The synthesis and characterization of novel PAH-capped oligosilane monomers: toward self-assembling, ball-and-socket polysilane-fullerene hybrids

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Abstract:

Several PAH-capped \((\text{SiMe}_2)_6\) tethers will be prepared and characterized and their electronic properties explored; an example is shown in Figure 1. The most promising will be used in future research projects that hope to exploit \(\pi-\pi\) (non-covalent) interactions between buckminsterfullerene, \(\text{C}_{60}\), and PAH moieties to achieve electronically interesting (e.g. photoconducting), ball-and-socket oligo/polysilane-fullerene hybrids that are able to self-assemble into stable monolayers (Figure 2).

Figure 1

![Figure 1](image1.png)

Figure 2

![Figure 2](image2.png)
I. Statement of the Problem/Purpose

There is a growing and significant interest in designing more efficient photovoltaic devices using organic and organosilicon materials. Photovoltaic devices are used to construct solar cells that convert solar energy into electrical energy. This electrical energy, which is clean and environmentally friendly, can be used to supplement chemical energy derived from non-renewable resources such as petroleum and coal. Even though the maximum efficiency of present organic photovoltaic devices is less than 7%, organic photovoltaic cells are more flexible, sturdier, and cheaper than their crystalline silicon counterparts whose efficiencies have recently reached 28%.\(^1,2\)

This author proposes to investigate, through computational methods, and synthesize novel PAH-capped oligosilanes that form self-assembled monolayers. It is hoped that photovoltaic devices which exploit these monolayers will be used to build more efficient and cost-effective solar cells.

II. Significance of the Problem

Due to its ability to form long-lived excitons in the presence of electron donors, C\(_{60}\) can dramatically increase the charge mobility of a polycrystalline film, a very desirable characteristic for organic-based solar cells.\(^3-5\) C\(_{60}\), therefore, has become one of the most useful materials for the construction of organic-(polymeric) photovoltaic cells; examples of many optoelectronic devices that are composed of photoconductive organic thin films in a heterostructure with fullerenes in the electron conducting layer have been described.\(^3,4,6-8\) The most recent of these devices have been shown to be very efficient but are relatively complex and difficult to construct and usually include separate, light-harvesting chromophores in a distinct layer with an additional exciton blocking layer to protect the delicate acceptor and donor substrates (Figure 3).\(^9\)

It has been shown, by the author and other researchers, that fullerene-doped polysilanes also exhibit significant photoconductivity, similar in efficiency and hole mobility to the best organic devices.\(^10-15\) Photodevices utilizing PAH-capped polysilane-fullerene SAMs of the type the author proposes should be relatively simple to construct, once the preparation of the various monomers has been optimized, and may yield quantum efficiencies an order of magnitude higher than current available organic devices as the fullerene will be directly and intimately associated with the polysilane cores where photoelectron

![Figure 3](image1)

![Figure 4](image2)
generation and charge separation occurs, negating the need for complex heterostructures (Figure 4).\textsuperscript{5,12,16,17} One problem when using polysilanes, however, is their tendency to degrade over time when exposed to ultraviolet radiation.\textsuperscript{18} It has been recently suggested, however, that self-assembling monomers may be able to reorganize themselves spontaneously to exclude cross-linked and/or photo-degraded domains, thus increasing the longevity of the entire photovoltaic device.\textsuperscript{19}

In addition, as no examples of PAH-capped oligo/polysilane fullerene hybrids have been reported, a published synthesis and characterization of one or more of these macromolecules may increase interest and stimulate further investigations into their electronic properties in other laboratories.

