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Final Report: Photochromism as a Switching Mechanism for Electronically Active Organic Materials

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**Final Report: Photochromism as a Switching Mechanism
for
Electronically Active Organic Materials**

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Abstract

Recent discoveries in the field of conjugated polymers in environmental stability, regiochemical regularity, and electrical conductivity, particularly of polythiophene and polyaniline, have intensified interest in device applications. Present or anticipated applications include development of electrical circuitry on a molecular scale, as well as conducting and semiconducting materials for a variety of applications including thin film transistors and batteries. We have investigated a series of compounds comprising conjugated segments coupled to photochromic elements. The photochromic reaction in these compounds reversibly alters the conjugation length and provides a mechanism for switching both the electrical and optical properties of these materials. We are currently investigating the nature and scope of this switching mechanism and preparing extended materials that take advantage of this novel form of switching behavior. Preparation and photochromic behavior of several of these materials are described.

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Preface

This report reviews the goals and accomplishments of Sandia LDRD #xxxx entitled "Photochromism as a switching mechanism for electronically active organic materials." This LDRD project was initiated on 10/1/94, renewed on 10/1/95, but terminated soon thereafter when the principal investigator (S.J.J.) left the corporation. Consequently, the research efforts described in this report are reflective of a "work in progress" rather than a completed research project.

INTRODUCTION

Since the first proposal that building electrical circuits on a molecular scale might be possible, a wide variety of molecules and supramolecular systems have been studied around the world for application in "molecular electronics."¹ Molecules that may serve as analogs of electronic circuit elements in nanoscale systems have recently drawn increased attention.²

We would like to develop a number of tools for use in designing inexpensive, highly functional microdevices based on organic molecules and polymers. To have utility in this regard, a molecular system must include discrete, interconvertible molecular states that are readily polled. Easy external control of such devices and their processes might be realized with light. In unison, these features suggest advantages obtainable by coupling easily polled, bistable switchable molecules to conducting or semiconducting polymers that could serve as active electronic elements in microscale devices.

To address these requirements, we have undertaken the synthesis and characterization of a family of organic compounds containing thiophene oligomers and polymers whose conjugation length and electronic properties may be reversibly altered by means of a photochromic reaction involving the oligothiophene chain. This report describes the synthesis and photophysical behavior of **1**, a thiophene trimer coupled to a dimethylenesuccinic anhydride (fulgide) (Figure 1), a well-known element of many organic photochromes.³ In addition, our approach to preparing a variety of polymers in which **1** is used as a building block is described. Under the influence of UV light, **1** should isomerize to 7,7a-dihydrobenzo[b]thiophene (7,7a-DHBT) **2**, which should in turn be converted by visible light back into **1** (Figure 1). Research on these and similar molecules will provide a foundation for a device we have dubbed a "molecular transistor." Our molecular transistors will be designed to operate analogously to conventional transistors, except that instead of being controlled by a bias electrical current, these molecular transistors are controlled photonically (Figure 2).

