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

Gilbert M. Brown, Peter V. Bonnesen, and Reza Dabestani
Chemical Sciences Division, Oak Ridge National Laboratory

David R. Walt
Department of Chemistry, Tufts University

Samuel A. Bryan
Pacific Northwest National Laboratory

Postdoctoral Fellows:
Gudrun Goretzki,[1] Maryna Gorbunova,[1] and David J. Monk[2]
[1]ORNL and [2]Tufts University

Program Objective

Develop sensors for cesium, strontium, and pertechnetate that can be used in real-time to characterize high-level waste (HLW) process streams

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

Principles of molecular recognition utilized to achieve selectivity

Current work on Cs^{+} and Sr^{2+}, future effort on TcO_4^{-}

DOE Site Specific Problems

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

DOE Hanford Site: Cs^{+} removed in columns; Sr^{2+} removed by precipitation; TcO_4^{-} removed by ?

Need sensors to monitor separation process for breakthrough.

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

The future: an array of sensors

fiber optic sensors based on bead approach of David Walt

Fluorescent Sensors

Cs^{+} and Sr^{2+} detection based on calix[4]arene 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

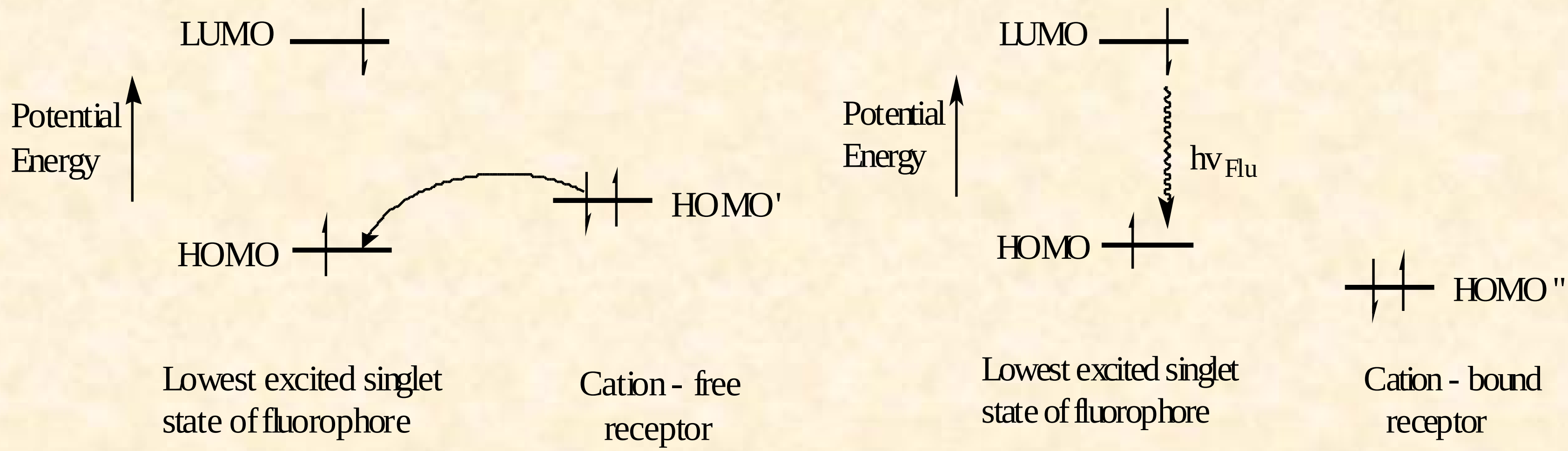
Develop an array of chemically selective sensors to correct for interference from K^{+}, etc. that can be coupled to fiber optics for remote analytical applications

Several methods are being investigated to signal complexation:

