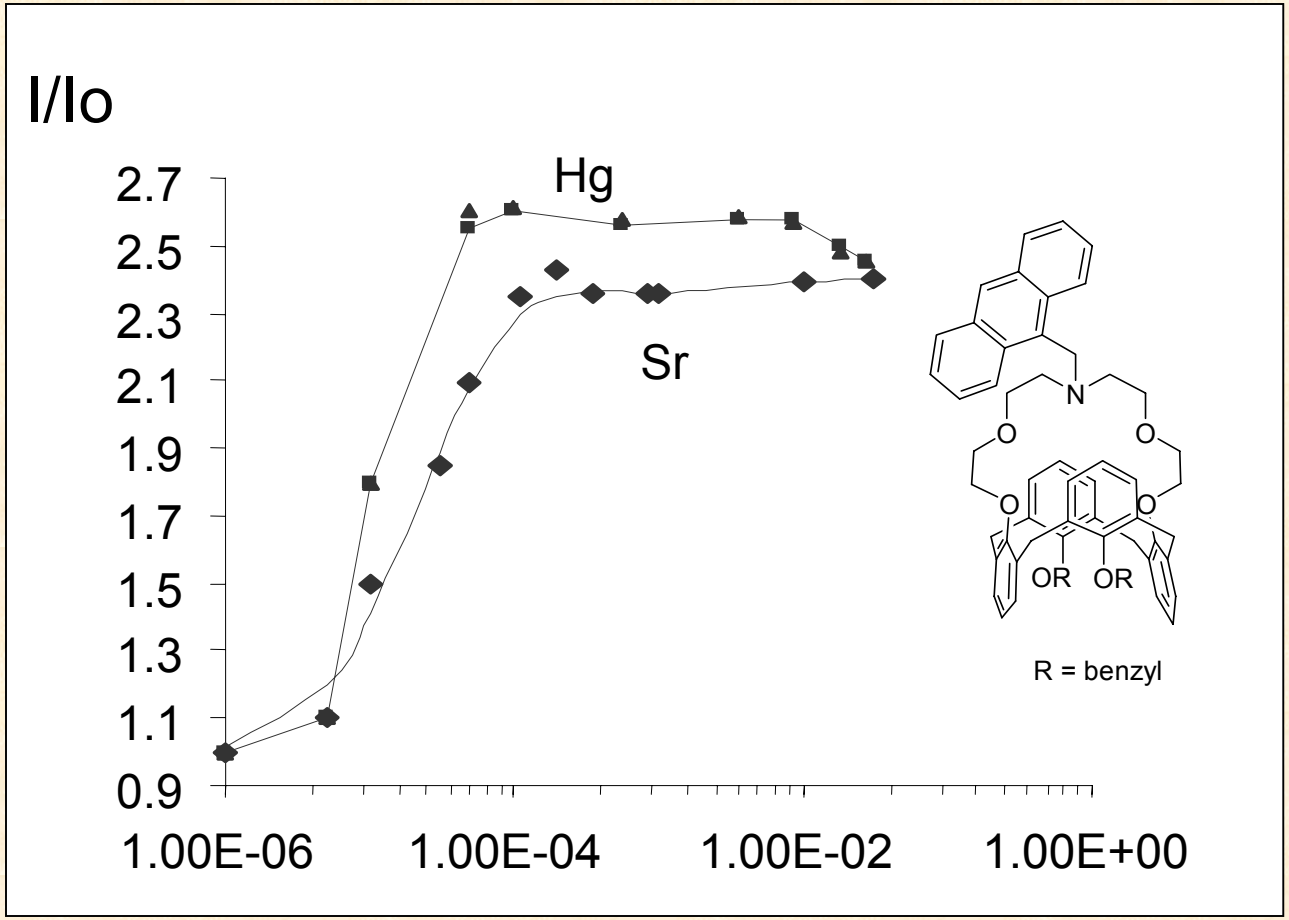


Synthesis crown compounds, anthracene fluorophore



(IV)

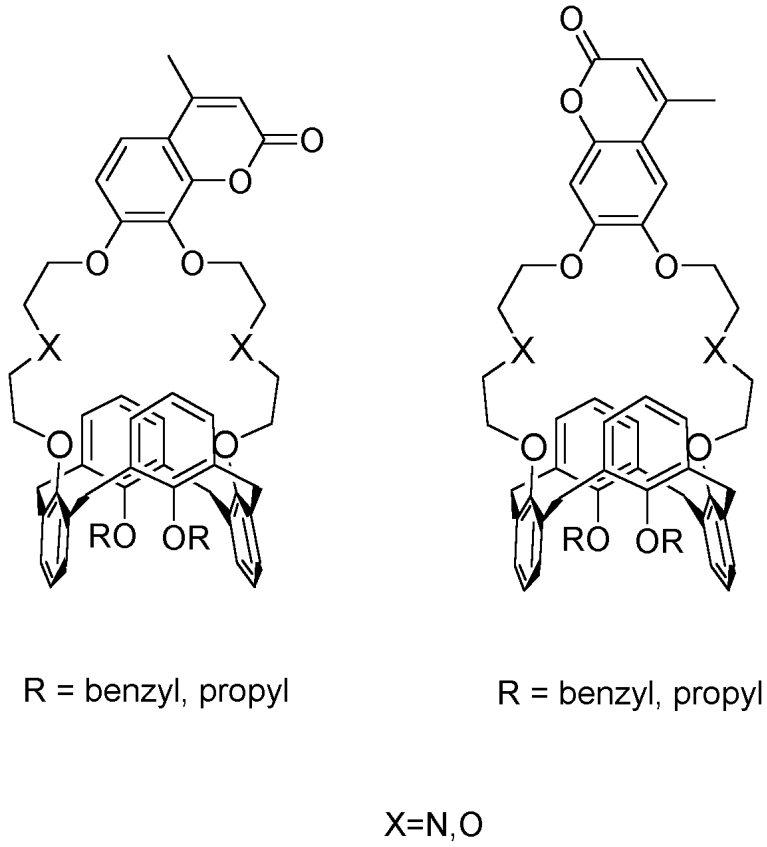
R = benzyl



Changes in the emission intensity of **(IV)** as the concentration of Sr(II)/Hg(II) ion is increased,
solvent was ethanol, (λ_{ex} = 380 nm)

