

科技资料

**Photochemistry &
Photoelectrochemistry of
Organic & Inorganic
Molecular Thin Films**



PROCEEDINGS

 SPIE—The International Society for Optical Engineering

Photochemistry and Photoelectrochemistry of Organic and Inorganic Molecular Thin Films

Marcus F. Lawrence
Arthur J. Frank
S. Ramasesha
Carl C. Wamser
Chairs/Editors

23-24 January 1991
Los Angeles, California

Sponsored and Published by
SPIE—The International Society for Optical Engineering



Volume 1436

SPIE (Society of Photo-Optical Instrumentation Engineers) is a nonprofit society dedicated to advancement of optical and optoelectronic applied science and technology.



The papers appearing in this book comprise the proceedings of the meeting mentioned on the cover and title page. They reflect the authors' opinions and are published as presented and without change, in the interests of timely dissemination. Their inclusion in this publication does not necessarily constitute endorsement by the editors or by SPIE.

Please use the following format to cite material from this book:

Author(s), "Title of Paper," *Photochemistry and Photoelectrochemistry of Organic and Inorganic Molecular Thin Films*, Marcus F. Lawrence, Arthur J. Frank, S. Ramasesha, Carl C. Wamser, Editors, Proc. SPIE 1436, page numbers (1991).

Library of Congress Catalog Card No. 91-60512
ISBN 0-8194-0526-4

Published by
SPIE—The International Society for Optical Engineering
P.O. Box 10, Bellingham, Washington 98227-0010 USA
Telephone 206/676-3290 (Pacific Time) • Fax 206/647-1445

Copyright © 1991, The Society of Photo-Optical Instrumentation Engineers.

Copying of material in this book for internal or personal use, or for the internal or personal use of specific clients, beyond the fair use provisions granted by the U.S. Copyright Law is authorized by SPIE subject to payment of copying fees. The Transactional Reporting Service base fee for this volume is \$4.00 per article (or portion thereof), which should be paid directly to the Copyright Clearance Center (CCC), 27 Congress Street, Salem, MA 01970. Other copying for republication, resale, advertising or promotion, or any form of systematic or multiple reproduction of any material in this book is prohibited except with permission in writing from the publisher. The CCC fee code is 0-8194-0526-4/91/\$4.00.

Individual readers of this book and nonprofit libraries acting for them are permitted to make fair use of the material in it, such as to copy an article for teaching or research, without payment of a fee. Republication or systematic or multiple reproduction of any material in this book (including abstracts) is prohibited except with the permission of SPIE and one of the authors.

Permission is granted to quote excerpts from articles in this book in other scientific or technical works with acknowledgment of the source, including the author's name, the title of the book, SPIE volume number, page number(s), and year. Reproduction of figures and tables is likewise permitted in other articles and books provided that the same acknowledgment of the source is printed with them, permission of one of the original authors is obtained, and notification is given to SPIE.

In the case of authors who are employees of the United States government, its contractors or grantees, SPIE recognizes the right of the United States government to retain a nonexclusive, royalty-free license to use the author's copyrighted article for United States government purposes.

Printed in the United States of America

PHOTOCHEMISTRY AND PHOTOELECTROCHEMISTRY OF ORGANIC
AND INORGANIC MOLECULAR THIN FILMS

Volume 1436

CONFERENCE COMMITTEE

Conference Chair

Marcus F. Lawrence, Concordia University (Canada)

Cochairs

Arthur J. Frank, Solar Energy Research Institute

S. Ramasesha, Indian Institute of Science (India)

Carl C. Wamser, Portland State University

Session Chairs

Session 1—Surface Modification and Photosensitization of Semiconductor
Electrodes: Photovoltaic and Photoelectrochemical Cells

Arthur J. Frank, Solar Energy Research Institute

Marcus F. Lawrence, Concordia University (Canada)

Session 2—Mechanisms of Photoinduced Charge Separation
and Charge Transport in Molecular Films

Arthur J. Frank, Solar Energy Research Institute

Marcus F. Lawrence, Concordia University (Canada)

Session 3—Nonlinear Optical Properties of Polymeric Materials

Carl C. Wamser, Portland State University

Conference 1436, *Photochemistry and Photoelectrochemistry of Organic and Inorganic Molecular Thin Films*, was part of a three-conference program on Instrumentation for Chemical Sensing of the Environment, held at SPIE's Symposium on Laser Spectroscopy, a part of OE/LASE '91, 20–25 January 1991, in Los Angeles, California. The other conferences were:

Conference 1435, *Optical Methods for Ultrasensitive Detection and Analysis: Techniques and Applications*

Conference 1437, *Applied Spectroscopy in Material Science*.

Program Chair: **David E. Cooper**, SRI International

PHOTOCHEMISTRY AND PHOTOELECTROCHEMISTRY OF ORGANIC
AND INORGANIC MOLECULAR THIN FILMS

Volume 1436

INTRODUCTION

It has been approximately 40 years since the first detailed studies of the electrical and photoelectrical behaviors of organic and inorganic molecular solids were undertaken. These were basically motivated by the interest in gaining a greater understanding of important photochemical processes such as photosynthesis and vision, and in advancing their use as photographic sensitizers. Since then, the molecular engineering of chemical structures and molecular assemblies has lead to widespread technological applications such as photovoltaic energy conversion, photocatalysis, electrocatalysis, and electrophotography.