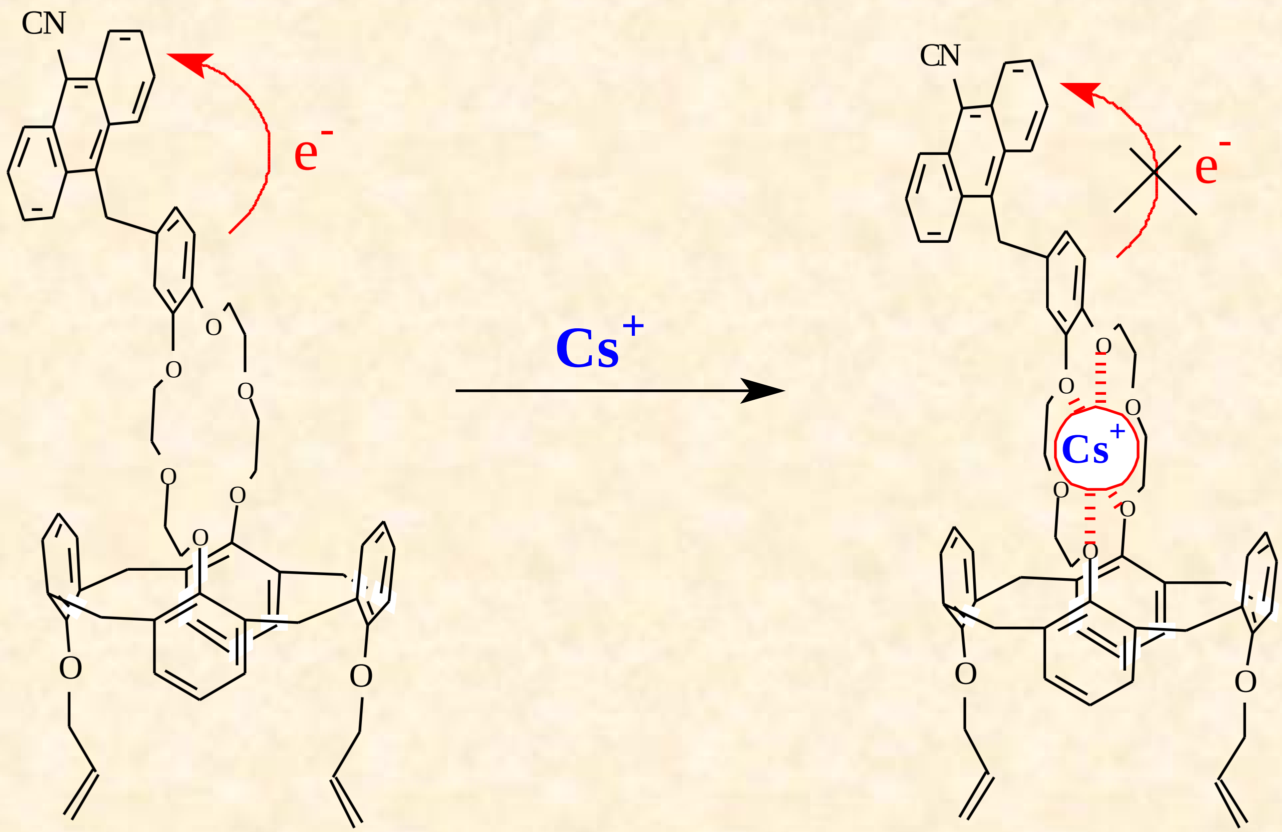
(1) PET (2) cation controlled PCT (3) excimer formation

Fluorescence Turn-On: Photoinduced Electron Transfer (PET)

