OFFICE OF NAVAL RESEARCH

END-OF-THE YEAR REPORT

PUBLICATIONS/PATENTS/PRESENTATIONS/HONORS/STUDENTS REPORT

for

GRANT : N00014-89-J-3062

R&T Code 400x056yip01&02

Organometallics for Conducting Polymer Synthesis and Starburst Polymer Synthesis

James M. Tour

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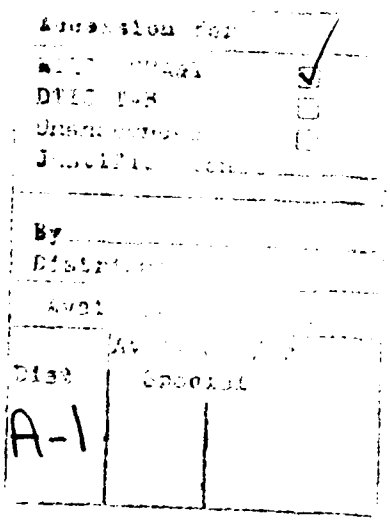
Department of Chemistry
Columbia, SC 29208

May 16, 1991



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PUBLICATIONS/PATENTS/PRESENTATIONS/HONORS REPORT

R&T Number: 400x056yip01&02
Contract/Grant Number: N00014-89-J-3062
Contract/Grant Title: Organometallics for Conducting Polymer Synthesis and Starburst Polymer Synthesis.
Principal Investigator: James M. Tour
Mailing Address: Department of Chemistry
University of South Carolina
Columbia, SC 29208

Phone Number: (803) 777-9517 **Fax Number:** 803-777-9521

E-mail Address:

a. Number of papers submitted to refereed journals, but not published: 1
b. Number of papers published in refereed journals (list attached)*: 2
c. Number of Books or chapters submitted, but not yet published: 1
d. Number of books or chapters published (list attached)*: 0
e. Number of printed technical reports & non-refereed papers (list attached)*: 11
f. Number of patents filed: 1
g. Number of patents granted (list attached)*: 0
h. Number of invited presentations at workshops or professional society meetings: 13
i. Number of presentations at workshops or professional society meetings: 4
j. Honors/Awards/Prizes for contract/grant employees (list attached)*: 2
(This might include Scientific Society Awards/Offices, Promotions, Faculty Awards/Offices)
k. Total number of Graduate Students and Post-Doctoral associates supported by at least 25% during this period under this R&T project number:
Graduate Students: 5
Post-Doctoral Associates: 0
including the number of,
Female Graduate Students: 1
Female Post-Doctoral Associates: 0
the number of
Minority* Graduate Students: 0
Minority* Post-Doctoral Associates: 0
and, the number of
Asian Graduate Students: 1
Asian Post-Doctoral Associates: 0
l. Other funding (list agency, grant title, amount received this year, total amount, and period of performance)*

* Use the letter and an appropriate title as a heading for your list, e.g.:
b. Published Papers in Refereed Journals, or, d. Books and Chapters published

* Minorities include Blacks, Aleuts, AmIndians, Hispanics, etc. NB: Asians are not considered an under-represented or minority group in science and engineering.

PART I

a. Papers submitted to Refereed Journals (and not yet published):

Extended Orthogonally Fused Conducting Oligomers for Molecular Electronic Devices. Tour, J. M.; Wu, R.; Schumm. J. S. *J. Am. Chem. Soc.* **1991**, submitted. Other support: National Science Foundation EPSCoR Program (RII-8922165).

b. Papers published in Refereed Journals:

Approaches to Orthogonally Fused Conducting Polymers for Molecular Electronics. Tour, J. M.; Wu, R.; Schumm. J. S. *J. Am. Chem. Soc.* **1990**, *112*, 5662. Other support: National Science Foundation EPSCoR Program (RII-8922165), and the University of South Carolina Venture Fund.

Facile Li/HMPA-Promoted Polymerization Method for the Synthesis of Soluble Poly(phenylenes). Tour, J. M.; Stephens, E. B. *J. Am. Chem. Soc.*, **1991**, *113*, 2309. Other support: National Science Foundation EPSCoR Program (RII-8922165).

c. Books or chapters submitted, but not yet published.

Approaches to Orthogonally Fused Conducting Polymers for Molecular Electronics. Tour, J. M.; Wu, R.; Schumm. J. S. *Contemporary Topics in Polymer Science*, Plenum, Vol 7. Other support: National Science Foundation EPSCoR Program (RII-8922165).

d. Books or chapters published: none.

e. Technical Reports Published and Papers Published in Non-Refereed Journals:

Extension of Branches for Orthogonally Fused Molecular Switches. Tour, J. M.; Wu, R. *Polymeric Mater., Sci. Engin.* **1991**, *64*, 178. Other support: National Science Foundation EPSCoR Program (RII-8922165).