In recent years, the use of polymers and other organic materials to obtain nonlinear optical effects is emerging as a frontier of science and technology. The intense research in this field is motivated by the prospect of using molecular materials showing nonlinear optical properties for optical signal processing, optical switching and logic operations in optical computing, and optical fiber communications. Again, the principal reason for this lies in the great versatility of molecular structures, which allows for modification of a system's architecture through chemical synthesis.

In view of the important current developments brought on by the use of molecular materials and their multidisciplinary nature, this volume is intended to provide a broad coverage of recent work by some of the leading scientists in their respective areas. The content should be of interest to researchers in the fields of photoelectrochemistry, photovoltaic energy conversion, and optoelectronics.

Session 1 deals with the use of molecular thin films for surface modification, semiconductor photosensitization, and applications in photovoltaic and photoelectrochemical cells. Session 2 looks at some of the mechanistic aspects of photoinduced charge separation and charge transport in molecular films. Session 3 presents both theoretical and experimental contributions in the area of nonlinear optical properties of polymeric materials.

Marcus F. Lawrence
Concordia University (Canada)

Arthur J. Frank
Solar Energy Research Institute

S. Ramasesha
Indian Institute of Science (India)

Carl C. Wamser
Portland State University

PHOTOCHEMISTRY AND PHOTOELECTROCHEMISTRY OF ORGANIC
AND INORGANIC MOLECULAR THIN FILMS

Volume 1436

CONTENTS

	Conference Committee	v
	Introduction	vii
SESSION 1	SURFACE MODIFICATION AND PHOTSENSITIZATION OF SEMICONDUCTOR ELECTRODES: PHOTOVOLTAIC AND PHOTOELECTROCHEMICAL CELLS APPLICATIONS	
1436-01	Charge separation in functionalized tetrathiafulvalene derivatives (Invited Paper) M. A. Fox, H. Pan, Univ. of Texas/Austin.	2
1436-02	Soluble polyacetylenes derived from the ring-opening metathesis polymerization (ROMP) of substituted cyclooctatetraenes: electrochemical characterization and Schottky barrier devices (Invited Paper) T. H. Jozefiak, M. J. Sailor, E. J. Ginsburg, C. B. Gorman, N. S. Lewis, R. H. Grubbs, California Institute of Technology.	8
1436-03	UV laser-induced photofragmentation and photoionization of dimethylcadmium chemisorbed on silicon A. P. Simonov, V. N. Varakin, A. M. Panesh, Karpov Institute of Physical Chemistry (USSR).	20
1436-04	Electric field effect on the persistent hole burning of quinone derivatives T. Nishimura, E. Yagyu, M. Yoshimura, N. Tsukada, T. Takeyama, Mitsubishi Electric Corp. (Japan).	31
1436-05	Modified chloroaluminium phthalocyanine: an organic semiconductor with high photoactivity (Invited Paper) J. Dodelet, L. Gastonguay, G. Veilleux, R. G. Saint-Jacques, INRS-Energie (Canada); R. Côté, Concordia Univ. (Canada); D. Guay, G. Tourillon, Univ. Paris-Sud (France).	38
1436-06	P-n heterojunction and Schottky barrier formation between poly(3-methylthiophene) and n-type cadmium sulfide A. J. Frank, S. Glenis, Solar Energy Research Institute.	50
1436-07	Pulsed photoconductivity of chlorophyll α H. Kassi, S. Hotchandani, R. M. Leblanc, N. Beaudoin, M. Déry, Univ. du Québec à Trois-Rivières (Canada).	58
1436-09	Artificial photosynthesis at octane/water interface in the presence of hydrated chlorophyll α oligomer thin film A. G. Volkov, M. I. Gugeshashvili, M. D. Kandelaki, V. S. Markin, A.N. Frumkin Institute of Electrochemistry (USSR); B. Zelent, G. Munger, R. M. Leblanc, Univ. du Québec à Trois-Rivières (Canada).	68
SESSION 2	MECHANISMS OF PHOTOINDUCED CHARGE SEPARATION AND CHARGE TRANSPORT IN MOLECULAR FILMS	
1436-10	Photochemistry and photophysics of stilbene and diphenylpolyene surfactants in supported multilayer films (Invited Paper) S. P. Spooner, D. G. Whitten, Univ. of Rochester.	82
1436-11	Light energy conversion with pheophytin α and chlorophyll α monolayers at the optical transparent electrode (Invited Paper) R. M. Leblanc, P. Blanchet, D. Côté, Univ. du Québec à Trois-Rivières (Canada); M. I. Gugeshashvili, A.N. Frumkin Institute of Electrochemistry (USSR); G. Munger, Univ. du Québec à Trois-Rivières (Canada); A. G. Volkov, A.N. Frumkin Institute of Electrochemistry (USSR).	92

(continued)