Frontier orbital energy diagram for the fluorophore-receptor pair



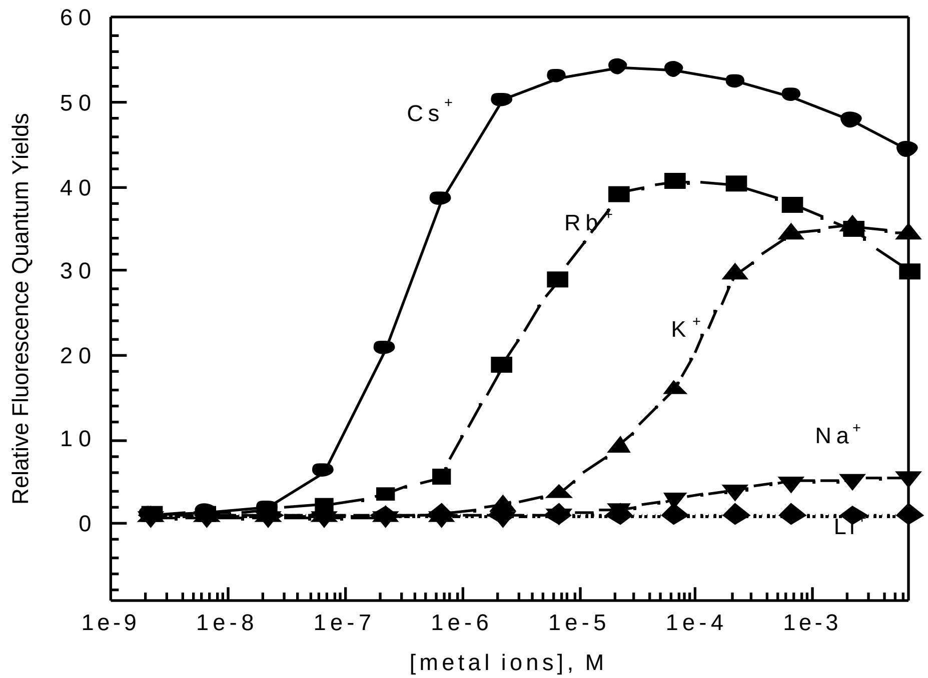
Cation Free **Cation Bound**

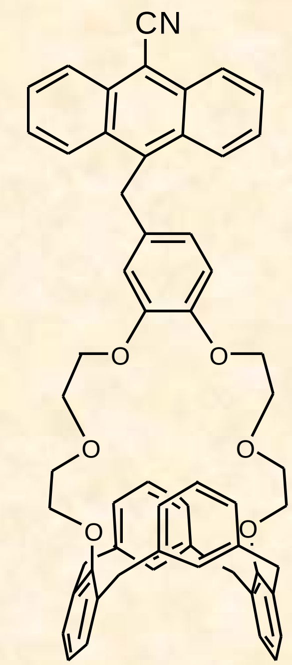


Weak Emission **Strong Emission**

Most efficient fluorescent Cs^{+} selective ligand developed to date

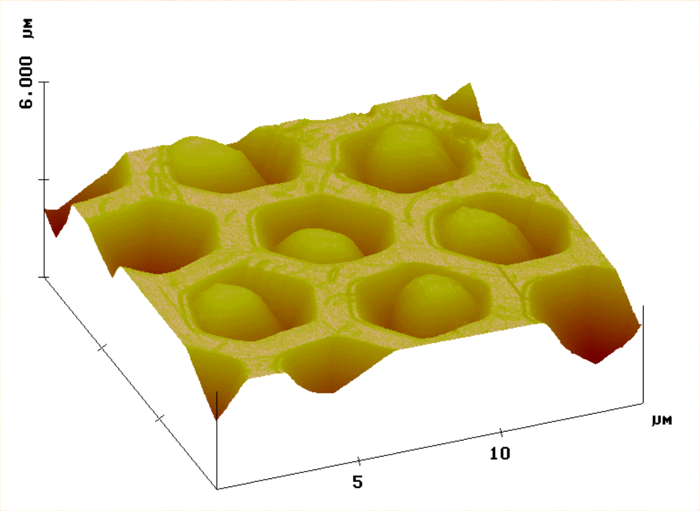
X-ray crystallography of related systems shows shortest Cs-benzocrown-oxygen distances



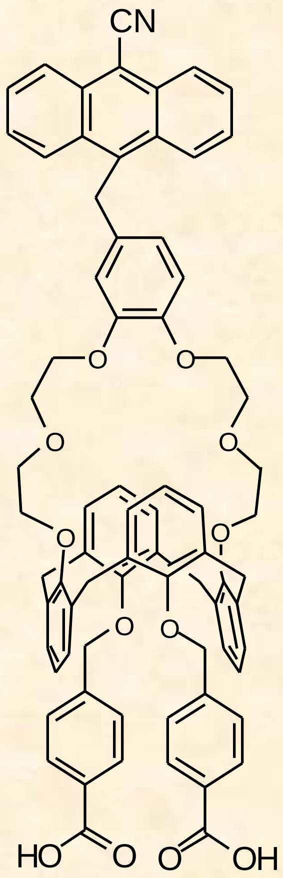


Changes in the emission intensity of 1 ($1x10^{-6}$ M) as a function of alkali metal ion concentration in aerated CH_2Cl_2:MeOH (1:1 v/v), l_{ex}= 376nm, l_{em} = 400-600 nm (integrated).

Goal - Array of Optical Sensors



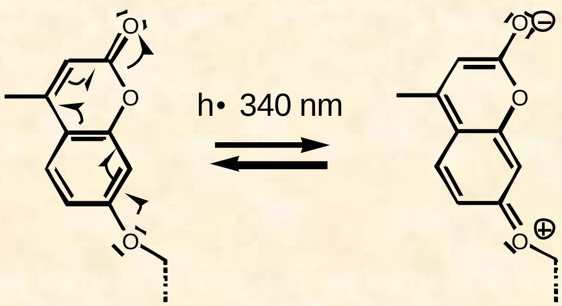
Atomic force microscopy image of microwells etched in the distal end of an imaging optical fiber, plastic microbeads derivatized with fluorescent molecular recognition agent reacted with surface of beads