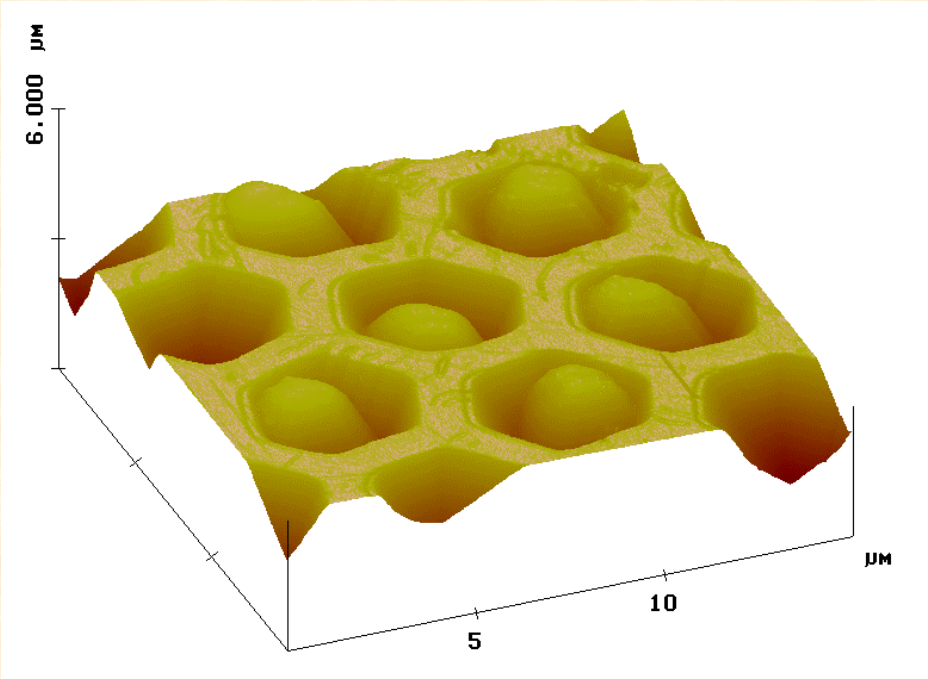
Current and Future Plans

Test fiber optic sensor with waste simulants (FY 03) and then actual waste in (FY 04)



- Investigate two derivatives of coumarin as fluorescent reporter groups
- Investigate pyrene excimer with cyclic ether for improved selectivity
- Pyrene excimer works in celulose acetate film – donor-acceptor pairs as reporter
- Translate solution to solid matrix

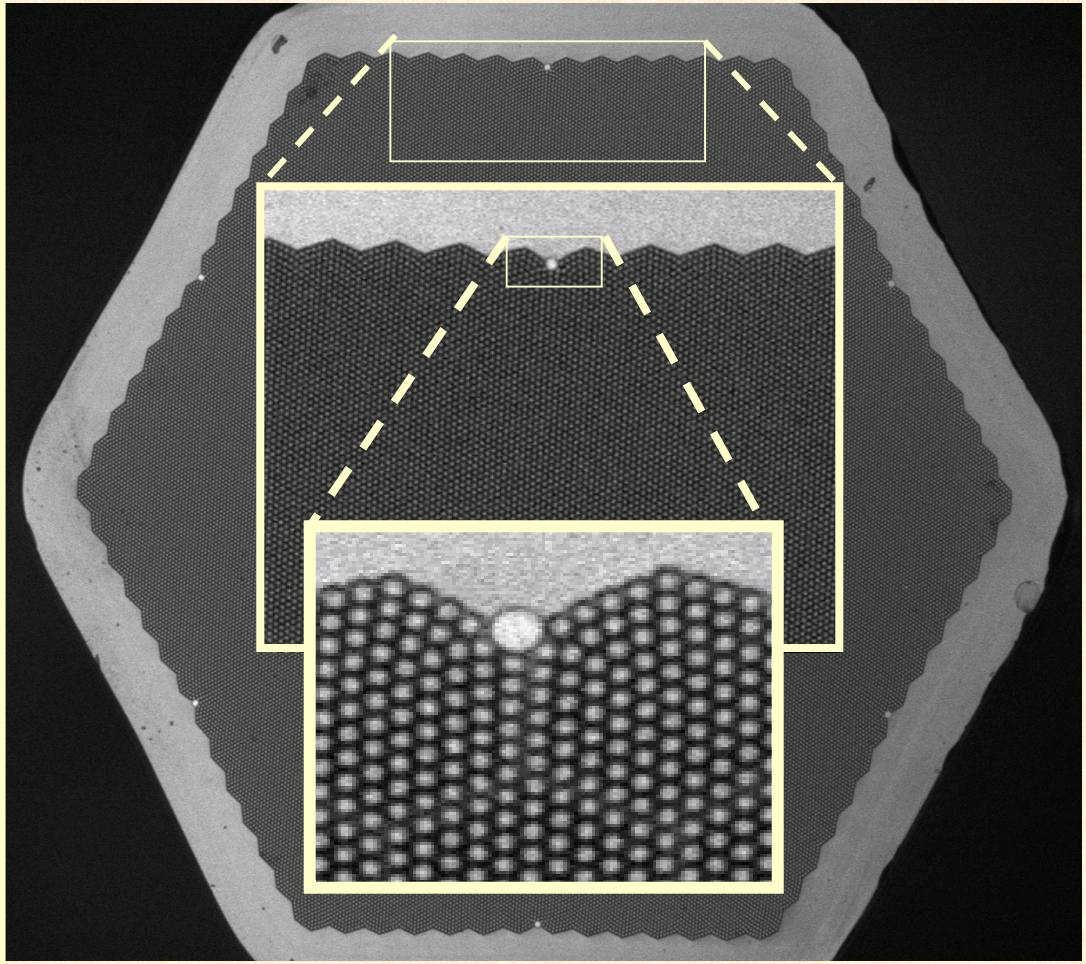
Sensors Based on Modified Fiber Optic Bundle