**PHOTOCHEMISTRY AND PHOTOELECTROCHEMISTRY OF ORGANIC
AND INORGANIC MOLECULAR THIN FILMS**

Volume 1436

1436-12	Solid state conductivity and photoconductivity studies of an ion-exchange polymer/dye system Z. Huang, I. Ordonez, A. A. Ioannidis, C. H. Langford, M. F. Lawrence, Concordia Univ. (Canada).	103
1436-13	Asymmetric photopotentials from thin polymeric porphyrin films C. C. Wamser, V. Senthilathipan, W. Li, Portland State Univ.	114
1436-19	Photophysics of 1, 3, 5-triaryl-2-pyrazolines M. R. Sahyun, G. P. Crooks, 3M Co.; D. K. Sharma, Concordia Univ. (Canada).	125
SESSION 3	NONLINEAR OPTICAL PROPERTIES OF POLYMERIC MATERIALS	
1436-14	Microscopic mechanism of optical nonlinearity in conjugated polymers and other quasi-one-dimensional systems (Invited Paper) S. Mazumdar, D. Guo, Univ. of Arizona; S. N. Dixit, Lawrence Livermore National Lab.	136
1436-15	Nonlinear absorbance effects in bacteriorhodopsin (Invited Paper) G. W. Rayfield, Bend Research, Inc.	150
1436-16	Progress in organic third-order nonlinear optical materials (Invited Paper) M. G. Kuzyk, Washington State Univ.	160
1436-17	Linear and nonlinear optical properties of polymeric Langmuir-Blodgett films T. L. Penner, C. S. Willand, D. R. Robello, J. S. Schildkraut, A. Ulman, Eastman Kodak Co.	169
1436-18	Theoretical study of optical pockels and Kerr coefficients of polyenes I. D. Albert, S. Ramasesha, Indian Institute of Science (India).	179
	Addendum.	190
	Author Index.	191

PHOTOCHEMISTRY AND PHOTOELECTROCHEMISTRY OF ORGANIC
AND INORGANIC MOLECULAR THIN FILMS

Volume 1436

SESSION 1

**Surface Modification and Photosensitization
of Semiconductor Electrodes: Photovoltaic
and Photoelectrochemical Cells Applications**

Chairs

Arthur J. Frank

Solar Energy Research Institute

Marcus F. Lawrence

Concordia University (Canada)

Charge separation in functionalized tetrathiafulvalene derivatives

Marye Anne Fox and Horng-Long Pan

Department of Chemistry, University of Texas at Austin
Austin, Texas 78712

ABSTRACT

The synthesis of a family of symmetrical derivatives of tetrathiafulvalene bearing long chain ether groups is discussed. A comparison will be made between this family of compounds and those obtained with symmetrically substituted zinc octakis(alkoxyethyl)porphyrins, which have been shown to exhibit unusual photoeffects when dispersed as liquid crystals in symmetrical cells consisting of indium tin oxide electrodes as windows.

1. INTRODUCTION

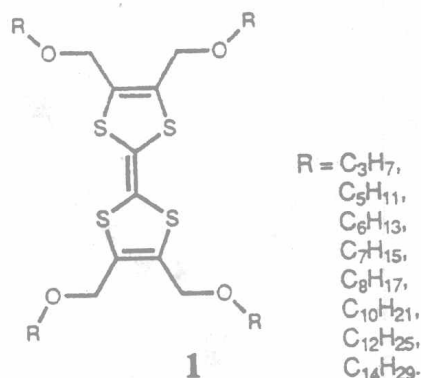
Our research group has recently reported the construction of a solid state photovoltaic device in which a zinc porphyrin symmetrically substituted with long chain alkyl groups is sandwiched between identical conductive, optically-transparent indium tin oxide electrodes.¹ Upon irradiation with visible light into either the Soret or Q-bands of the porphyrin, a photopotential develops. The highly ordered thin layer of absorber is prepared by exploiting the liquid crystallinity of the discotic phase of zinc octakis(β -octyloxyethyl)porphyrin to preserve order while being capillary-filled between the precisely spaced optically transparent electrodes. In this cell, the illuminated electrode acts as a photoanode and the direction of current flow inverts upon reversal of the direction of illumination. Photocurrents of up to ca. 0.4 mA/cm² have been measured under illumination with a 150 W Xe lamp of about 150 mW/cm² intensity. The short circuit photocurrent is found to be a strong function of thickness and open circuit photovoltages of ca. 120-250 mV can be routinely observed. After a small initial decay, the short circuit current is unaffected by the passage of more than 10⁴ electrons per porphyrin unit in the thin layer. The observed photovoltage increases linearly with light intensity at low incident intensities and saturates at higher intensities. In the dark, conductivity in the cell is negligible, implying a dark resistivity of more than 10¹³ Ω -cm. The degree of correspondence between the action spectrum of the photocell and the solid state absorption spectrum of the porphyrin absorber depends on cell thickness: as thickness increases, a decreased response in the Soret band relative to the Q bands is observed.

This cell appears to be the first clear example of an organic-based photovoltaic device with reasonable efficiency for photon-to-electrical energy conversion which is controlled entirely by interfacial kinetics.¹ The magnitude of the observed photoeffects make unlikely the possibilities that a Dember effect or diffusion photovoltage, which have been suggested as operative current generating mechanisms in other organic photovoltaic devices, are operative here. Instead a model coupling photoinjection at the illuminated interface with enhanced photoconductivity in the bulk of the liquid porphyrin is suggested to rationalize the experimental results.