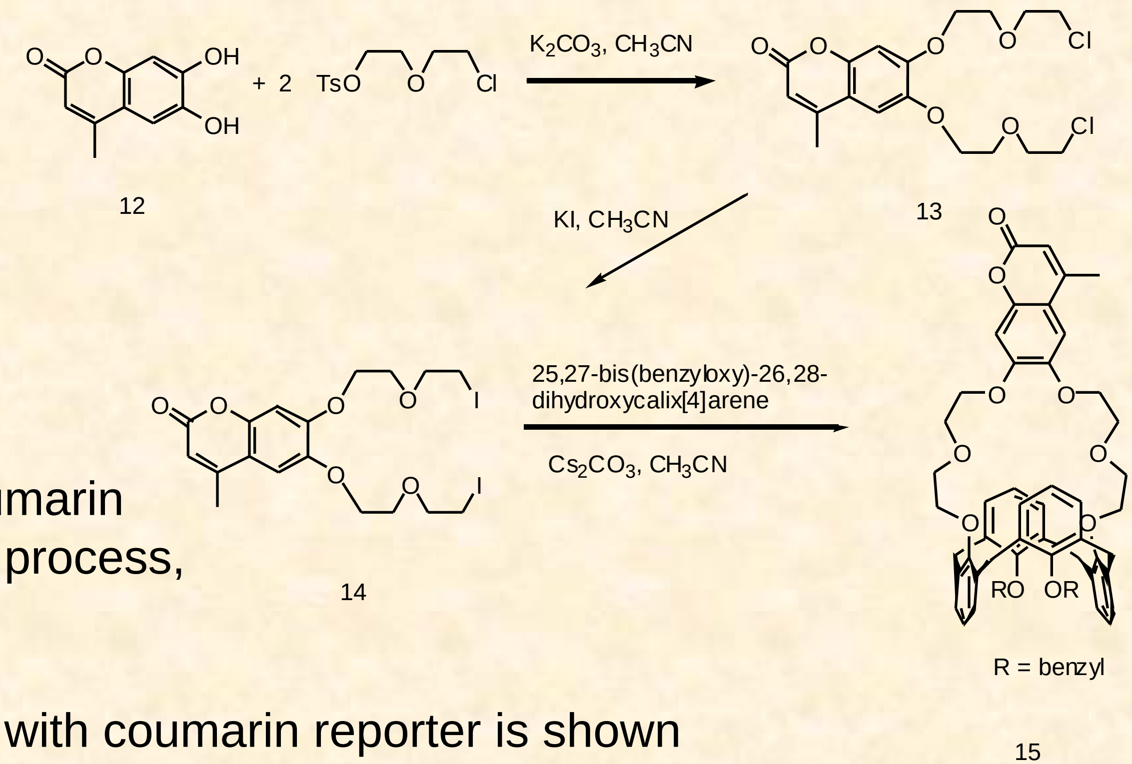


Beads derivitized with NH_2 groups reacted with NHS ester of Cs^+ selective calix-crown

Use cation-controlled photoinduced internal charge transfer as a sensing mechanism (PCT-sensor)

Coumarin dyes have intense fluorescence spectra, internal charge transfer process

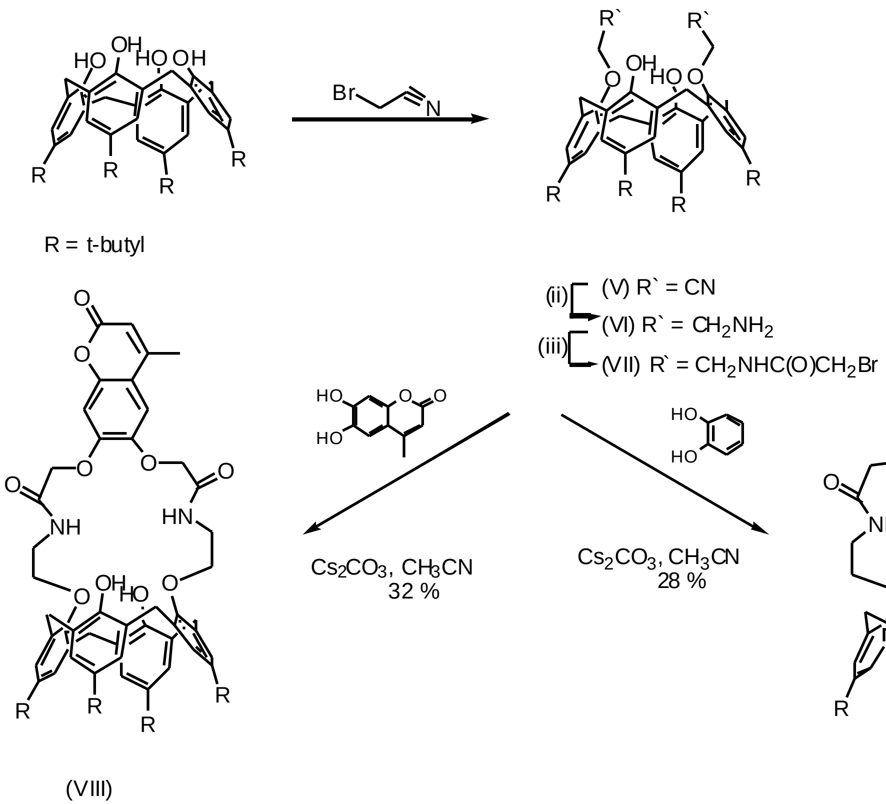




Metal ion coordination to the oxygen in the 7-position of coumarin interferes with charge transfer process, quenching fluorescence