Synthesis of Poly(phenylenes) by a Rapid Polymerization of 1-Bromo-4-lithiobenzene Using HMPA. Tour, J. M.; Stephens, E. B. *Polymeric Mater., Sci. Engin.* **1991**, *64*, 233. Other support: National Science Foundation EPSCoR Program (RII-8922165).

Our work on molecular electronics was the topic of several technical magazines and notices:

a. American Chemical Society News Release on July 4, 1990. *Molecules for Molecular Electronic Systems That Could Replace Computer Chips.*

b. Science News 1990, 138(2), 22. *Inching Closer to Molecular Electronics.*

c. Scientific American Magazine, November, 1990, pp 136-138. *Not Biochips? There May Yet Be Computers Made With Organic Molecules.*

d. Advanced Materials 1990, 2, 504. *Joining Molecular Wires.*

e. What's Happening in Chemistry: American Chemical Society, 1991. *Molecular Electronic Devices.*

f. Electronic Packaging & Production, October, 1990, p 134. *Microminiaturization Goes to the Limit.*

g. Inside R&D, July 11, 1990, Vol 19(28). *Part of Main Biochip Molecule Formed.*

h. USC Times, September 14, 1990. *Organic Molecules May One Day Replace Computer Chips.*

i. Carolinian, September, 1990. *'Organic' Computers.*

f. Patents Filed:

Lithium/HMPA-Promoted Synthesis of Poly(phenylenes). Tour, J. M.; Stephens, E. B. No. 07/543,673. Filed June 25, 1990.

g. Patents Granted: none.

h. Invited Presentations:

(A) Synthesis of Conjugated Organic Oligomers and Polymers for Electronic and Photonic Applications. (B) Metal(0) Deposition in Sol-Gel Materials for Heterogeneous Catalysis. Dow Corning Corporation, Midland, Michigan, April 24, 1991.

(A) Synthesis of Conjugated Organic Oligomers and Polymers for Electronic and Photonic Applications. (B) Metal(0) Deposition in Sol-Gel Materials for Heterogeneous Catalysis. Shell Development Company, Westhollow Research Center, Houston, Texas, March 16, 1991.

Conjugated Oligomers and Polymers for Electronic and Photonic Applications. Informal seminar given to Professor Alan MacDiarmid's research group at the University of Pennsylvania, Philadelphia, PA, March 1, 1991.

Molecules for Molecular Electronics. Presented to High School Students of South Carolina at the Science Day Presentation Sponsored by the Army ROTC at the Holiday Inn, Columbia, SC, November 12, 1990.

New Conjugated Organic Molecules. Office of Naval Research Conference on Future Directions in Polymer Chemistry, Wilmington, NC, November 1, 1990.

New Conjugated Organic Molecules for Electronic and Photonic Applications. Eastman Kodak Company, Rochester, NY, October 25, 1990.

Conducting Organic Molecules for Molecular Electronics. Francis Marion College, Florence, SC, October 18, 1990.

Synthesis of Soluble Poly(phenylenes) and Catalysis with Metals in Sol-Gel. Ethyl Corporation, Central Research and Development, Baton Rouge, LA, October 26, 1990.

Molecules for Electronics Applications. The Citadel, the Military College of South Carolina, Charleston, SC, September 21, 1990.

Molecules for Electronic Applications. The College of Charleston, Charleston, SC, September 20, 1990.

Homogeneous Deposition of Transition Metal(0) Species Into Sol-Gel Derived Materials and Their Use In Aqueous Hydrogenation Processes. Westinghouse Savannah River Laboratories, Aiken, SC, August 9, 1990.

Organometallic for the Synthesis of Novel Monomeric and Polymeric Materials with Potential Electronic and Photonic Applications. E. I. duPont de Nemours and Company, Inc., Experimental Station, Wilmington, DE, June 26, 1990.

Organometallics for the Preparation of (1) Conducting Polymers and NLO Related Materials (2) Metal(0)-Impregnated Sol-Gel Derived Ceramics. Ethyl Corporation, Central Research and Development, Baton Rouge, LA, April 12, 1990.

i. Contributed Presentations:

Synthesis of Poly(phenylenes) by a Rapid Polymerization of 1-Bromo-4-lithiobenzene Using HMPA. Tour, J. M.; Stephens, E. B. 201st National Meeting of the American Chemical Society, Atlanta, GA, April, 1990, Polymeric Materials Science and Engineering Division.

