3-28-2014

Isolation of Various Endohedral Metallofullerenes with a More Efficient Lewis Acid

Khristina A. Rottinger
Indiana University - Purdue University Fort Wayne

Muska Fahim
Indiana University - Purdue University Fort Wayne

Kristine Arvola
Indiana University - Purdue University Fort Wayne

Follow this and additional works at: http://opus.ipfw.edu/stu_symp2014

Recommended Citation
http://opus.ipfw.edu/stu_symp2014/18

This Poster is brought to you for free and open access by the IPFW Student Research and Creative Endeavor Symposium at Opus: Research & Creativity at IPFW. It has been accepted for inclusion in 2014 IPFW Student Research and Creative Endeavor Symposium by an authorized administrator of Opus: Research & Creativity at IPFW. For more information, please contact admin@lib.ipfw.edu.
**Abstract**

**Goal:** We strive to develop new separation strategies for isolating endohedral metallofullerenes, which contain clusters of metals, carbides, nitrides, or oxides that are trapped inside fullerene cages. We seek a non-chromatographic approach that will take advantage of differences in chemical reactivity among the 50+ different types of fullerenes and metallofullerenes. Metallofullerenes possess an electron-rich carbon cage surface that can react with electron-deficient Lewis acids. We report an improved separation method to replace the currently used aluminum chloride technique with more selective Lewis acids. Results indicate a successful and selective separation of a diverse array of metallofullerene types.

**Experimental**

- **MALDI Analysis:** Mass spectral data (positive ion mode) is obtained from a Bruker Microflex LT mass spectrometer. Samples are deposited on a stainless steel plate without using a matrix.
- **SAFA (Stir and Filter Approach):** 500 mg of extract containing Gd metallofullerenes is dissolved in 750 mL xylene. 30 g of dried monoaminosilica is added to uptake the reactive fullerenes and reactive metallofullerenes until only C60 C70 and the most inert metallofullerene (Gd,N@C60) remain in solution.
- **Lewis Acid Precipitation and Decomplaxation:** Metallofullerene samples are dissolved in C54. A Lewis acid (e.g., ZnCl₂, MgCl₂) is added to the SAFA filtrate to selectively precipitate Gd or Sc metallofullerenes. After filtration, the precipitate is placed in a beaker for decomposition with ice water for subsequent workup in a separatory funnel. Metallofullerenes re-dissolve in the C54 organic layer. MALDI data demonstrate the successful separation and isolation of metallofullerene samples.

**Results: Fractionation of Gadolinium Metallofullerenes via Selective Reactions**

<table>
<thead>
<tr>
<th>Scandium Metallofullerenes</th>
<th>Gadolinium Metallofullerenes</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sc AntiSAFA Extract</td>
<td>Gd Extract</td>
</tr>
<tr>
<td>Sc @C60 @C70</td>
<td>Gd,N@C60</td>
</tr>
<tr>
<td>ScO@C60</td>
<td>Gd@C60</td>
</tr>
<tr>
<td>Sc,N@C60</td>
<td>Gd @C60</td>
</tr>
<tr>
<td>Sc,N@C70</td>
<td>Gd,N@C70</td>
</tr>
<tr>
<td>Sc,N@C80</td>
<td>Gd,N@C80</td>
</tr>
<tr>
<td>LaSc @C60</td>
<td>LaSc @C70</td>
</tr>
<tr>
<td>LaSc @C80</td>
<td>LaSc,N@C60</td>
</tr>
<tr>
<td>LaSc,N@C70</td>
<td>LaSc,N@C80</td>
</tr>
<tr>
<td>MgCl₂,PPT After 2 d</td>
<td>Unreacted Fullerenes</td>
</tr>
<tr>
<td>Step 1 ZnCl₂, PPT After 1 h</td>
<td></td>
</tr>
<tr>
<td>Step 2 ZnCl₂, PPT After 2 h</td>
<td></td>
</tr>
<tr>
<td>Step 3 MgCl₂, PPT After 4 h</td>
<td></td>
</tr>
<tr>
<td>Step 4 MgCl₂, PPT After 7 h</td>
<td></td>
</tr>
</tbody>
</table>

**SAFA (Stir and Filter Approach)**

- **Scalable from microgram to grams**
- **Isomerically purified samples**
- **No expensive equipment or costly reagents**
- **Selective fullerene uptake, unattended**
- **Non-chromatographic approach**
- **No refluxing solvent, ambient separations**

**Conclusions**

- **New Isolation Method:** By manipulating our selection of Lewis acid, we can separate metallofullerenes based on their reactivity differences.
- **Multi-Stage, Non-HPLC Approaches:** Combining our Stir and Filter Approach (Stage 1) with our Lewis Acid method (Stage 2), we demonstrate powerful non-HPLC techniques toward separating different types of metallofullerenes.
- **Array of Metallofullerenes:** Our methods work for LaSc, Sc, and Gd metallofullerene.

**Funding**

- NSF RUI CHE #1151668

---

**“Isolation of Various Endohedral Metallofullerenes with a More Efficient Lewis Acid”**

Kristina A. Rottinger, * Muska Fahim, Kristine Arvola, and Steven Stevenson (Advisor)

Stevenson Research Group, Chemistry, IPFW, Fort Wayne, IN 46805

stevenss@ipfw.edu (260-481-6290)