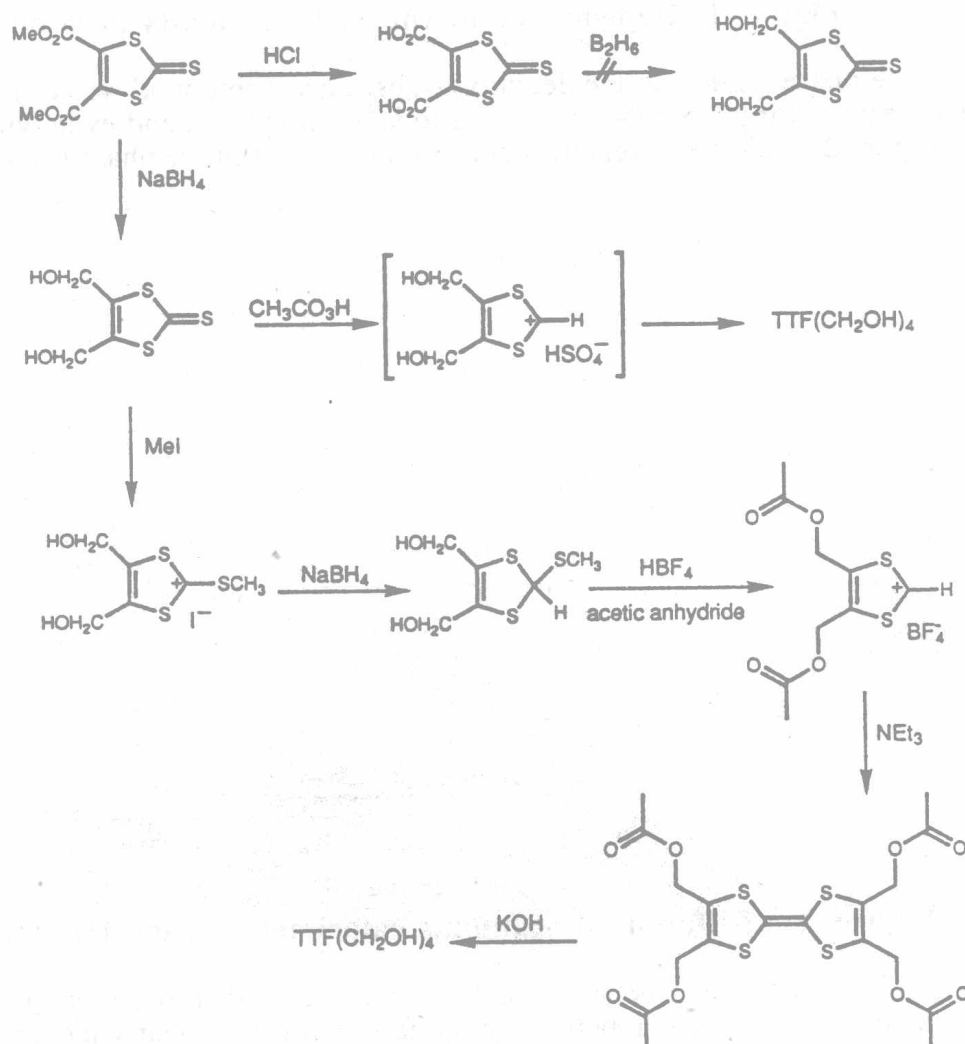
We now describe our attempts to evaluate the physical parameters of the absorptive material which allow for construction of such cells. Specifically, we have synthesized a series of symmetrically substituted tetrathiafulvalene derivatives **1** which, like the liquid crystalline porphyrin discussed above, bear symmetrically placed long chain alkyl groups. Unlike zinc octakis(β -alkyloxyethyl)porphyrin, this family shows no stable mesophases, although the low melting points of several members of the series does still allow for capillary filling of a photocell. We have found that the photoeffects attainable with this family in either the doped or undoped state are significantly poorer than are observed with the liquid crystalline porphyrin. The dark conductivity is appreciably higher in this family with and without iodine doping.

2. RESULTS AND DISCUSSION

The synthesis of tetrakis(alkoxymethyl)tetrathiafulvalenes **1**, which is described in detail



elsewhere,² is summarized in Scheme 1. The penultimate tetraalcohol shown in the Scheme is converted to long chain ether or ester derivatives by standard Williamson etherification and esterification methods, respectively. We have evaluated here only the ethers for photoeffects in the solid photovoltaic cell.



Scheme 1. Synthesis of tetrakis(alkoxymethyl)tetrathiafulvalenes **1**

Although the melting points for the series were found to depend on the length of the appended alkyl chain, Figure 1, no evidence from differential scanning calorimetry could be found to implicate a

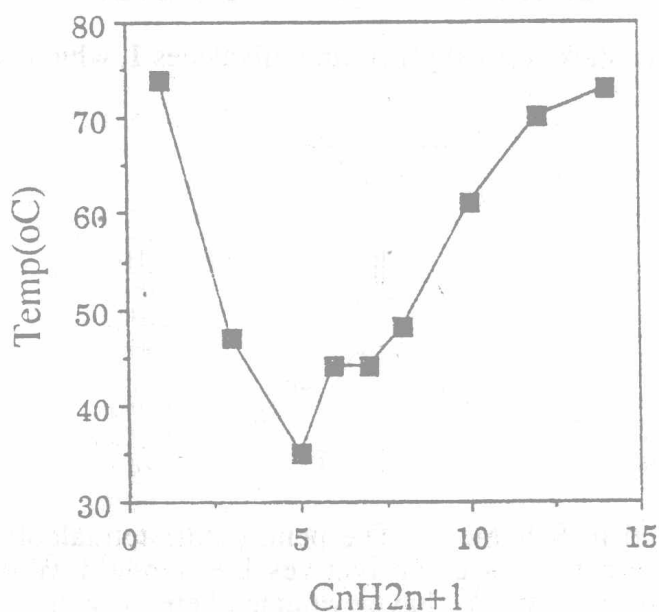


Figure 1. Dependence of the melting points of **1** on chain length

metastable phase. Only for the decyloxy-substituted compound was any evidence detected for other than a clean melting from the crystalline to isotropic phase, and even with this compound, the extra peak, Figure 2, could be assigned as a crystalline-to-crystalline phase transition.