### III. Summary of Pertinent Literature

Since the discovery of a method for the macroscopic synthesis of buckminsterfullerene ($\text{C}_{60}$) in 1990, this crystalline allotrope of carbon has been studied extensively, revealing many interesting chemical and physical properties.\textsuperscript{20-21} For example, $\text{C}_{60}$, with a relatively low lying $\pi$ LUMO, has one of the highest electron affinities of any nonderivitized organic compound.\textsuperscript{22,23} In contrast, polysilanes, macromolecules in which silicon atoms are bonded directly to themselves in long, uninterrupted chains, have delocalized
σ-electrons with relatively high energy HOMOs. These respective properties provide an interesting opportunity for the synthesis of fullerene-polysilane adjuncts with extensive σ-π conjugation; it has been shown that photoexcitation of such a system may induce promotion of an electron from the polysilane σ-electron backbone into the conjugated fullerene cage creating a hole(+) charge carrier (Figure 5). In fact, merely doping (mixing) a polysilane with C₆₀ can increase the photoconductivity of the organosilicon polymer by an order of magnitude, presenting the possibility of using polysilane-fullerene hybrids to construct molecular wires and/or organic photocells. Fullerene-polysilane covalent hybrids that have been synthesized and reported, by this and other researchers, are extensively cross-linked, a consequence of the polymerization process. Such cross-linking significantly inhibits hole mobility drift by isolating conducting domains. It would be useful, therefore, to have high control over the polymerization process to prepare polymers of well-defined structure with little or no cross-linking.

Another characteristic of C₆₀, also related to its extensive π-network and one it shares with most aromatic compounds, is the ability to form relatively stable complexes through hydrophobic, π-π stacking interactions. Several recent examples have been reported that take advantage of these forces to form fullerene-organopolymer aggregates or macromolecules. No example, however, has been published of a fullerene-polysilane that depends primarily on these π-π interactions to drive a self-assembly process. Monomers that spontaneously form well-defined, macroscopic layers are attractive as one can effect direct orientation at the time of polymerization using physical or chemical means. Highly oriented polymers, including ones that self-assemble, are much more efficient photoconductors and are therefore necessary to construct the most photosensitive optoelectronic devices.

After thoughtful and thorough consideration of the relevant literature, including the author’s own research experience and previous attempts to produce fullerene-polysilane hybrids with well-defined structure, the author proposes the synthesis of one or more PAH-capped polysilane hybrids in a three-phase, 1.5-2 year project that will study not only the physical properties of these compounds, but will also explore the ability of these monomers to self-assemble due to π-π stacking interactions in the presence of C₆₀ to form highly oriented ball-and-socket monolayers (Figure 6). A culminating project will incorporate the sturdiest of these SAMs into an organosilicon photocell so that the quantum efficiency of these hybrid structures can be investigated.

Figure 6

A. PAH-capped oligosilanes (solvated)  B. Self-assembled monolayers

\[ C_{60} \]
IV. Not applicable.

V. Design and Methods by Schedule (A – D)

Phase 1. Fall 2007-Spring 2008

Choosing the PAH candidates using molecular dynamics (semi-empirical computations)
In collaboration with Dr. Mark Freitag, Creighton University. 37

Using recently published computational methods, one or two promising PAH caps will be chosen after considering the following questions:

i. Does the PAH have sufficient $\pi$-$\pi$ interaction with $C_{60}$ to initiate and sustain a self-assembly process of the type previously described?

ii. Does the PAH and $C_{60}$ share solubility in one or more common solvents?

iii. Is the PAH synthesized using readily available laboratory equipment?

iv. Will this laboratory be able to purify and characterize the PAH with available instrumentation?

v. Is the synthesis relatively cost effective and safe for an undergraduate laboratory?

Methods: One or more of the following PAH caps will be chosen after molecular dynamics analysis using the effective fragment potential (EFP) method to determine equilibrium geometries and interaction energies between $C_{60}$ and the PAH motif. The EFP method has been recently shown to be a reliable and computationally inexpensive means for determining these types of intermolecular attractions. 38

![Diagram of PAH caps](image-url)
A literature search has revealed published procedures for the synthesis of compounds 1 - 5 above. Due to the amount of computer time needed for these calculations using the EFP method, it is reasonable to assume that at least one candidate can be found by April 2008. As detailed computational studies of these types of π-stacking systems have not been previously reported, it will be important to publish the results of Phase 1 as soon as feasible.

**Phase 2A. Summer 2008 (The period covered by this fellowship.)**

**Synthesizing the PAH caps**

The unique data and results of the molecular dynamics project (computational studies) from Phase 1 will be submitted for publication.