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

David Walt, et al, Tufts University

Imaging Fiber Bundles



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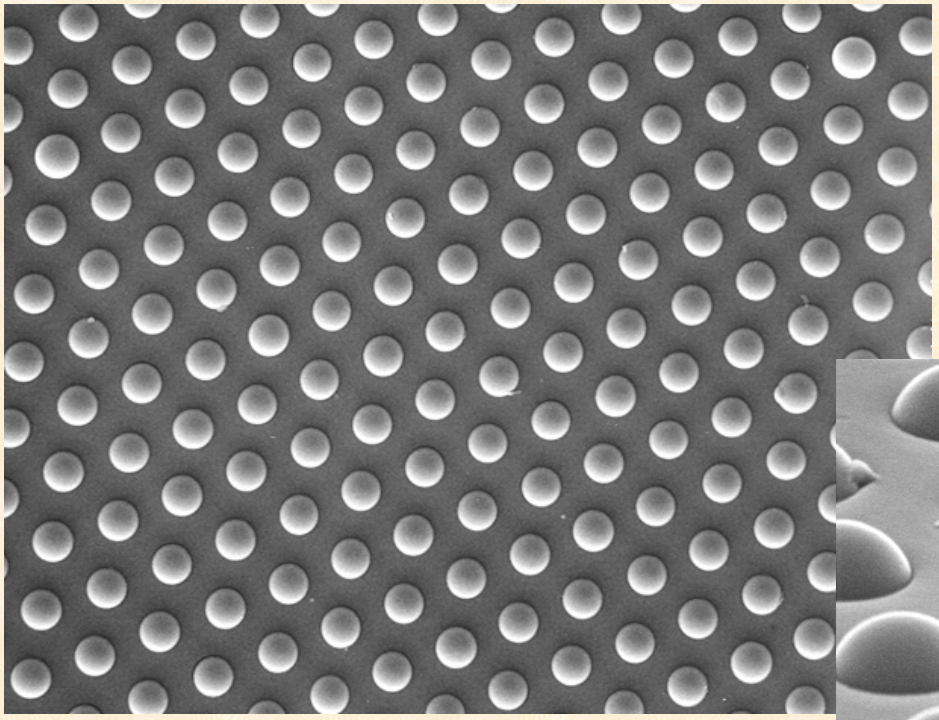
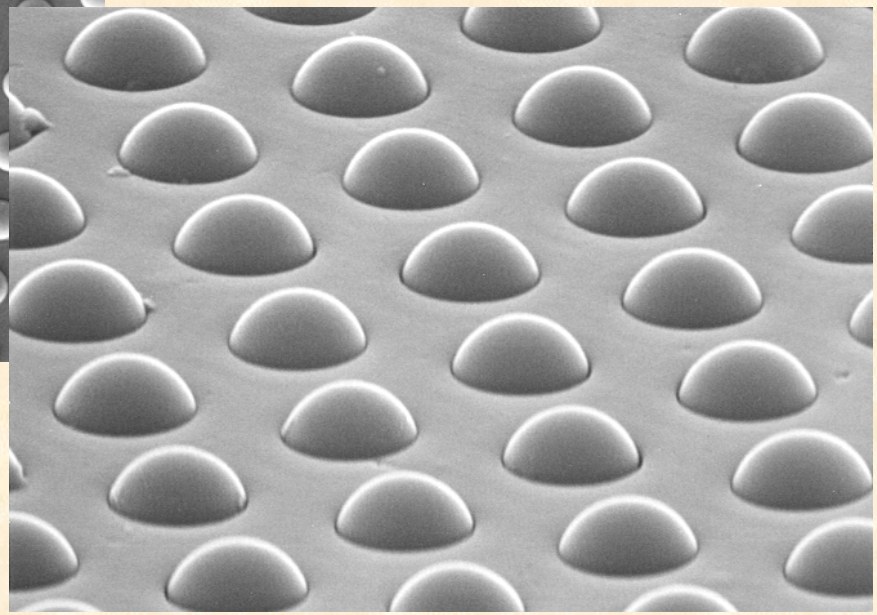
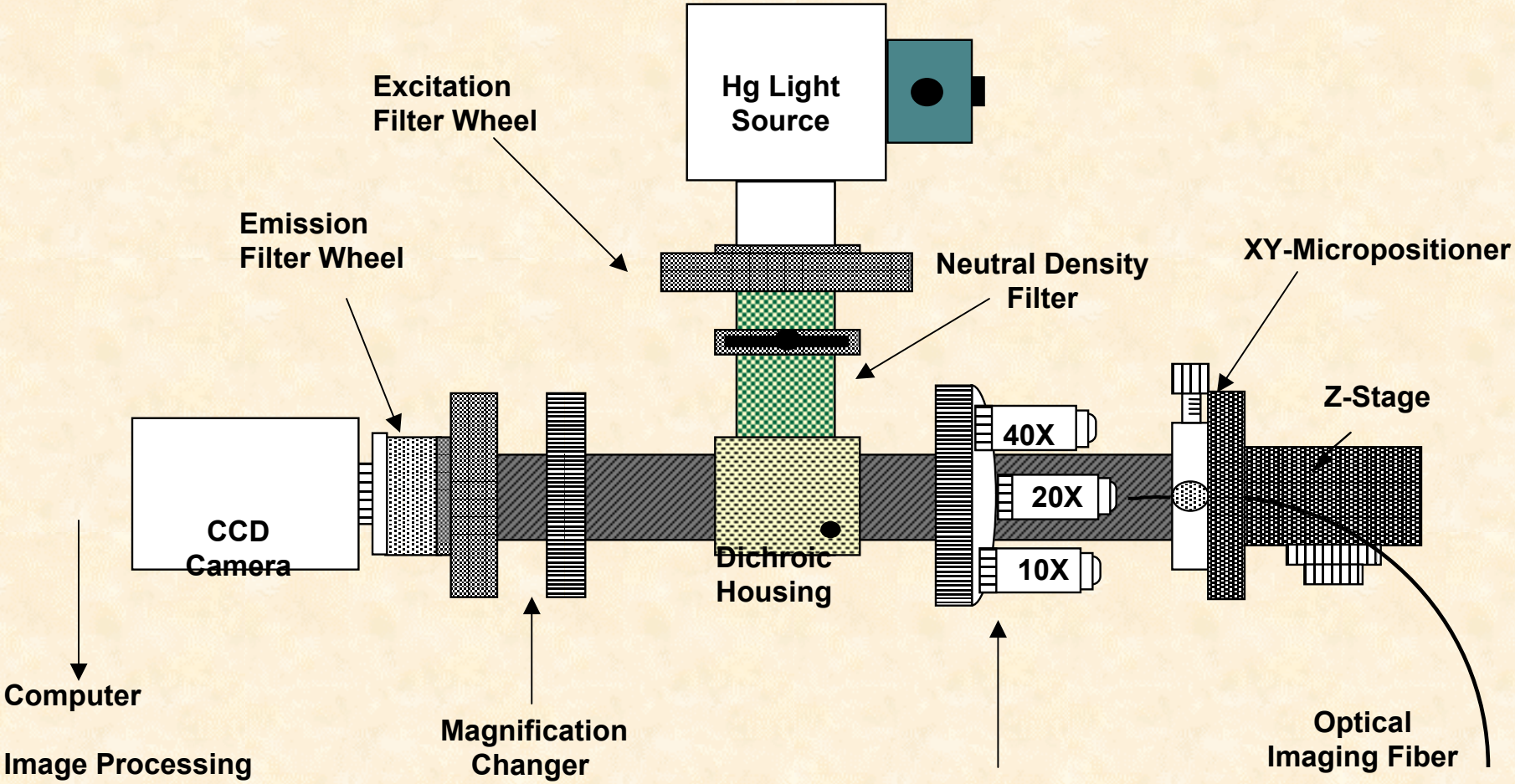
Tufts Univ.