Heating Rate: 5 deg/min

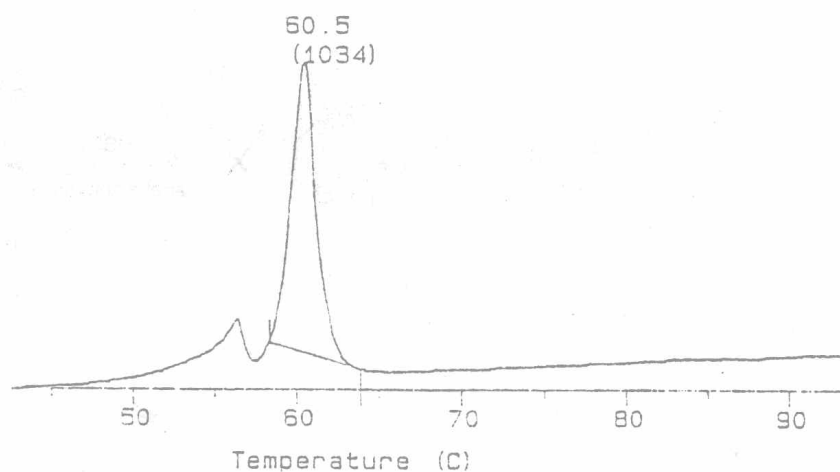


Figure 2. Differential scanning calorimetry trace for decoxy-substituted **1**

The electrochemical behavior of **1** was parallel to that of the parent tetrathiafulvalene. Cyclic voltammetric traces for each member of the family revealed nearly ideal reversibility, with nearly the same potentials for the first and second oxidations, 0.01 and 0.33 V vs. SCE, respectively.²

Consistent with the observed redox potentials, **1** could be converted to the corresponding cation radical salt upon doping with iodine.² The resulting dark black 1:1 charge transfer solid exhibited an absorption spectrum (Figure 3), an electron spin resonance spectrum (Figure 4), and an infra-red spectrum (Figure 5) consistent with a singly oxidized organic species.