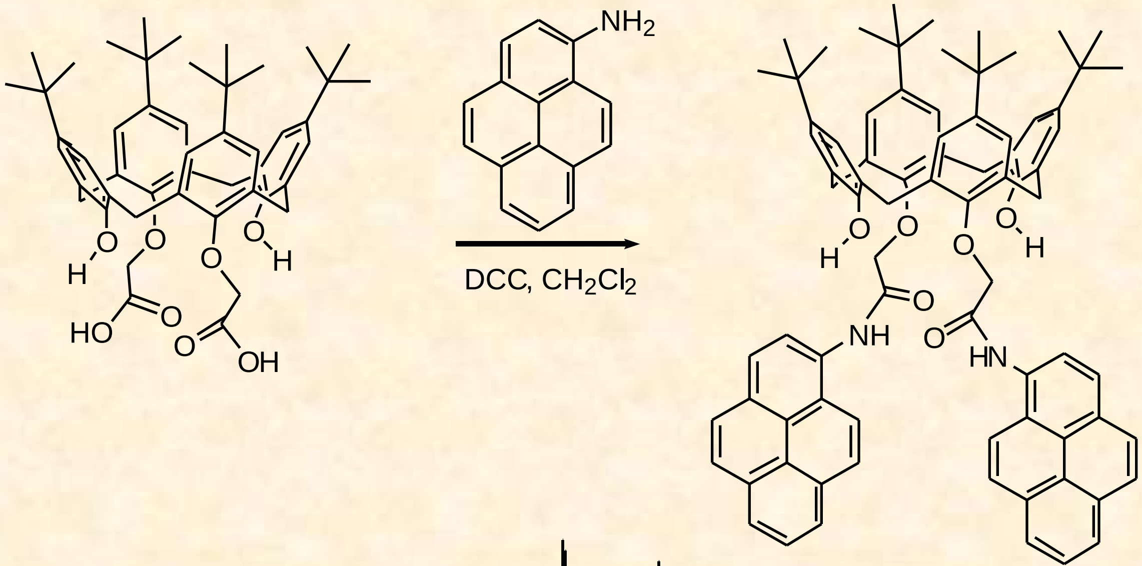
Synthesis of calix-crown ether with coumarin reporter is shown