Recent Beads in Wells SEMs

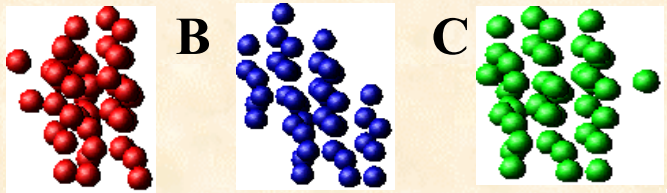




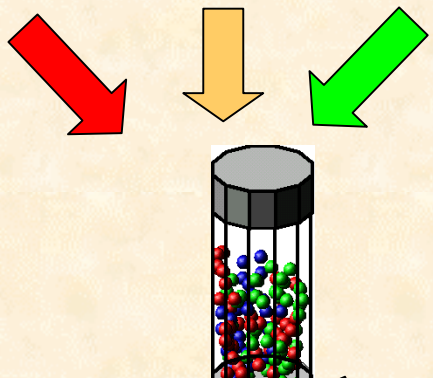
Instrumentation: Modified Fluorescence Microscope



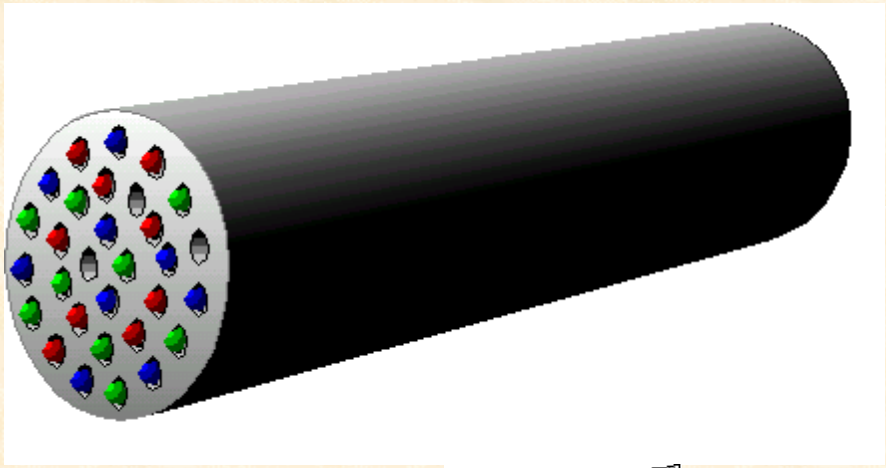
Randomly-distributed Addressable High-density Sensor Array



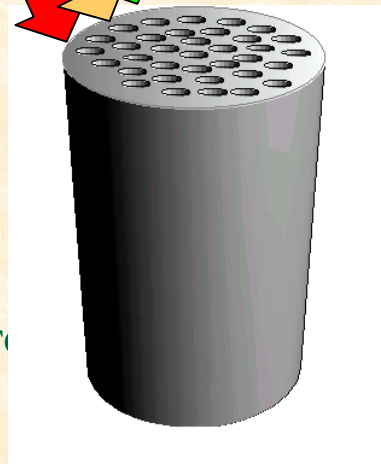
Michael et al., **1998** *Anal. Chem.*, ***70***, 1242-1248.