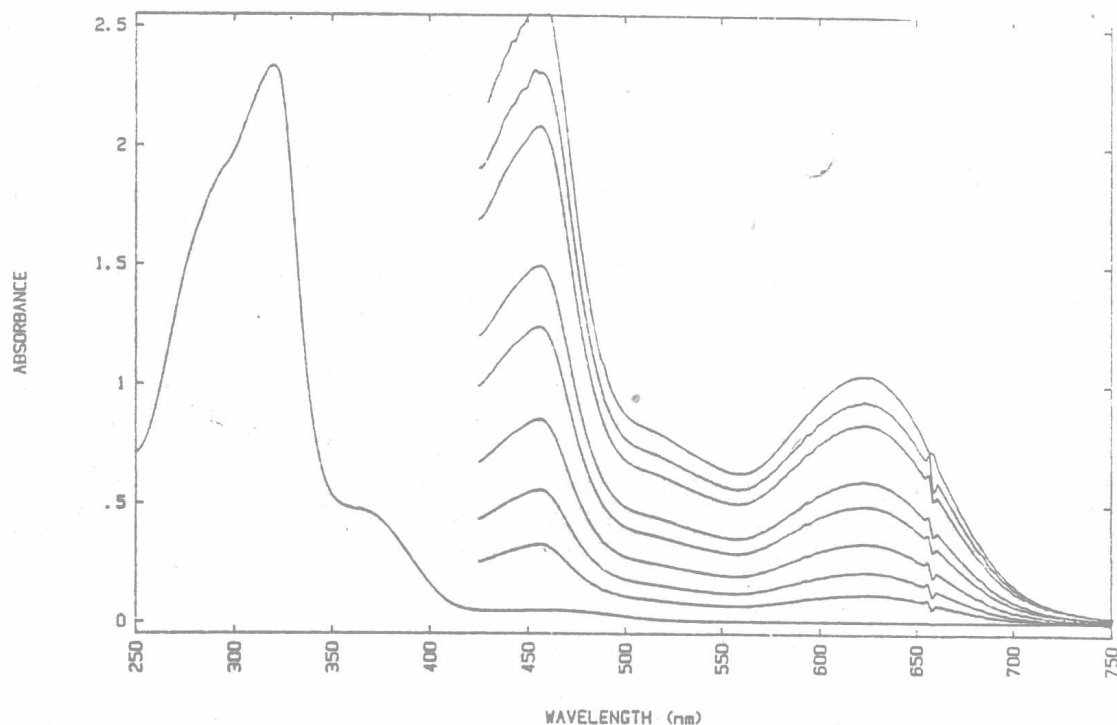


Figure 3. Absorption spectrum of propyloxy-substitute **1** doped with I_2

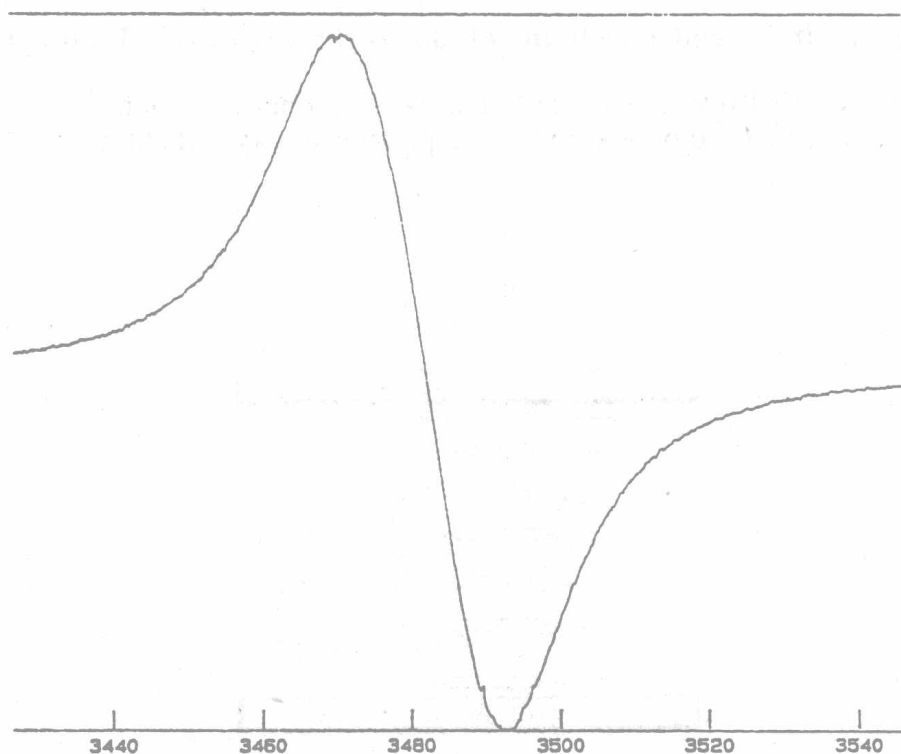


Figure 4. Electron spin resonance spectrum of dodecyl-substituted **1** doped with I_2

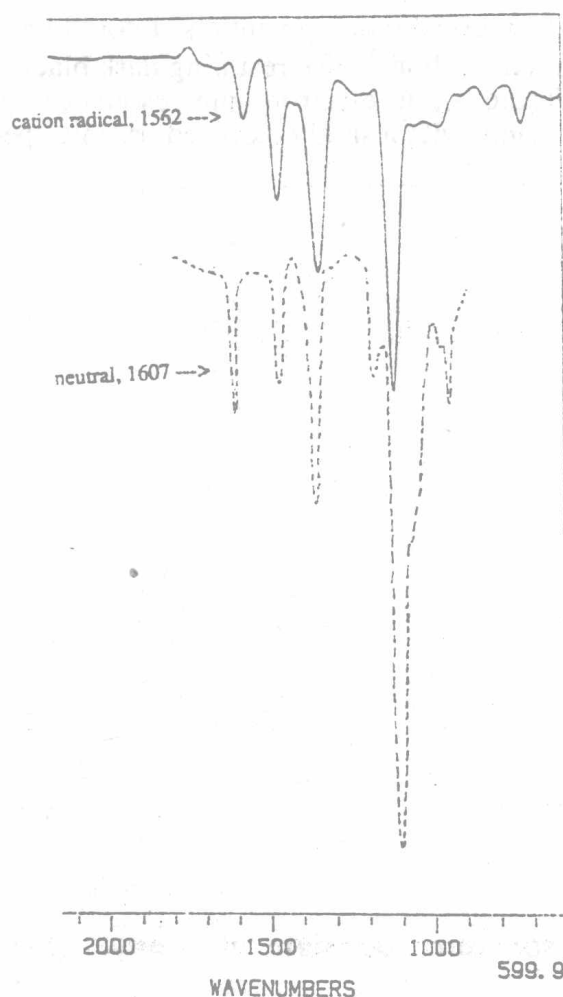


Figure 5. Infra-red spectrum of dodecyl-substituted 1 doped with I₂

When capillary-filled into a photocell, a working model of which is shown schematically in Figure 6, 1 showed no enhanced photoeffects, irrespective of alkyl substitution. Dark resistivity

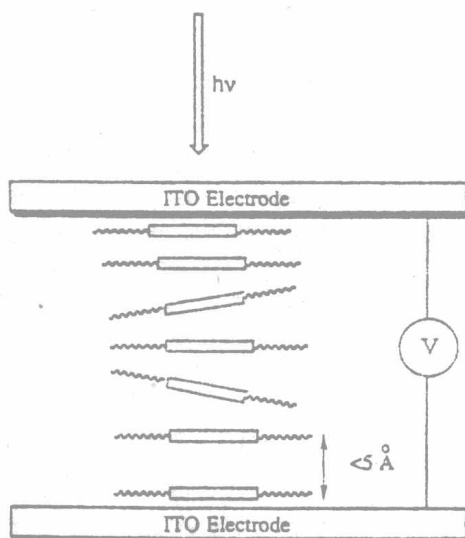


Figure 6. A schematic representation of a discotic-ordered photovoltaic cell

was much lower than with the zinc octakis(alkoxyethyl)porphyrins, decreasing to $10^6 \Omega\text{-cm}$ in the undoped state and to $10^{-3} \Omega\text{-cm}$ as the charge transfer complex with iodine. The contrasting behavior of these two materials presumably relates to the requirement for partial ordering with self-healing of defects during capillary-filling of the photocell and to the necessary differences in dark conductivity for bulk materials within the thin absorptive layer. Differences in excited state behavior and efficiency of charge injection at the illuminated interface are also likely to be important. Quantitative evaluation of these effects is currently being conducted in our laboratories.

