WATER QUALITY

Molecular Recognition Based Sensing of Critical and Emerging LaMP Pollutants: A Versatile New Nano-engineered Materials Approach

Final Report

During our first year of funding, we evaluated currently available thin film testing materials used for detecting toxic agents such as volatile organic compounds (VOCs) and other pollutants that may cause cancer and other human health problems. The materials were able to distinguish between small aromatic and aliphatic molecules of almost identical size and volatility as well as an array of benzene molecules. For our second year of funding, we worked to improve upon the detection levels and chemical selectivity by developing a new family of candidate sensors designed with expanded cavity volumes and restricted entry ports. A second new family of host molecules featuring rectangular cavities, suitable for recognition of planar aromatic contaminant molecules was designed and synthesized. The new sensors demonstrate a greater chemical selectivity for VOCs and other pollutants as well as being capable of detecting these materials at much lower concentrations. Currently, the sensors are still in the developmental stages however, the successful development and use of the sensors will facilitate the ongoing efforts to remediate Lake Michigan. Also, the sensors will be useful for water quality assessment efforts currently underway by providing simple, quantitative, chemically specific measures for critical and emerging pollutants.

Objectives
Design, construction, demonstration and optimization of versatile new sensors and sensor materials for critical and emerging LaMP and EPA pollutants.

Summary of Progress
Screening of thin film materials for recognition and sensing of putative chemical pollutants was performed. An expanded library of mesoporous chemosensory materials was designed and assembled. Improved host materials based on molecular rectangles were designed and evaluated.

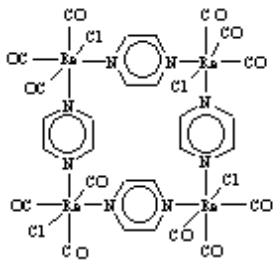
Accomplishments
Chemical discrimination (selectivity in contaminant recognition) has been demonstrated for mesoporous thin film materials featuring ~5 D and ~10 D diameter binding cavities. Studies indicated that the cavities serve a useful role in the solid state. A new class of host molecules featuring expanded cavity volumes and restricted entry ports was designed and constructed. A second new family of host molecules featuring rectangular cavities, suitable for recognition of planar aromatic contaminant molecules, was designed and synthesized. Materials based on these molecules were found to exhibit greater sensitivity and greater selectivity than first-generation materials in pollutant molecule sensing studies. ;

Benefits
Successful sensor development and utilization will facilitate Lake Michigan remediation, compliance and water-quality assessment efforts by providing simple, quantitative, chemically specific measures of critical and emerging pollutants, including non-point source pollutants.

Narrative Report

Molecular recognition based sensors have the potential to deliver inexpensive, highly selective, robust, real time, field-portable, water-contaminant-evaluation capabilities that can be applied to extant great lakes water quality problems. Successful sensor development could facilitate Lake Michigan remediation, compliance, and water-quality assessment efforts by providing simple, quantitative, chemically specific measures of critical and emerging pollutants, including non-point-source pollutants. In year 1 the project focused largely on the evaluation of chemosensory materials already in existence (part a, below). In year 2 the project focused on the design and characterization of new chemosensory materials displaying better molecular recognition and chemical sensing capabilities (part b and c, below).

*Part a: Thin film materials using compounds **1** and **2** have been evaluated for sensitivity to volatile organic compounds (VOCs) by quartz crystal microgravimetry (QCM). The sensing of VOCs was conducted in the gas phase at concentrations ranging from 0.05 to 1 mM. QCM studies with these materials allowed for distinction between the following VOCs: 1) small aromatic versus aliphatic molecules of almost identical size and volatility, and 2) an array of benzene molecules derivatized with electron donating/withdrawing substituents. These experiments indicate that the porous molecular square films act as hosts to VOC guest molecules through both van der Waals and electronic interactions. The films have a much stronger affinity for aromatic molecules versus aliphatic molecules which indicates p–stacking van der Waals interactions. The films also have a preference for electron rich benzene derivatives like toluene or fluorotoluene over electron poor derivatives like fluorobenzene and hexafluorobenzene, supporting the hypothesis that the imine and azine walls of the squares are relatively electron deficient, thus having greater attraction for the electron rich guests. In addition, measurement of host:guest binding constant (M-1) allows for selective VOC detection. Size selectivity is demonstrated by exposure of the "molecular squares" to cyclic ethers of variable size. Thickness dependence plots for dioxame (a 6 membered ring) show no thickness dependence, indicating that the analyte permeates through out the film. On the other hand, 18-crown-6 (an 18 membered ring) shows a significant thickness dependence showing that it cannot permeate through the pores of the film. Also of note are the control experiments run with thin films of **3** and 4 which do not align to form channels in the solid state. In these experiments, the films demonstrated a greatly reduced responsiveness to benzene vapor when compared to the corresponding films derived from the square complexes **1** and **2**.*



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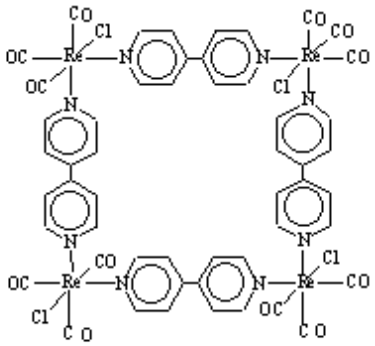

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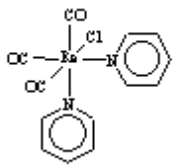

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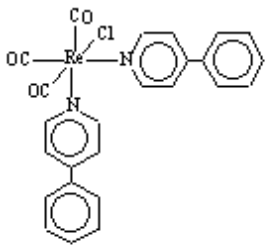