Extension of Branches for Orthogonally Fused Molecular Switches. Tour, J. M.; Wu, R. 201st National Meeting of the American Chemical Society, Atlanta, GA, April, 1990, Polymeric Materials Science and Engineering Division.

Approaches to Orthogonally Fused Conducting Polymers for Molecular Electronics. Tour, J. M.; Wu, R.; Schumm, J. S. Advances in New Materials Conference sponsored by the American Chemical Society, Polymer Division, Fort Lauderdale, FL, November 19, 1990.

Approaches to Orthogonally Fused Conducting Polymers for Molecular Electronics. Tour, J. M.; Wu, R., Schumm, J. S. Gordon Research Conference on Electronic Processes in Organic Materials, Plymouth, NH, June 30 - August 8, 1990.

j. Honors/Awards/Prizes:

Office of Naval Research, Young Investigator Award, Chemistry Division/Polymers, 1989-92.

National Science Foundation, Presidential Young Investigator Award, Materials Division/Polymers, 1991-96. Award starts June 1991.

k. Number of Graduate Students and post-doctoral associates supported by at least 25% during this period:

Graduate students: 5
Post-docs: 0
Female Graduate students: 1
Female postdocs: 0
Minority Graduate Students: 0
Minority Postdocs: 0
Asian Graduate Students: 1
Asian Postdocs: 0

l. Other Funding:

ACS-Petroleum Research Fund Type G:21011-G1 (Starter Grant). *Transition Metal-Catalyzed Polymerizations and Macrocyclization Reactions.* Period 9/1/89 - 8/31/91; Total support $18,000 + $4,500 for a summer research fellow. (direct cost). Received $11,500 this year.

National Science Foundation, EPSCoR Program to foster a Materials Research Program at the University of South Carolina, targeted for the development of Perpendicularly Arranged Conducting Polymers Period 3/1/90 - 2/28/92; Total Support $60,000 (direct cost), $40,000 received this year.

PART II

a. Principal Investigator: James M. Tour

b. Phone: (803) 777-9517

c. Cognizant ONR Scientific Officers: Dr. Kenneth J. Wynne and Dr. JoAnn Milliken

d. Brief Description of Project:

New synthetic organometallic reactions can be used to synthesize novel conjugated polymer systems with interesting electronic and photonic characteristics. (1) The first synthesis of a pi/sigma/pi conducting oligomer is described. It has two polythiophene backbones affixed at 90° angles to each other by a spiro carbon core. Proposed was a two step synthesis of the key spiro core and a total four step synthesis of the entire polymer system. This class of polymers has never before been synthesized. It has, however, been suggested by workers at the IBM Corporation that these polymers may be suitable for memory, logic, and amplification applications in molecular electronic devices. (2) An unprecedented method for aryl-aryl coupling has been developed which allows the facile preparation of soluble polyphenylenes. (3) A silicon-based starburst polymer synthesis has been proposed. (4) A route to planar phenylene oligomers has been proposed.

e. Significant Results during the last year:

(1) We have succeeded in coupling oligomeric chains onto the pi/sigma/pi semiconductor core units providing two orthogonally-fused systems that are 25 and 30 Å long. Our final targets are molecules that are 50 Å long. Additionally, we are soon to submit a joint publication with Art Diaz at IBM-Almaden on the conductive properties of end-capped oligothiophenes. (2) Our soluble polyphenylenes have interesting electronic and thermal characteristics with degrees of polymerization ~65. These polymers may be well suited for high temperature organic materials with high char yields and low shrinking and voids for carbon composites. We are collaborating with Dr. Teddy Keller at the NRL-Washington. (3) We have continued to peruse methods necessary to make conjugated silicon-based starburst oligomers. Along with this project, we developed a convenient method for the preparation of $R_2R'SiH$ compounds which have tremendous applications in hydrosilylation research. (4) Planarization of conjugated organic polymers should provide materials with low electrical resistance as well as excellent third order nonlinear optical (NLO) susceptibilities.

f. Brief summary of plans for next year:

(1) We will continue on the synthesis of the required pi/sigma/pi semiconductor systems with the hope of completing two target molecules that are 50 Å long and we will work closely with IBM scientists as we finish these molecules. We will continue to investigate the properties of the oligophenylenes (conductivity and NLO) and we hope to append these onto other polymer backbones (i.e. polyphosphazenes). This will allow us to address through-space conductivities rather than through bond conductivities. (2) We will be collaborating with Dr. Keller at the NRL on the functionalization of the polyphenylenes for suitable high temperature organic materials with low shrinking and voids for carbon composites. We will also continue to study the electronic properties of these polymers. (3) The synthesis of the silicon starburst polymers will be addressed by outer to central unit growth. (4)