3. ACKNOWLEDGEMENTS

This research was sponsored by the U.S. Department of Energy, Office of Basic Energy Sciences, and by the Texas Advanced Research Program.

4. REFERENCES

1. B.A. Gregg, M.A. Fox, and A.J. Bard, "Photovoltaic Effect in Symmetrical Cells of a Liquid Crystal Porphyrin," *J. Phys. Chem.*, 94, 1586, 1990.
2. M.A. Fox and H.-L. Pan, "Synthesis and Properties of 2,3,6,7-Tetrakis(alkoxymethyl)tetrathiafulvalenes," submitted for publication, 1991.

Soluble polyacetylenes derived from the ring-opening metathesis polymerization (ROMP) of substituted cyclooctatetraenes:
electrochemical characterization and Schottky barrier devices

Thomas H. Jozefiak, Michael J. Sailor, Eric J. Ginsburg, Christopher B. Gorman,
Nathan S. Lewis*, Robert H. Grubbs*

*Contribution #8376 from The Arthur A. Noyes Laboratory of Chemical Physics and
Arnold and Mabel Beckman Laboratory of Chemical Synthesis, The Division of Chemistry and Chemical Engineering,
California Institute of Technology, Pasadena, California 91125, USA*

ABSTRACT

Recent developments in ring-opening metathesis polymerization (ROMP) have enabled the synthesis of poly-cyclooctatetraene (poly-COT), a material which is isostructural to polyacetylene. This liquid-phase polymerization method allows facile construction of interfaces, films, and devices with polyacetylene-like materials. The ROMP method also allows the preparation of soluble, yet highly conjugated polyacetylene analogs from substituted cyclooctatetraenes (R-COT). The redox characteristics of R-COT polymers were investigated at electrodes modified with thin polymer films. Voltammetric methods were used to characterize the redox response, band gap, electrochemical doping, and cis-trans isomerization properties of these polyenes. We have applied poly-COT technology to the fabrication of Schottky diodes and photoelectrochemical cells, by forming poly-COT films on semiconductor surfaces. The resultant semiconductor/organic-metal interfaces behave more ideally than semiconductor contacts with conventional metals, in that changes in the work function of the conducting polymer exert a large and predictable effect on the electrical properties of the resulting Schottky diodes. Transparent films of the solution-processible polymer poly-trimethylsilyl-cyclooctatetraene (poly-TMS-COT) have been cast onto n-silicon substrates and doped with iodine to form surface barrier solar cells. These devices produce photovoltages that are much larger than can be obtained from n-silicon contacts with conventional metals.

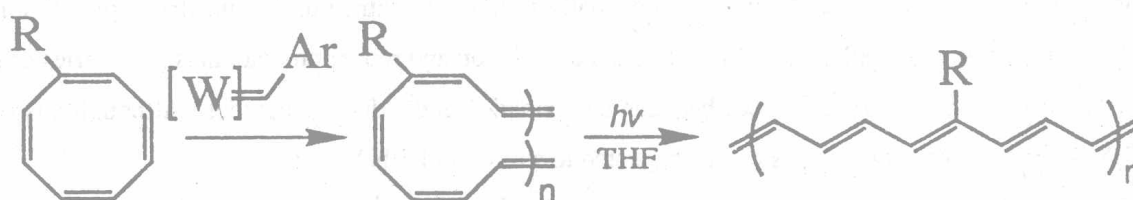
1. INTRODUCTION

Within the last 15 years, a large volume of work¹ exploring the synthesis and properties of polyacetylene has generated tremendous interest within the scientific community. As a one-dimensional semiconductor capable of either n- or p-type doping to high metallic conductivities, polyacetylene is a material with many potential applications² in diverse fields such as sensors, solar energy conversion, and lightweight batteries. However, the use of polyacetylene in many of these applications is hindered by an inherent lack of processability that is found in nearly all highly conjugated, and necessarily rigid, organic conducting polymers. Polyacetylene is a brittle, insoluble, and unprocessable material, classically formed by the exposure of acetylene gas to catalyst-treated surfaces. The polymer films which result have a fibrillar morphology and are semi-crystalline. Both the lack of processability of this material and its method of synthesis have hindered many potential applications where uniformly thin, mechanically strong films are required for casting onto a variety of substrates.

Considerable effort has been directed toward the preparation of soluble prepolymers from which polyacetylene may be obtained after processing.³

The synthesis of polyacetylene from the transition-metal catalyzed ring-opening metathesis polymerization (ROMP) of cyclooctatetraene, reported by Grubbs in 1988,⁴ represents a liquid-phase route to polyacetylene. The resulting polymer, poly-cyclooctatetraene (poly-COT), has many of the same properties as polyacetylene formed by the classical (Shirakawa) polymerization of acetylene over Ziegler-Natta type catalysts. However, the liquid-phase ROMP method of synthesis is more amenable to the preparation of thin films and the fabrication of devices. More importantly, this method can be generalized to the polymerization of substituted cyclooctatetraenes.⁵⁻⁷ Polymers from substituted cyclooctatetraenes (poly-R-COT), bear a substituent group every eight carbons on the average. Thus, the ROMP procedure provides substituted polyacetylenes not accessible from other monomers. It has been found that the appropriate choice of substituent results in a polymer which is soluble in common organic solvents (tetrahydrofuran, CH₂Cl₂) while retaining the high conjugation length required for doping to the metallic state.

