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PREVIEW

**SYNTHESIS AND ELECTRONIC PROPERTIES OF METALLOCENE-
VINYLENE OLIGOMERS AND FERROCENYL PHENYLENE-VINYLENE
OLIGOMERS**

by

Hookun Lee

A DISSERTATION

Presented to the Faculty of

The Graduate Collage at the University of Nebraska

In Partial Fulfillment of Requirements

For the Degree of Doctor of Philosophy

Major: Chemistry

Under the Supervision of Robert T. Hembre

Lincoln Nebraska

August, 1996

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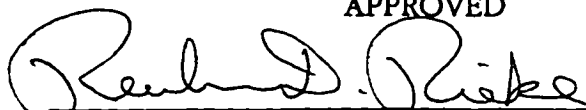
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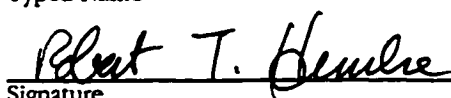


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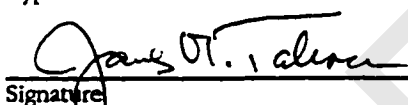


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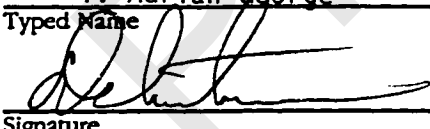


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GRADUATE COLLEGE
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SYNTHESIS AND ELECTRONIC PROPERTIES OF METALLOCENE-VINYLENE OLIGOMERS AND FERROCENYL PHENYLENE-VINYLENE OLIGOMERS

Hookun Lee, Ph.D.

University of Nebraska, 1996

Advisor: Robert T. Hembre

This dissertation presents the study of metallocene-vinylene (McV) oligomers and ferrocenyl phenylene-vinylene oligomers (FcPV). They have been synthesized via palladium catalyzed coupling reaction and volatile alkene metathesis (VAM) reaction. Redox potentials and spectroscopic data with their structures have been investigated to understand electron transfer (ET) properties related to the structural nature of its bridging group.

Iron, ruthenium, and osmium McV dimers and their heterometallic counterparts including diferrocenyl-butadiene and -hexatriene derivatives were synthesized via palladium catalyzed vinylferrocenylation and VAM. The crystal structure of trans- and cis-1,2-diferrocenylethylene have been determined. The monocations of ferrocenyl dimers linked by a vinyl-, butadiene-, and hexatriene, bridge are moderately localized class II ions based on their intervalence transfer band analysis and redox potential data.

McV trimers and tetramers have been prepared via above two methods. Useful precursors to polymers such as 1,2-divinyl-ferrocenyl-vinylene dimers and 1,3-divinyl-ferrocenyl-vinylene trimer have been synthesized by VAM. Evidence that long-range effects may exist in related polymers is found in the redox behavior of ferrocenyl-vinylene trimers.

(E)-Ferrocenylstyrenes, (E,E)-1-ferrocenyl-4-aryl-1,3-butadienes, phenylene-vinylene oligomers including phenylene-vinylene precursors have been synthesized in good yields with high regio- and stereoselectivity via palladium catalyzed arylation. The relatively high Hammett ρ -values for styryl ($\rho = 1.44$) or arylbutadiene ($\rho = 0.93$) substituents have been obtained. The structure of (E)- β -ferrocenyl-p-fluorostyrene has been determined. In addition, the redox potential of ferrocene of phenylene-vinylene dimer in a remote distance (11 C-C bonds) is influenced by a substituent (NO_2 or NH_2). The pH dependence of the redox properties, UV-spectra and solvatochromic effects for (E)-1-ferrocenyl-2-(4-pyridine)ethene and (E,E)- β -ferrocenyl- β' -(4-pyridinyl)-p-divinylbenzene with their corresponding salts are discovered. Ferrocenyl-phenylene-vinylene-thiol oligomers have been developed as a molecular wire.

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mistakes everyday. I thank to my God that I came to Lincoln and have worked with all peoples whom I have met.

Psalms 23 in the King James Version

The LORD is my shepherd, I shall not want.

He maketh me to lie down in green pastures: He leadeth me beside the still waters.

He restoreth my soul; He leadeth me in the paths of righteousness for His name's sake.

Yea, though I walk through the valley of the shadow of death, I will fear no evil; Thou art with me; Thy rod and Thy staff they comfort me.

Thou preparest a table before me in the presence of mine enemies; Thou anointest my head with oil; my cup runneth over.

Surely goodness and mercy shall follow me all the days of my life, and I will dwell in the house of the LORD for ever.

Maranatha.

To My Wife and Son
Ae-Ran and Victor

PREVIEW

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List of Abbreviations

Ac	acetyl
ADMET	acyclic diene metathesis
amu	atomic mass unit
Å	Angstrom unit, 10^{-8} cm
AIBN	azobis(isobutyronitrile)
AN	acetonitrile
c	light speed in vacuum
calcd	calculated value
cm^{-1}	wave number
com	comproportionation
Cp	cyclopentadienyl
Cp*	pentamethylcyclopentadienyl
DMF	dimethylformamide
E_b	binding energy
E_{in}	absorption energy contributed from innersphere
E_n	midpoint potential
E_{op}	absorption energy
E_{out}	absorption energy contributed from outersphere
equivs.	equivalents
ESCA	electron spectroscopy for chemical analysis
ESR	electron spin resonance