**4. TITLE AND SUBTITLE**
Structures and Energetics of Macromolecular Systems: POSS, Metal Clusters and Other Oligometric Molecules

**6. AUTHOR(S)**
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University of California Santa Barbara

**14. ABSTRACT**
Work has been completed in three areas of research. The first is in characterization of polyhedral oligomeric silsesquioxanes (POSS) and their attachment to backbones of organic-based oligomers. Using ion mobility, we have structurally characterized a wide variety of POSS species attaining good agreement with x-ray structures when available. We have also characterized di- and tri-siloxanes, POSS cages covalently bound via oxygen bridges. Most recently we have been able to insert a fluoride ion into the cage which should make detection of larger POSS/oligomer systems feasible. The second area of research deals with organic oligomeric systems. We have focused on systems with potential for opto-electronic or organo-electronic device formation. Successful work has been completed on a series of polyphenyl vinylenes and several paracyclophanes. Finally, we have generated and characterized the structures and ligand binding energies of both anionic and cationic gold and silver clusters (n = 2 to 13). These systems have been shown to have size-dependent catalytic behavior for double bond oxidation in small alkenes when dispersed on titanium oxide surfaces. We have focused on C2H4 and CH3CHCH2 due to their industrial importance.
Final Report
March 31, 2006

Structure and Energetics of Macromolecular Systems: POSS, Metal Clusters and Other Oligomeric Molecules

AFOSR Grant F49620-03-1-0046

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Santa Barbara, CA 93106-9510

I. Progress has been made on the objectives listed below since the grant was initiated on January 1, 2003. Work that was discussed in previous reports (Sept. 1, 2003, Sept 1, 2004 and Sept. 1, 2005) will not be repeated here. In addition, a renewal proposal was submitted in February, 2005 that both summarized work completed and gave updated descriptions of work in progress. That work also will not be repeated here. Only new work initiated or completed since September 2005 will be discussed.

II. Objectives

A. Structure and Characterization of Polyhedral Oligomeric Silsesquioxanes (POSS)
B. Organic Oligomers
C. Metal Clusters: Structure and Ligand Energetics

III. Progress and Accomplishments

As noted above, there have been detailed annual reports filed giving progress up to September, 2005. Here we will briefly summarize work done between September 1 and December 31, 2005.

A. POSS

We have nearly completed studies on a series of R7T8-POSS monomers, in which fluoride ion is trapped in the POSS cage as demonstrated by both NMR chemical shifts and mass spectroscopy. These derivatives are prepared easily by reacting equi-molar amounts of the neutral POSS with tetramethylammonium fluoride in THF under rigorous anhydrous conditions. X-ray studies have shown that the F\(^-\) ion is situated in the center of the cage when R = phenyl and vinyl. The Edwards group has synthesized new well-characterized POSS systems with R = isobutyl, styryl, phenyl, trifluoropropyl, fluorohexyl, fluoroocyl, and fluorodecyl, in addition to these previously known phenyl and vinyl species. We have
negative ion ESI studies on all of these monomers and positive ion MALDI and ion mobility data (fluoride species cationized to R_7T_8-POSS (HF)_Na^+) were obtained for several of these species. Experimental cross-sections agree within 2% with x-ray structures and with modeled structures (see Tables 1 and 2). Fluoride ion is also incorporated into cages in the presence of water, but side reactions occur which open cages and create a complicated series of oxo-anions. We have been able to determine many of these oxo-structures and model them. The fluoride monomer work is being written up for publication.

The monomer results are potentially very significant if the fluoride ion can be incorporated routinely into the POSS cage of oligomers. This simple derivatization would allow us to observe these systems and measure their cross sections. We have in hand a phenyl-POSS PMA 8-mer with one or two fluoride ions trapped in the POSS cages. We are in the process of characterizing it.

**Table 1. Collision Cross-Sections (Å²) of the POSS Fluoride Monomers.**

<table>
<thead>
<tr>
<th>Species</th>
<th>Mass</th>
<th>X-ray^a</th>
<th>ESI (MALDI)</th>
<th>Theory</th>
</tr>
</thead>
<tbody>
<tr>
<td>[(CF_3CF_2_3(CH_2)_2)_8T_8F^-</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sty_8T_8F^-</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ph_8T_8F^-</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Vi_8T_8F^-</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Vi_10T_10F^-</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Vi_12T_12F^-</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>i-Bu_7StyT_8F^-</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>i-Bu_6Sty_2T_8F^-</td>
<td></td>
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<td></td>
</tr>
<tr>
<td>i-Bu_3Sty_3T_8F^-</td>
<td></td>
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</tr>
<tr>
<td>i-Bu_4Sty_4T_8F^-</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(CF_3CH_2CH_2)_8T_8F^-</td>
<td></td>
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<td></td>
<td></td>
</tr>
</tbody>
</table>