As prepared, COT polymers have a high content of cis double bonds. In the case of the soluble poly-R-COT materials, a photochemical means of cis-trans isomerization has been developed,⁵ which results in a mostly trans polyene. This serves as an alternative to the thermal isomerization method commonly employed for insoluble polyacetylene films (see Scheme 1).



Scheme 1. Synthesis of *trans*-poly-RCOT from a substituted cyclooctatetraene.

In this report, we describe the electrochemical characterization of poly-R-COT materials, demonstrating the ease with which surfaces (such as electrodes) can be modified. As a potential application of this technology, we also describe the properties of Schottky barrier diodes formed by the interface between n-silicon and a metallically doped coating of poly-COT. Further, we describe Schottky barrier solar cells formed from thin transparent layers of poly-trimethylsilyl-COT deposited from solvent onto n-silicon. We have previously reported on the unique features of these semiconductor/organic-metal interfaces and found them to be superior to traditional semiconductor/inorganic-metal devices.

Substituted cyclooctatetraenes were polymerized as previously described⁵ by mixing the liquid monomer with the tungsten carbene catalyst:⁸ W(CHAr')(NAr)[OCMe(CF₃)₂]₂(THF) where Ar = C₆H₅ and Ar' = o-MeOC₆H₄. The polymer films were prepared and manipulated in a nitrogen filled dry-box. All electrochemical experiments were performed in the dry-box. All single-crystal silicon samples were ohmically contacted with gallium-indium eutectic, mounted in epoxy to cover the back contact and edges, and etched with 48% hydrofluoric acid before deposition of the polymer. n-Si samples were oriented along the (100) plane, and the p-Si samples were oriented in the (111) plane.

2. VOLTAMMETRIC STUDIES OF R-COT POLYMERS

2.1 Cyclic voltammetry and redox potentials

We have reported that, like polyacetylene, poly-R-COT films can be doped p-type with iodine vapour, or n-type with a tetrahydrofuran solution of potassium benzophenone. These redox processes have now been studied electrochemically. Voltammetry experiments were performed using carbon electrodes modified with thin ($<0.2\ \mu\text{m}$) films of R-COT polymers. Using a microliter syringe, a small amount (0.5–3.0 μl) of a tetrahydrofuran polymer solution (0.3 mg/ml) was placed on the surface of a glassy carbon electrode, and the solvent was evaporated. Voltammetry was performed using a standard three-electrode configuration in a single compartment cell. The polymer modified electrode was placed in a voltammetry cell along with a platinum counter electrode and a Ag/Ag^+ reference electrode. The solvent/supporting-electrolyte was acetonitrile/0.1M TBABF₄ (tetra-*n*-butylammonium tetrafluoroborate). Though soluble in nonpolar solvents such as tetrahydrofuran, dichloromethane and toluene, the R-COT polymers were found to be insoluble in more polar solvents such as acetonitrile. The voltammograms obtained show reversible couples for both anodic and cathodic redox processes (see Figure 1). The anodic couple was characterized by sharp peaks with small peak separation ($<100\ \text{mV}$). The cathodic couple generally shows slightly broader waves and a peak shape which is more dependent on scan rate and film thickness. The small voltammetric peak separations seen for these materials may be attributed to their amorphous morphology. Solvent cast films of R-COT polymers have been shown by microscopy^{7b} to be unusually smooth in contrast to the fibrillar or pitted morphology frequently found for conducting polymers. Table 1 lists the oxidation and reduction potentials for a series of R-COT polymers. Also listed is the energy difference between the oxidation and reduction couples. Although this is not a rigorous measure of the band gap, these two values can be expected to show similar behavior.

The data of Table 1 reveal some interesting trends. Particularly noteworthy is the effect of substitution on oxidation potential. Relative to alkyl-substitution, the trimethylsilyl (TMS) polymer is more difficult to oxidize by 130 mV, and the *tert*-butoxy polymer is more easily oxidized by 130 mV. The TMS group is known as a π -acceptor,⁹ while the *tert*-butoxy group is an electron donating substituent. There is also an observable effect of steric bulk on conjugation length. Within the series of butyl substituted polymers, *n*-butyl shows the smallest voltammetric "band-gap", while the bulky *tert*-butyl substituted polymer is so severely twisted that it cannot be doped anodically or cathodically within the available electrochemical window. This finding is supported by spectroscopic measurements in THF solution, where increasing conjugation length is indicated by a lower energy π - π^* transition.

The inability to measure the relative amounts of capacitive and faradaic charge in the electrochemical doping of a polymer film complicates the coulombic determination of stoichiometry.¹⁰ With this point in mind, coulometric analysis of the electrochemical doping was attempted. In this experiment, a polymer modified electrode was swept through its anodic or cathodic couple within limits that closely bracketed the peak region of the voltammetric wave. This portion of the wave should represent predominantly faradaic charging. The charge passed was measured for the anodic sweep of the oxidation couple (p-doping), and the cathodic sweep of the reduction couple (n-doping). This measurement was carried out on the