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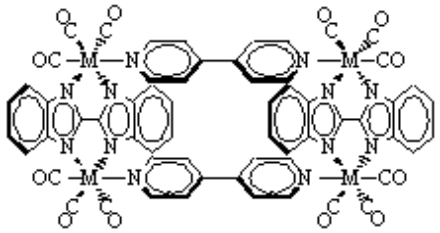
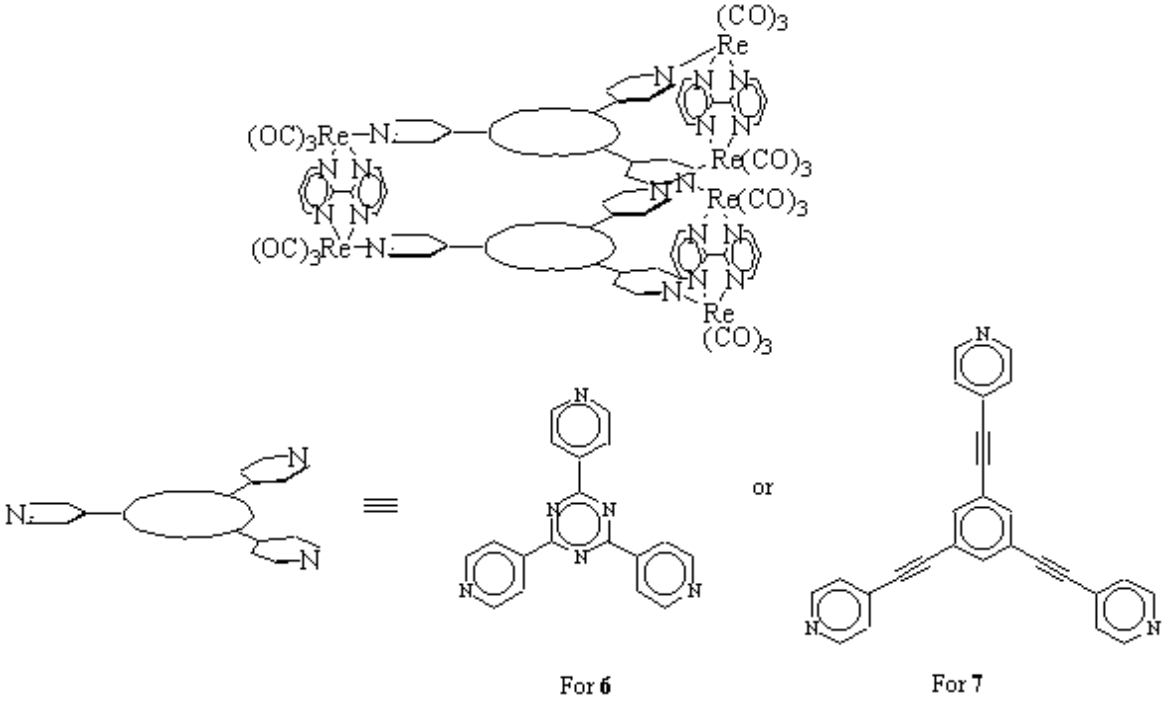
*Part b: The synthesis and characterization of the first two members, **5a** and **b**, of a new family of candidate sensor molecules featuring rectangular cavities for pollutant molecule binding was accomplished. In thin film form both behave as high internal surface area, microporous materials. These new materials display significantly higher affinities (lower detection limits) and greater chemical selectivity with respect to candidate guest molecules (potential pollutants) than do the first-generation materials described in part a.*



5a M = Mn^I

5b M = Re^I

*Part c: The synthesis and characterization of new compounds which may serve as host molecules for sensing VOCs and other pollutants has also been explored. Two haxametallic host molecules have recently been developed (**6** and **7**) which utilize 2, 2'-bipyrimidine to bridge rhenium(I) tricarbonyls at three points along the short edge of the cavity, and triply functional pyridine-based ligands (2,4,6-tripyridyl-1,3,5-trizaine or 1,3,5-tris(4-ethynylpyridyl)benzene) as a top and bottom. Modeling has been done to determine the volumes of the cavities and the sizes of the entry ports for the host molecules. The volumes for the new species are two to three times as large as related "molecular rectangle" complexes which should allow for the sequestering of several potential guests, and which should provide a more completely encapsulating, and thus more hydrophobic, cavity. The structure of the bridging ligands should also allow functionalization of the cavity entry ports which would allow further chemical and size selectivity.*



For **6** For **7**

Publications

"Luminescent Mesoporous Molecular Materials Based on Neutral Tetrametallic Rectangles", K. D. Benkstein, J. T. Hupp, and C. L. Stern Angew. Chem. Int. Ed., 2000, 39, 2891-2893.

"Synthesis and Characterization of Hexametallic Molecular Hosts Featuring Large Cavity Volumes and Constrained Cavity Port Sizes", K. D. Benkstein and J. T. Hupp, Mol. Cryst. Liq. Cryst., 1999, submitted.

"Mesoporous Thin Films of "Molecular Squares" as Sensors for Volatile Organic Compounds", M. H. Keefe, R. V. Slone, J. T. Hupp, K. F. Czaplewski, R. Q. Snurr, and C. L. Stern, Langmuir, 2000,

"Luminescent Sensor Molecules Based on Coordinated Metals: A Review of Recent Developments", M. H. Keefe, K. D. Benkstein, and J. T. Hupp, Coord. Chem. Rev., 2000, in press.

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Research Information

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