Vi = vinyl; Ph = phenyl; Sty = styryl; i-Bu = i-butyl; T_8 = Si_8O_12  
^a. Structures obtained from Dr. Tim Haddad at ERC Inc., Air Force Research Laboratory  
b. Calculated value for the neutral species.  
c. Values correspond to two possible isomers.  
d. Values identical for all possible isomers within experimental error.

**Table 2. Collision Cross-Sections (Å²) of the Sodiated POSS Fluoride Monomers.**

<table>
<thead>
<tr>
<th>Species</th>
<th>X-ray</th>
<th>MALDI (Na^+)</th>
<th>Theory (Na^+)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na^+Sty_8T_8·HF</td>
<td></td>
<td>321</td>
<td>325</td>
</tr>
<tr>
<td>Na^+Ph_8T_8·HF</td>
<td>263^b</td>
<td>254</td>
<td>257</td>
</tr>
<tr>
<td>Na^+Vi_8T_8·HF</td>
<td>168^b</td>
<td>165</td>
<td>167</td>
</tr>
</tbody>
</table>

Vi = vinyl; Ph = phenyl; Sty = styryl; i-Bu = i-butyl; T_8 = Si_8O_12  
a. Structures obtained from Dr. Tim Haddad at ERC Inc., Air Force Research Laboratory  
b. Calculated value for the neutral species.
B. Metal Clusters

The work on gold clusters has now been completed and a manuscript is in draft form.

IV. Papers published or in press


V. Personnel Supported

<table>
<thead>
<tr>
<th>A. Senior</th>
<th>B. Junior</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dr. Paul Kemper</td>
<td>Mr. Manuel Manard</td>
</tr>
<tr>
<td>Dr. Thomas Wyttenbach</td>
<td>Ms. Erin Baker</td>
</tr>
<tr>
<td>Dr. Jennifer Gidden</td>
<td>Mr. John Bushnell</td>
</tr>
<tr>
<td>Dr. Stan Anderson</td>
<td>Ms. Dena Bodzin</td>
</tr>
<tr>
<td>Ms. Connie Mitchell</td>
<td></td>
</tr>
</tbody>
</table>

VI. Papers Presented

A. Invited Lectures at Meetings

1. Field and Franklin Award Symposium, American Chemical Society Meeting, New Orleans, LA, Mar. 2003


6. Plenary Lecture, Department of Energy Basic Energy Sciences Analysis Program Contractors Meeting, Annapolis, MD, Feb. 2004

7. Plenary Lecture, German Mass Spectrometry Meeting, Leipzig, Germany, Mar. 2004


15. Air Force Contractors Meeting, Monterey, CA, May 2005

B. Contributed Papers at Meetings


3. Four Papers, Ion Chemistry Conference, Lake Arrowhead, CA, Jan. 2004


C. Seminars at Universities

1. UC San Diego, Jan. 2003

2. UC Santa Barbara, Apr. 2003

VII. Honors/Awards

New

none

Continuing/Prior

1. Honoree of a Special Issue of the International Journal of Mass Spectrometry (There were 84 papers comprising all of vols. 185, 186 and 187 -- June 1999)

2. Fellow, American Physical Society (elected 1987)

3. Fellow, American Association for the Advancement of Science (elected 1994)

4. Fellow, John Simon Guggenheim Foundation (1995 Calendar Year)

5. Nobel Laureate Signature Award, American Chemical Society (1989)

6. Faculty Research Lecturer, University of California at Santa Barbara (1994) (This is the highest award given by the UCSB Academic Senate. There is one award given each year campus-wide.)

7. Frank H. Field and Joe. L Franklin Award for Outstanding Achievement in Mass Spectrometry, American Chemical Society (1996)

8. Thomson Gold Medal, International Mass Spectrometry Society (1997) (This is the highest award given internationally in mass spectrometry. There is one award given each year.)

9. Distinguished Contribution Award, American Society of Mass Spectrometry (2004) (This is the highest award presented by ASMS. It is given to one person each year for a specific scientific contribution.)


VIII. Transitions

None in this time period
IX. New Discoveries, Innovations or Patent Disclosures

None