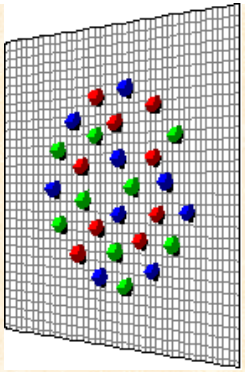
Sensor stock



Microwells on etched face



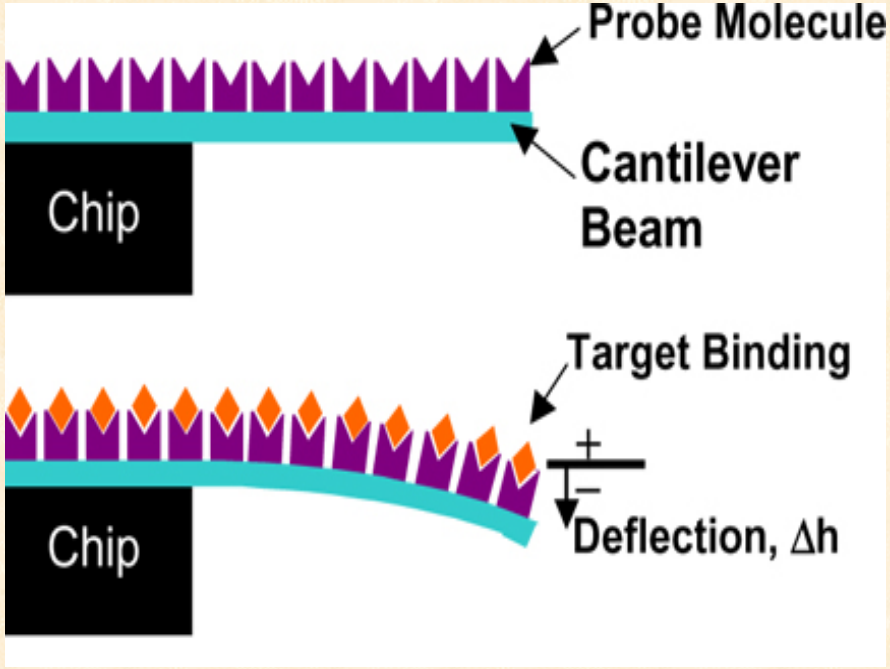
Distal face of imaging fiber



CCD chip

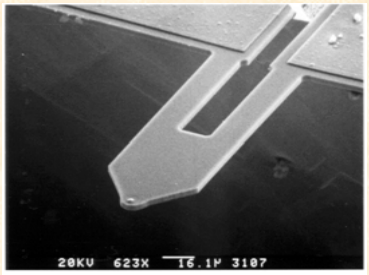
Nanomechanical Observation of Adsorption-Induced Forces - Microcantilever Sensors

- Adsorption Decreases Surface Free Energy
- Surface Stress N/m
- Changes In Stress As Small As 10^{-4} N/m Can Be Detected
- Mechanical Strengths of Bonds:
  - H - Bond 10^{-11} N
  - Covalent Bond 10^{-9} N

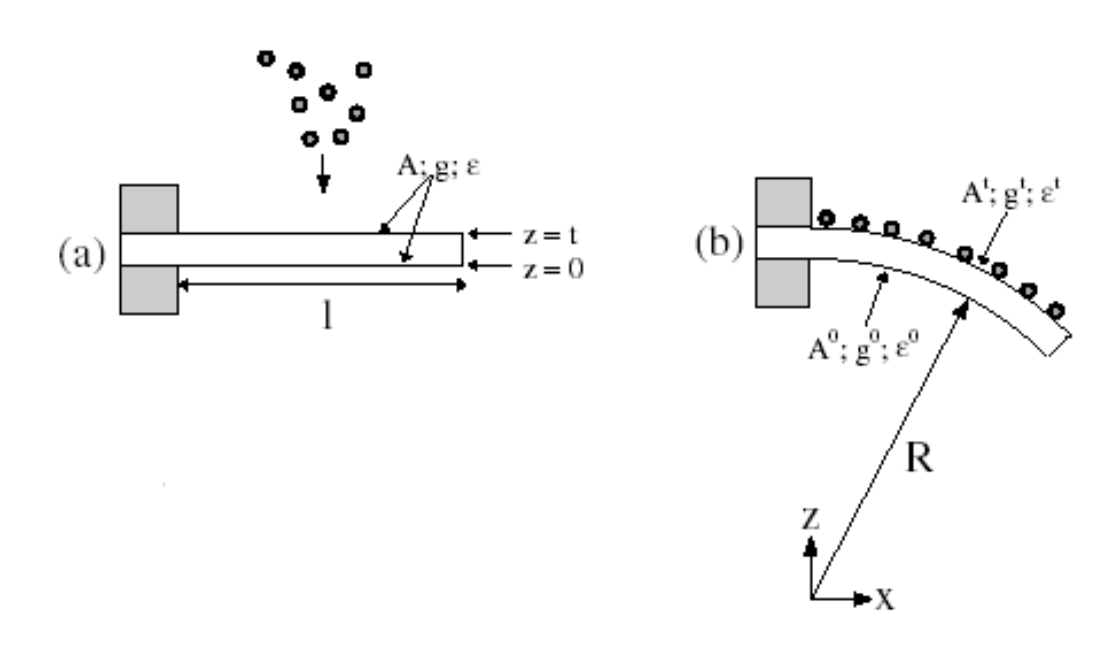


Cantilever beams with spring constant in the same order of magnitude as the free energy change undergo bending due to adsorption

Adsorption on One Surface of the Cantilever



electron micrograph of a 200 µm long cantilever



The length of the cantilever, L, is assumed to be large compared to its width, w, which is assumed to be large with respect to its thickness, t. The radius of curvature, defined for the Stoney equation, is R.

Relationship Between Surface Stress and Surface Free Energy

Surface stress, g, and surface free energy, γ, can be related using the Shuttleworth equation

$$g = \gamma + \left(\frac{\partial \gamma}{\partial \varepsilon} \right)$$

Surface strain $\partial\varepsilon$ is defined as ratio of change in surface area, $\partial\varepsilon = dA/A$

Bending of the cantilever is very small compared to the length; to a first approximation can neglect the contribution from surface strain effects and equate the free energy change to surface stress variation