Calix[4]arenes in the cone conformation for strontium selectivity

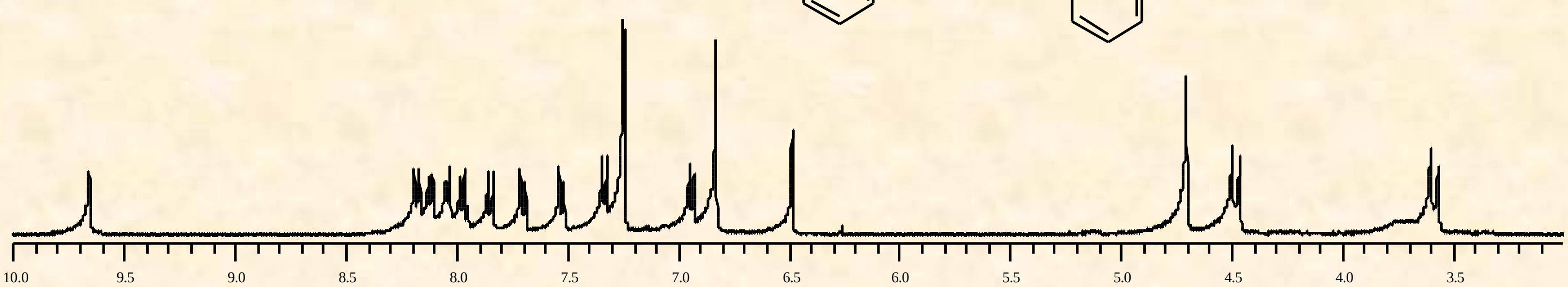


Excimer Formation as a Sensing Mechanism

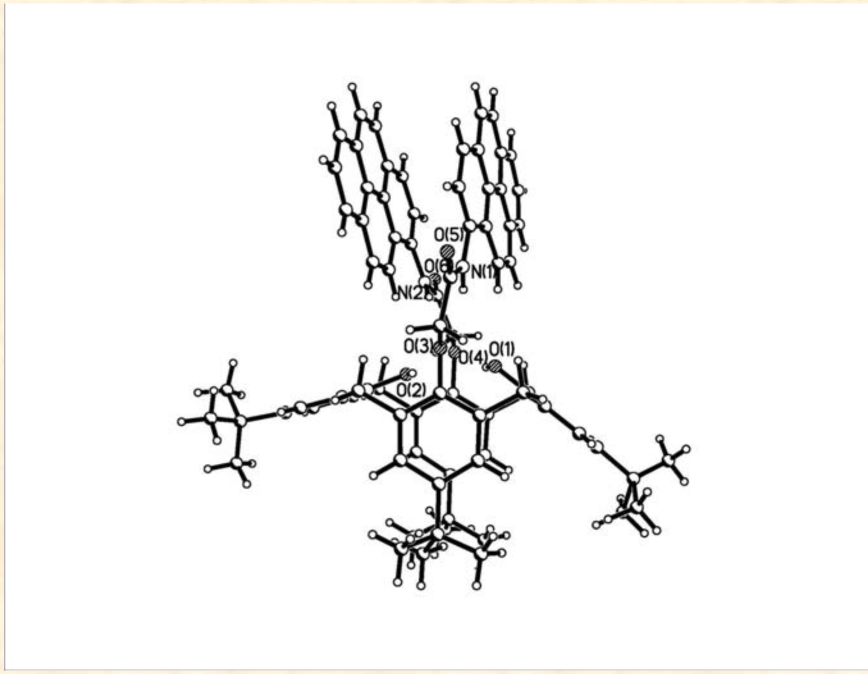
Excimer and exciplex formation and breaking is an attractive signaling mechanism; pyrene-pyrene interactions under investigation

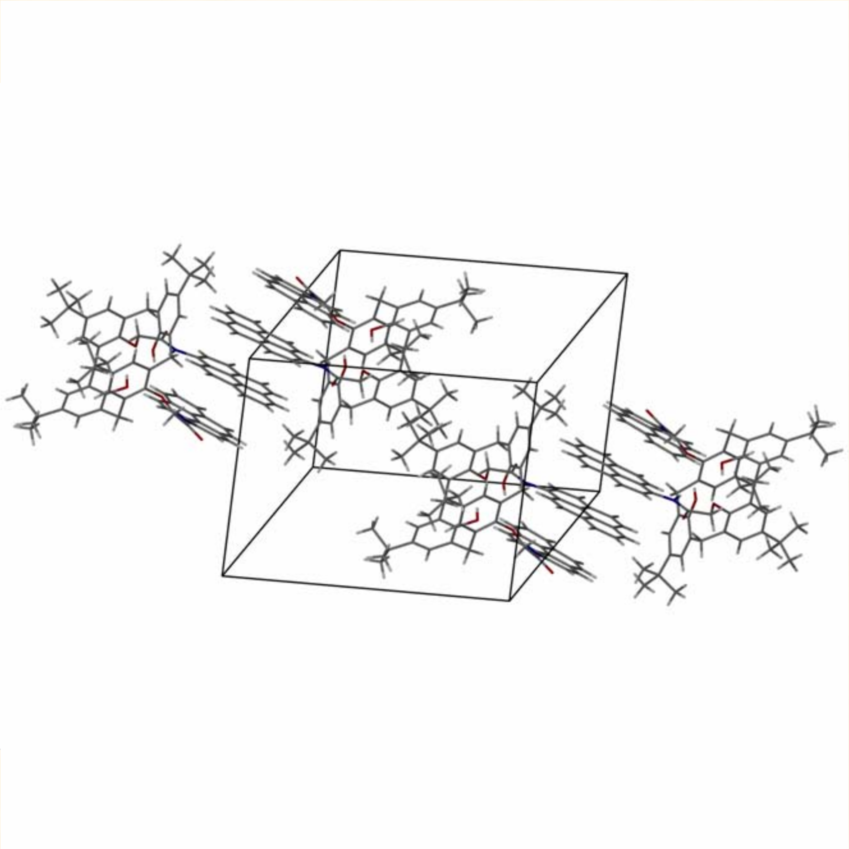


Pyrenes dimerized in solution; mutual ring currents result in significant chemical shift