**Methods:** One or two candidates chosen in Phase 1 will be prepared using either a published (modified) or de novo procedure developed in this laboratory. Products will be characterized using \(^1\)H-NMR, \(^{13}\)C-NMR, UV-Vis, IR, and MALDI TOF mass spectroscopy. As an example, a published partial synthesis of 5 was found in the literature and is described in Scheme 1.39

Scheme 1

![Scheme 1](image-url)
Phase 2B. Fall 2008

Synthesizing the PAH-capped oligosilane
A successful modified or de novo synthesis from Phase 2A will be submitted for publication.

Methods: The PAH oligosilane will be synthesized and characterized using $^1$H-NMR, $^{13}$C-NMR, UV-Vis, IR, and MALDI TOF mass spectroscopy. The final product will be purified by column chromatography. This procedure will be highly dependent on the PAH. As an example, a proposed synthesis is shown in Scheme 2 that begins with a methylated analog of compound 3. Steps 2 and 3 have not been published and are proposed by the author.40
Phase 3. Spring 2009

The interaction between C$_{60}$ and the PAH-capped oligosilane synthesized in Phase 2B will be investigated, paying special attention to its ability to form self-assembled polymers. Further investigation will probe the electronic properties of the PAH-oligosilane-fullerene hybrid using standard methodology familiar to this author.

Summer 2009: A final manuscript will be submitted for publication that summarizes the results from all phases of the project.

Initial funding will come from new faculty start up funds provided by the College of Arts and Sciences. The author will seek additional funding from ACS-PRF Grant B and Research Corporation.

VI. References

VII. Appendices
A. Biographical Sketch
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Academic Degrees

Ph.D. in Organic Chemistry, 1997
University of Wisconsin–Madison

B.S. in Chemistry, 1989, summa cum laude
Augusta State University (formerly Augusta College)

Brief Synopsis of Teaching and Professional Experience

Assistant Professor, Organic Chemistry
Creighton University, August 2007 – present

Resident Assistant Professor, Organic and General Chemistry
Creighton University, July 2004 – May 2007

Assistant Professor, Organic Chemistry
Utica College, August 1999 – May 2004

Postdoctoral Appointment, Chemical Education

Visiting Lecturer, General Chemistry
University of Wisconsin-Madison, August 1997 – May 1998

Senior Instructor and Coordinator
University of Wisconsin-Madison, Summer Enrichment Program, 1991–1999 (May - July)
Relevant Presentations at Local and National Conferences (Students in Bold)

The Reaction of Triphenylsilanilimine with Buckminsterfullerene; Anthony Di Pasqua and Michael Miller; Booklet of Abstracts, 5th Annual Research Conference, Utica College; Utica, NY (2003).

The Synthesis of Novel Fulleroids via Free-Radical Addition Reactions; Anthony Di Pasqua and Michael Miller; Abstracts and Proceedings; 5th Annual Research Symposium in the Chemical and Biological Sciences, University of Maryland-Baltimore County (2002).


Toward the Synthesis of Water-Soluble Fulleroids; Paul Sardina and Michael Miller; Booklet of Abstracts, 4th Annual Undergraduate Research Conference, Utica College; Utica, NY (2002).

The Reaction of AIBN with Buckminsterfullerene; Paul Sardina and Michael Miller; Abstracts and Proceedings; 4th Annual Research Symposium in the Chemical and Biological Sciences, University of Maryland-Baltimore County (2001).


The Hydrosilylation of Cyclohexene Fulleroid; Paul Sardina and Michael Miller; Booklet of Abstracts, 3rd Annual Undergraduate Research Conference, Utica College; Utica, NY (2001).

Relevant Publications and Preceedings

Platinum-Catalyzed Hydrosilylation of C_{60}; Synthesis of a Novel Fullerene-Siloxane Polymer; Michael Miller and Robert West, Chemical Communications, 1999, 1797-1798.