Adsorption on surface changes free energy which is a surface stress

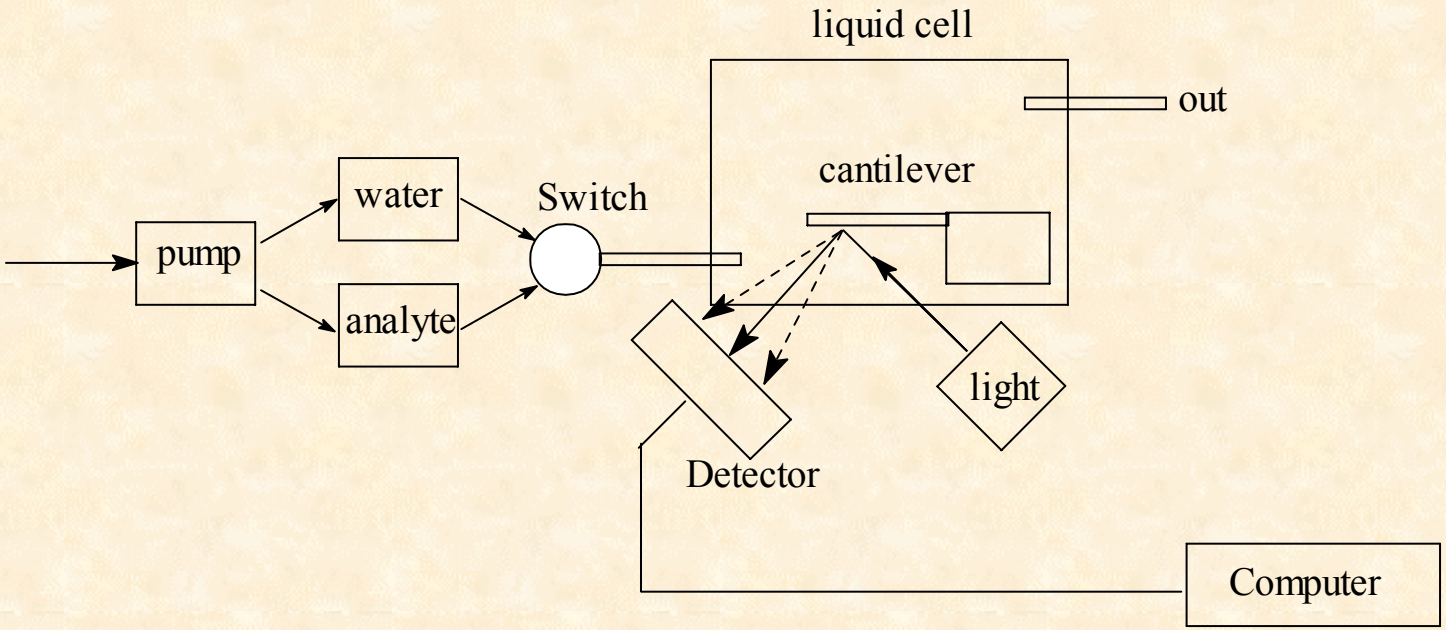
Stoney's formula relates displacement (Δz) in a bending cantilever to the change in surface stress (δg)

$$\Delta z = \left(\frac{3(1-\nu)L^2}{Et^2}\right)\delta g$$

where L is the length, ν is Poisson's ratio, E is Young's modulus, and t is the thickness of the cantilever

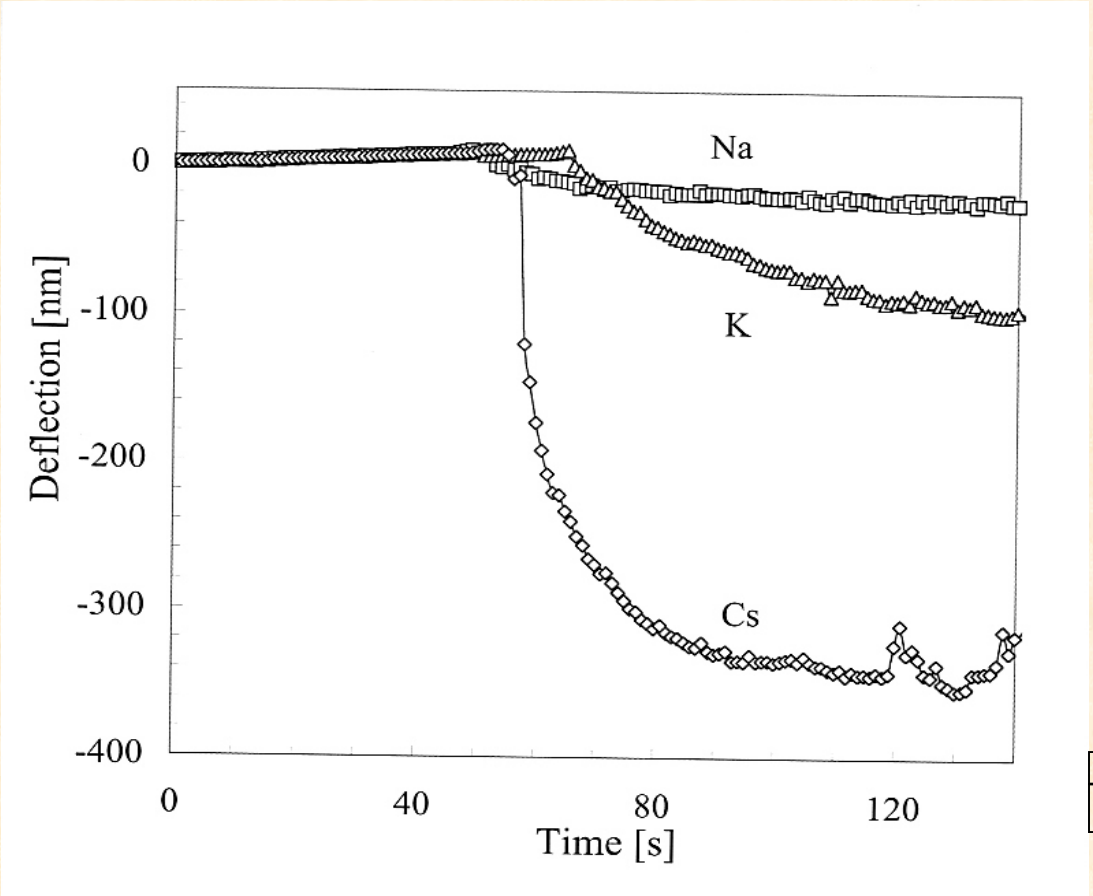
Molecular adsorption to one surface of a cantilever creates surface stress that is manifested as a bending