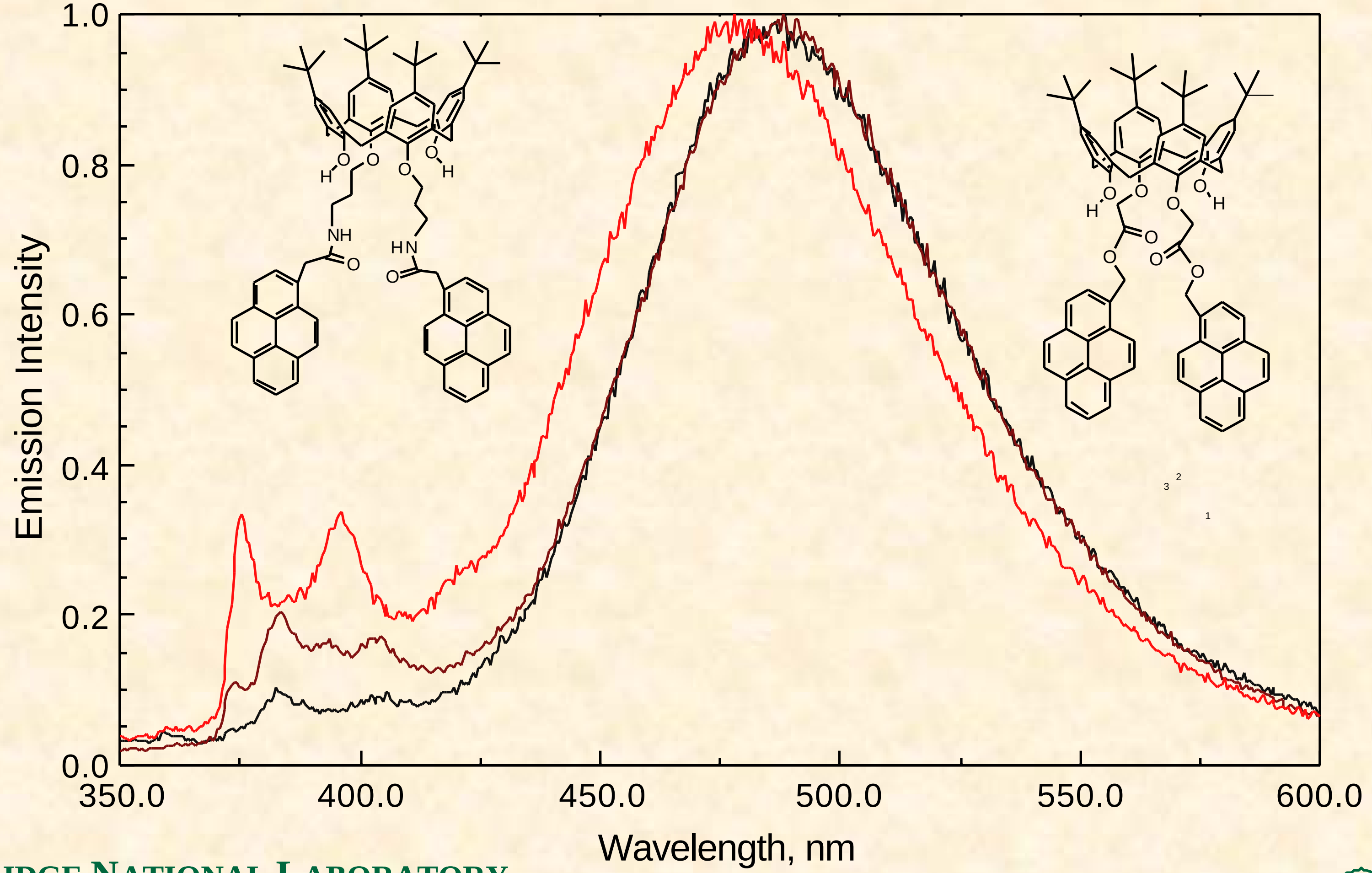


X-ray crystal structure of pyrene calix[4]arene compound – pyrene ground state dimer and pairs of molecules with pyrene interaction