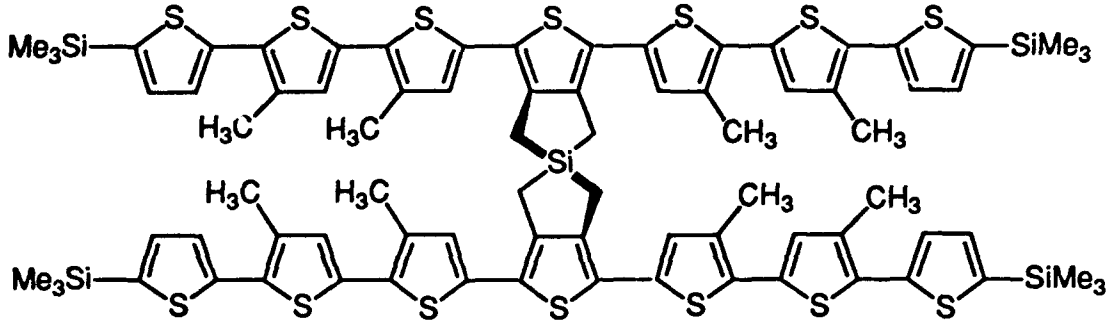
We hope to compete the synthesis of planar polyphenylene derivatives and study the conductivity and NLO properties.

g. Graduate Students Currently Working on the ONR Project:
Eric Stephens, Ruilian Wu, Jay Lamba, Jens John, Jeffry Schumm

PART III

Organometallic Routes to Conjugated Organic Oligomers and Polymers for Electronic and Photonic Applications.

(1) Molecules synthesized for molecular electronics.



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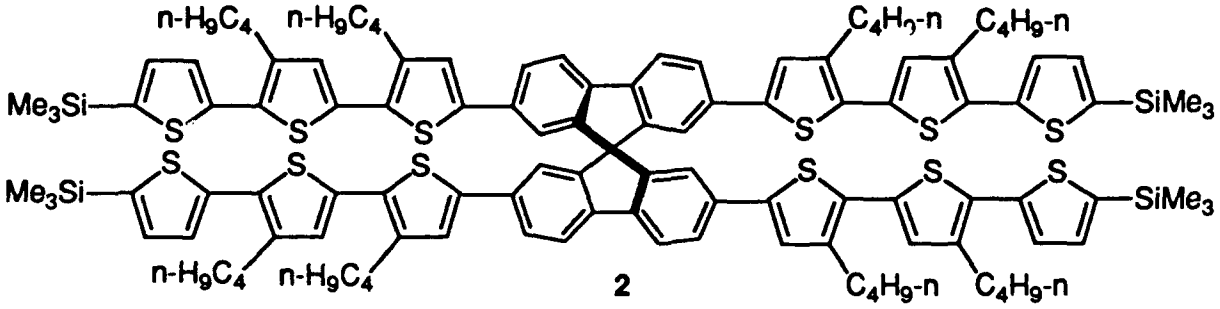

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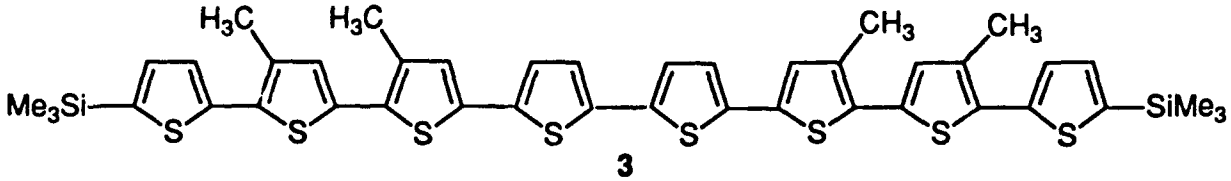
(One of many soluble oligothiophenes synthesized for CV studies.