Silicon Polymers of C_{60}; Robert West, Kunio Oka, Hideaki Takahashi, Michael Miller, and Takahiro Gunji, in Inorganic and Organometallic Polymers II, P. Wisian-Nielson, H. R. Allcock,

*Platinum Catalyzed Hydrosilylation of Buckminsterfullerene: Synthesis of a Novel C\textsubscript{60}-Siloxane Copolymer*; Michael Miller, Kunio Oka, Birgir Gudmundsson, and Robert West; Abstracts and Proceedings, 10th Symposium on Organosilicon Chemistry; Poznan, Poland, p. 114 (1993).

*Silicon Derivatives of Buckminsterfullerene*; Kunio Oka, Takahiro Gunji, Hideaki Takahashi, Michael Miller, and Robert West; Abstracts and Proceedings, 10th Symposium on Organosilicon Chemistry; Poznan, Poland, p. 235 (1993).

**Recent Grant Applications**

*Cisplatin-Peptide Conjugates*, ACS PRF, 10/14/2005
Consultant in collaboration with James C. Dabrowiak, PI, Syracuse University

*Mechanism of Cisplatin Resistance*, NIH, 9/26/2004
Consultant in collaboration with James C. Dabrowiak, PI, Syracuse University

**Professional Service (College/University)**

- 2005 – 2006 Chair, American Chemical Society-Omaha Chapter
- 2003 – 2004 Utica College Faculty Senate By-laws Review Committee
- 2003 – 2004 AAUP-UC, Governing Board Member (at large, elected)
- 2002 – 2004 Nominating Committee of the Faculty Senate, Chair (elected)
- 2002 – 2004 Coordinating Council of the Faculty Senate, *ex officio*
- 2001 – 2004 Office of Higher Education Opportunity Programs, Faculty Mentor
- 2001 – 2004 Nexus Seminar Series, Coordinator
- 2001 – 2004 Utica College Undergraduate Research Conference, Director
- 2000 – 2004 Advisory Committee for the Health Professions
- 2000 – 2004 Academic Advising Award Selection Committee
- 1999 – 2004 Student Affiliates of the ACS-UC Chapter, Faculty Advisor
- 2001 – 2003 AAUP-UC, Secretary (elected)
- 2001 – 2002 Utica College Commencement, Faculty Marshall
- 1999 – 2001 Nominating Committee, Secretary (elected)
- 1999 – 2000 Committee on Student Retention

**Professional Service (Community)**

- April 2006 Chemistry Field Day, Creighton University
- April 2005 Chemistry Field Day, University of Nebraska-Omaha
- 2002 – 2004 Big Brothers/Big Sisters Annual Fall Demonstration, Director
- 2000 – 2004 Board of Cooperative Educational Services, Student Research Mentor
- 2000 – 2004 Scientific Review Committee for ISEF affiliated science fairs
2001 – 2003  International Science and Engineering Fair, Regional Director
2001 – 2003  Chemical Research Symposium, University of Maryland, Invited Judge
2000 – 2001  International Science and Engineering Fair, Committee Member

Awards and Honors

Research Grant Award, Utica College, Spring 2003
Summer Research Fellowship, Utica College, 2000
Stonebridge Full Academic Scholarship, Medical College of Georgia, 1989
Phi Kappa Phi Honor Society, Augusta College, 1989
Mixon Chemistry Teaching Award, Augusta College, 1989
John Pierce Award in Organic Chemistry, Augusta College, 1989

B. Budget Justification
PI: Dr. Michael L. Miller

Stipend: $4300.00
Dr. Miller will plan, synthesize, and characterize one or more PAH-oligosilane hybrids as described in Section V, Phase 2A of this document (Summer 2008): 10 weeks.

Direct Costs Associated with Research Plan: $500.00
To be used to purchase reagents, solvents, and analytical support including MALDI TOF characterization.

C. Supporting Materials
Acronyms encountered in the text.
1) PAH: polycyclic aromatic hydrocarbon.
2) SAM: self-assembled monolayer (or self-assembling monomer)
3) LUMO: lowest unoccupied molecular orbital
4) HOMO: highest occupied molecular orbital
5) UV: ultraviolet
6) NMR: nuclear magnetic resonance
7) IR: infrared
8) MALDI TOF: matrix assisted laser desorption ionization, time of flight