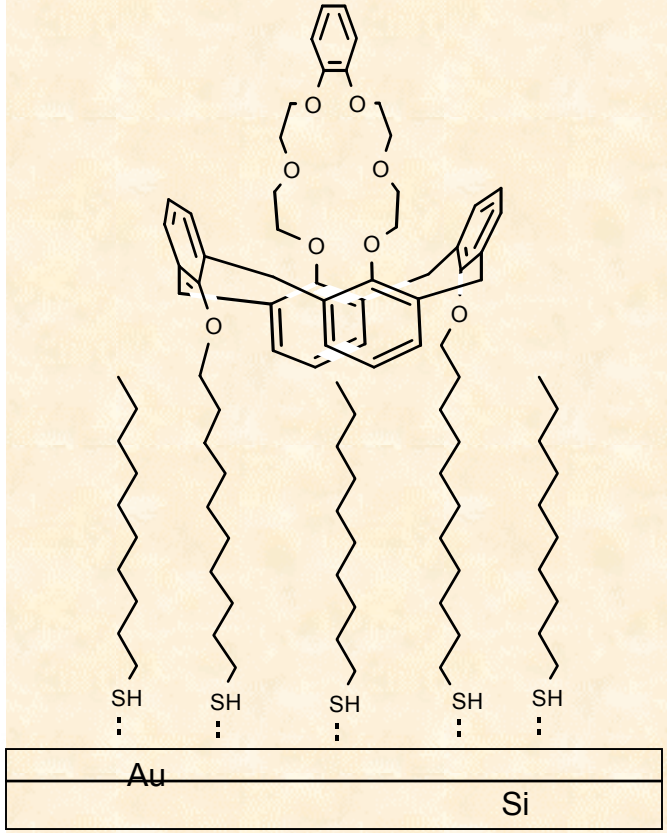
Schematic of Microcantilever Apparatus



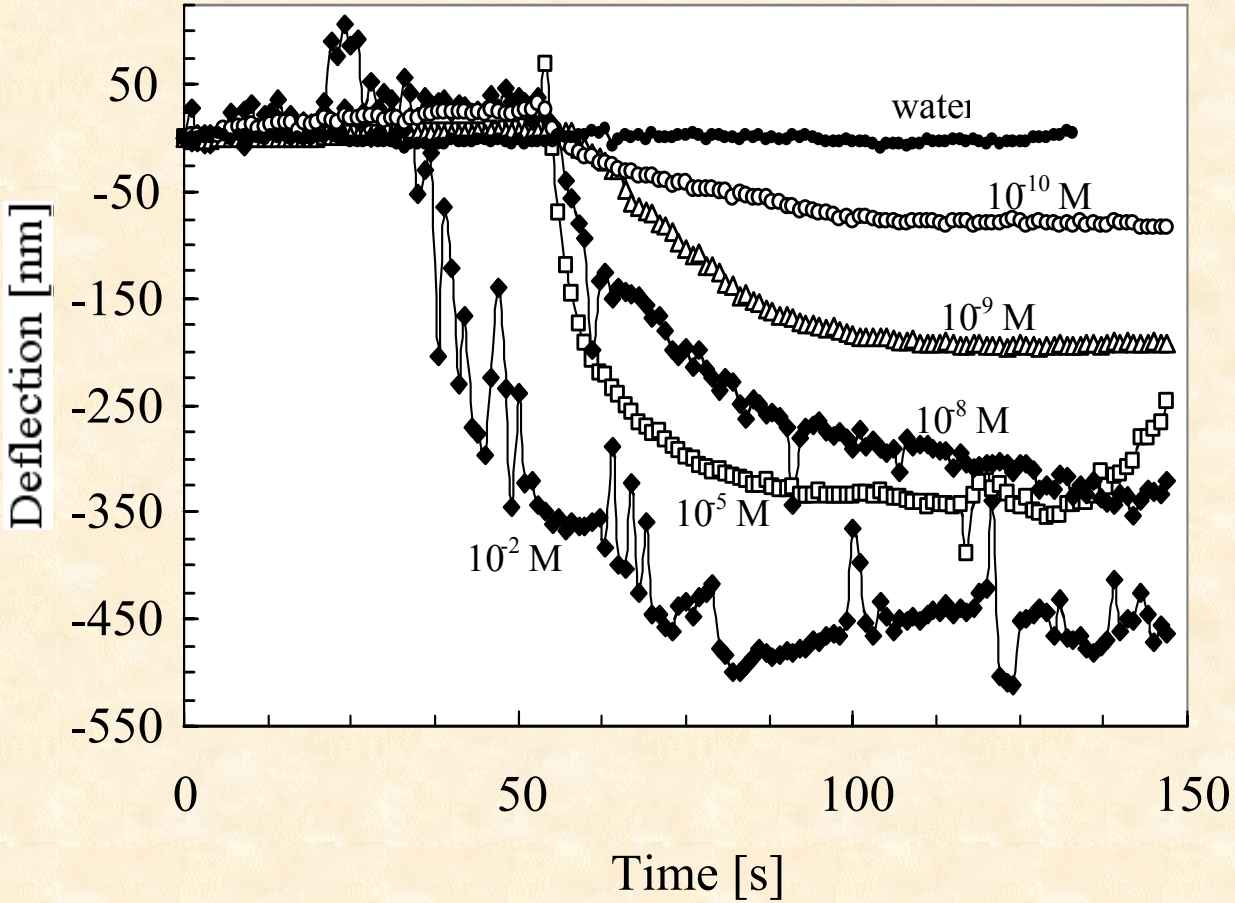
Measure cantilever deflection by reflection of a diode laser from the cantilever tip to a position sensitive detector

Molecular recognition agent attached to Au-coated Si cantilever as SAM – co-adsorbed with decanethiol