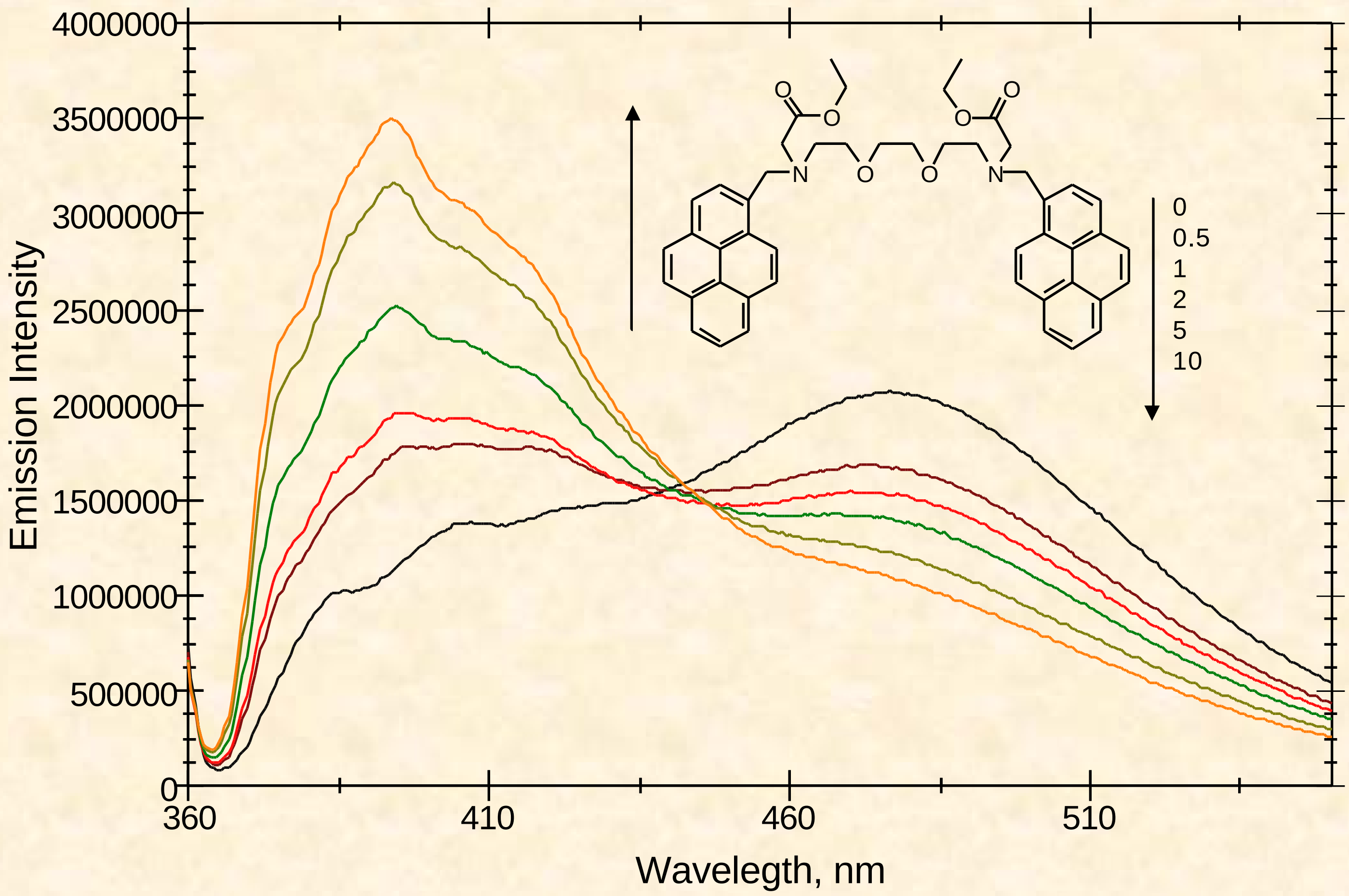




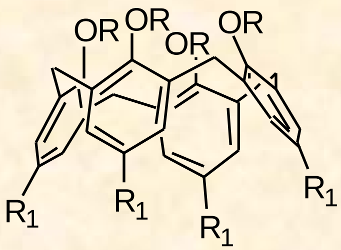
Emission spectra of pyrene-calix[4]arene derivatives shows clear presence of monomer, excited dimer, and excimer



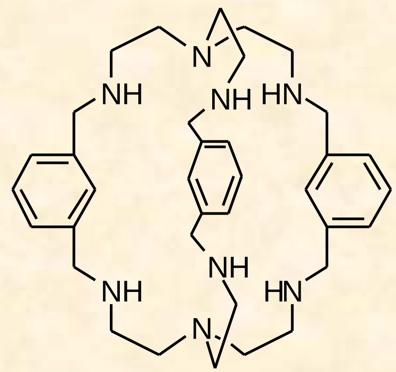
Fluorescence titration of open-chain pyrene ester with Sr^{2+} in acetonitrile - [L] = 5 x 10^{-5} M excitation at 320 nm

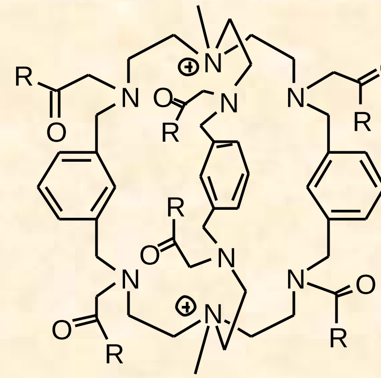


Optical Sensors for Pertechnetate Ion



R_1 = tert.-butyl, H
R = allyl, benzyl, propyl





Tl$^+$ complexed by calixarene will prefer large poorly hydrated anions, charge transfer will influence luminescence of the Tl$^+$ ion

Pertechnetate has been demonstrated to associate with tricyclic amine ligands; exploit the fluorescent properties of the derivative with R = pyrene

Acknowledgements

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