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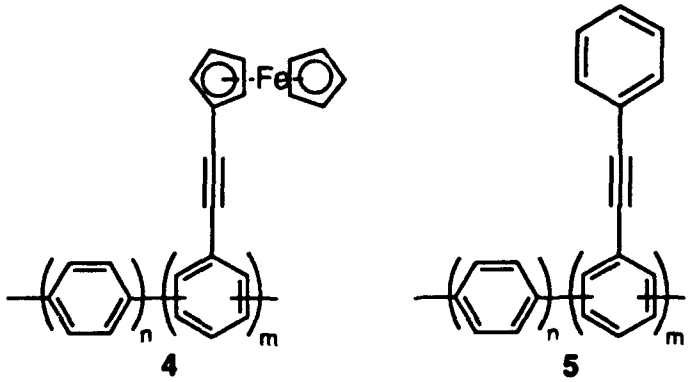
(2) Two of many functionalized and soluble polyphenylenes that we have synthesized.



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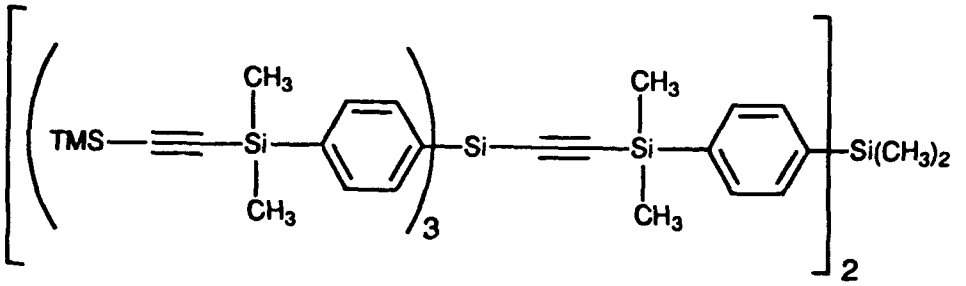
(3) In route to silicon-based starburst oligomers such as **6** and larger. We have developed new methods for the synthesis of silanes **7** from tetra(alkoxy)silanes.



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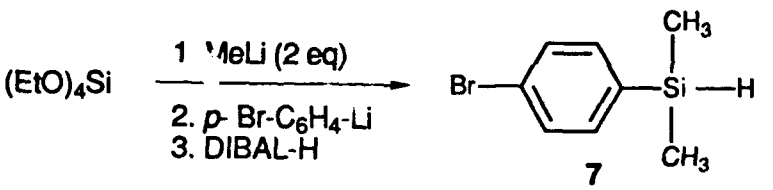

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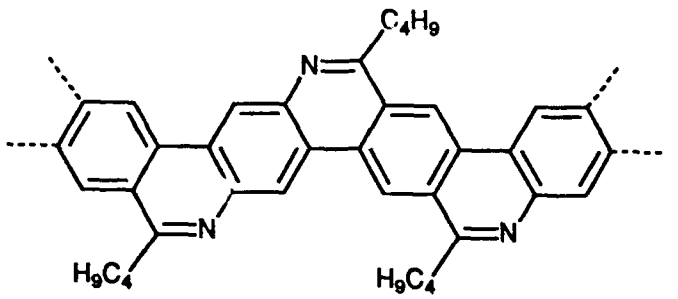
(4) Synthesis of planar polyphenylene derivatives such as **8**.



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Explanatory text for PART III:

(Project 1) Compounds **1** and **2** were prepared in 86 % and 60 % yields, respectively, from the spiro cores that were prepared last year. Compounds **1** and **2** are 25 Å and 30 Å long, respectively, excluding the TMS end groups. The target compounds need to be 50 Å according to the initial proposal by IBM researchers, hence, we are approaching the lengths necessary. IBM researchers will soon be able to study the feasibility of single molecule devices.

On a related topic, we have synthesized numerous soluble thiophene oligomers (monomer through octamer **3**). These all have TMS-capping groups so that we can study the electrochemical characteristics without getting further polymerization. At seven thiophene units in length, the materials are electrochemically identical to polythiophene exhibiting two reversible waves at 0.68 and 1.05 V. This work is being done in collaboration with Dr. A. Diaz at IBM-Almaden.

(Project 2) We have developed a new synthesis of functionalized and soluble polyphenylenes. For example, compound **4** gives us an internal handle in the oxidation indicating that the polymer undergoes a two electron oxidation per phenyl ring! Compound **5** is an excellent candidate for high temperature organic materials with high char yields for carbon composites. We are collaborating with Dr. Teddy Keller at NRL on this phase of the project.

(Project 3) We are continuing our work on silicon-based starburst oligomers and we are developing new synthetic methods along the way.

(Project 4) Planar ladder polymers with a polyphenylene core are being prepared. The planarity along with the increase in electron density between the consecutive aryl rings should provide materials with low electrical resistance and excellent third order NLO responses. Dr. L.-T. Cheng at DuPont Experimental Station is providing us with the NLO measurements.