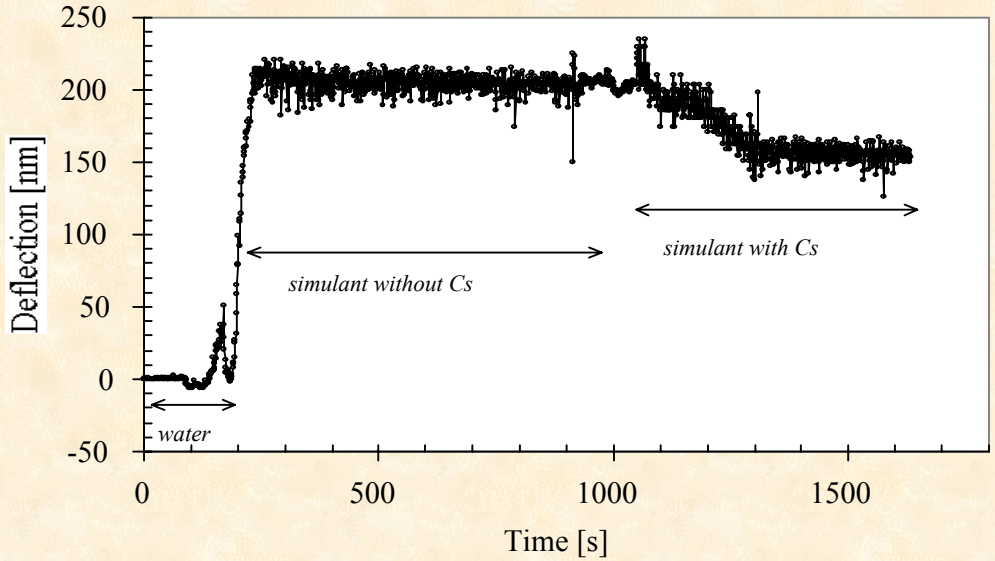


Bending deflection response of the coated microcantilever towards different alkali metal ions (10^{-5} M concentration of Cs^+, K^+, and Na^+).



Bending deflection response of the SAM coated microcantilever as a function of time, t, before and after exposure to different concentrations of Cs+ ions in solution at room temperature

Detection of Cs^+ in a tank waste simulant (pH 14)



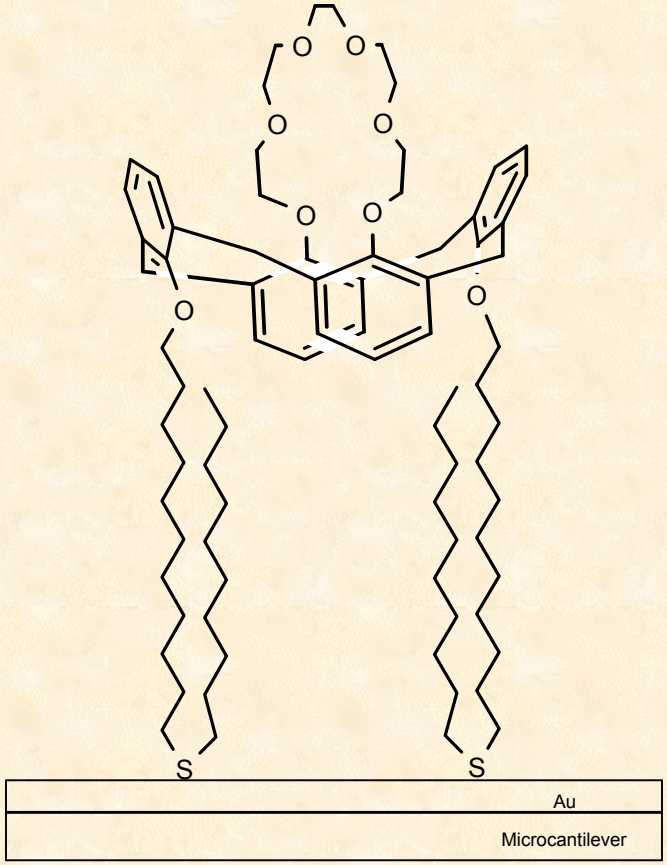
Simulant composed of NaOH (3.3 M), Al(NO3)3.9H2O (0.4 M), sodium dichromate (7x10-3 M), Na2CO3 (1.3 M), NaNO3 (1.3 M), KNO3 (1.7 M), Na2SO4 (0.2 M), NaCl (0.1M), NaF (0.05M), NaNO2 (0.8M).

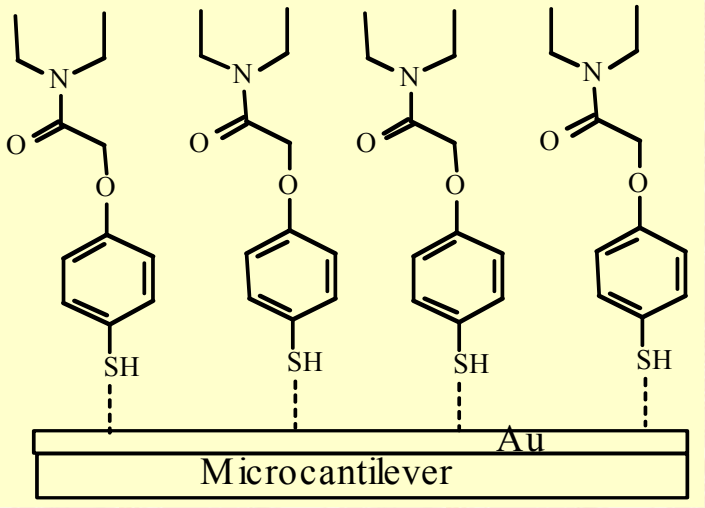
Cs^+ at 10^{-5} M

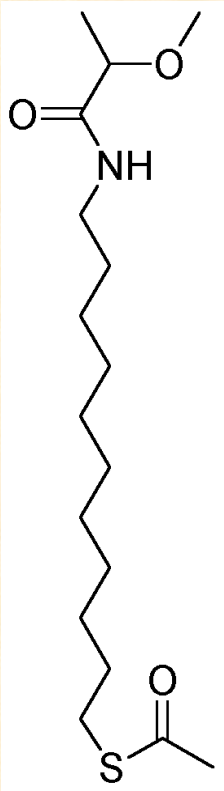
increased noise probably due to high pH value of the solution

Research in progress to protect microcantilever from alkaline solution; use materials that are more stable (SiC)

Research in progress to develop cesium and strontium selective molecular recognition agents







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