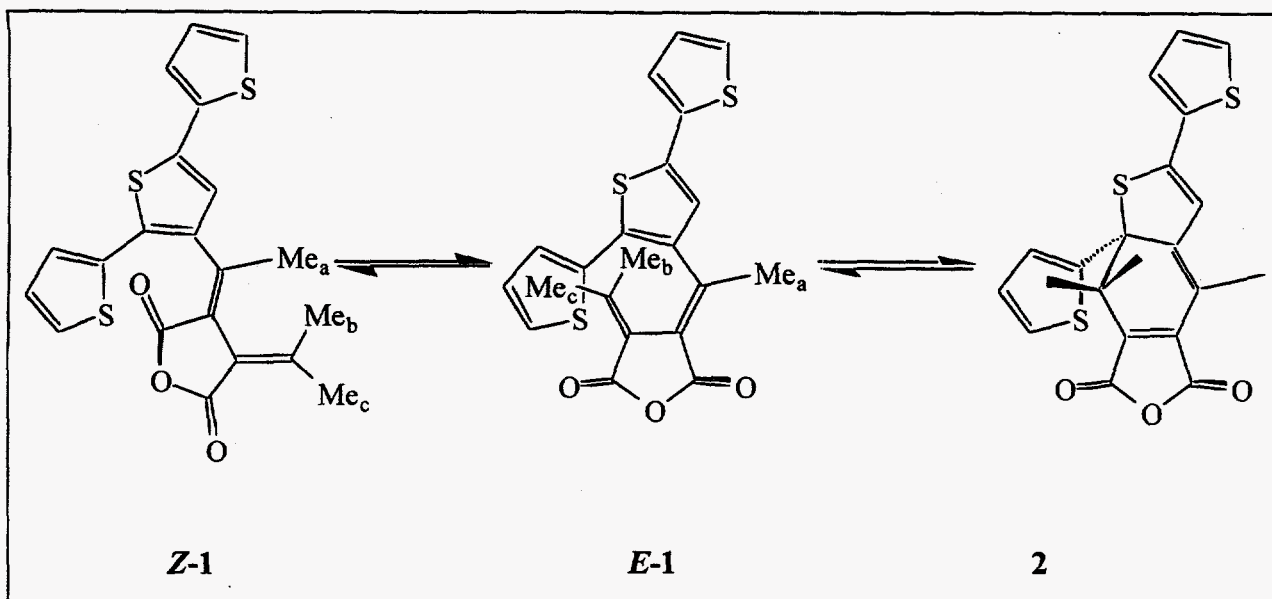


Figure 1. Interconversion of *Z*-1, *E*-1, and 2 via photoisomerization and photocyclization.

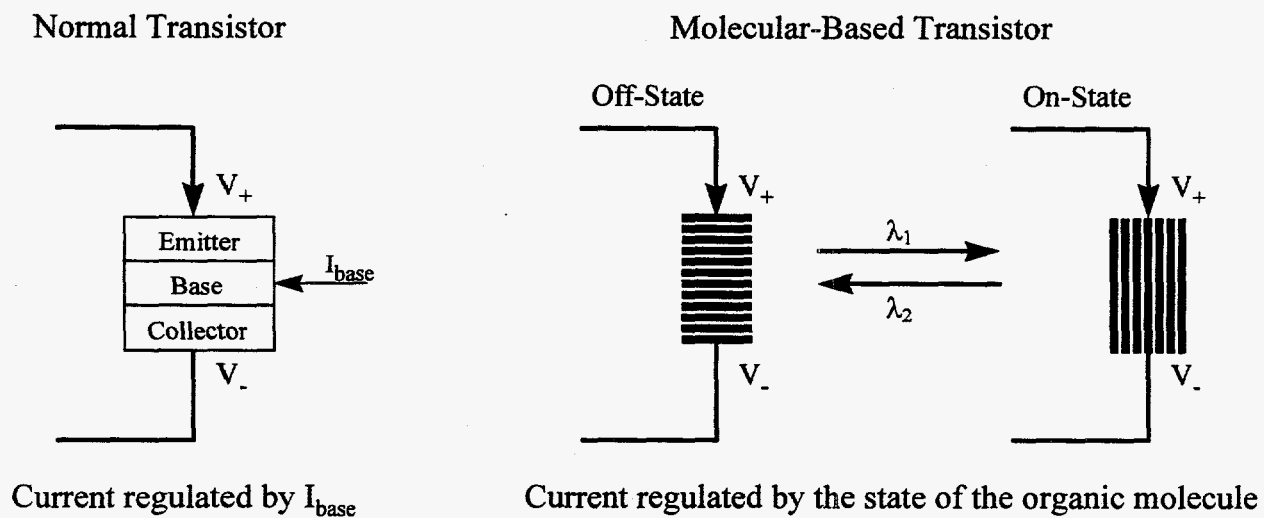


Figure 2. Comparison of conventional and molecular based transistors.

EXPERIMENTAL

Starting materials and solvents were of commercial grade and used and received. Synthetic precursors to 3'-fulgide-2:2'-5':2''-terthiophene (1) were characterized by GC-MS using a Hewlett-Packard 5890 Series II gas chromatograph coupled to a Hewlett-Packard 5972 Series mass selective detector using chemical ionization techniques. ¹H-NMR were obtained with a Bruker AM300-NMR spectrometer operating at 300 MHz. Chemical shifts are reported relative to TMS (δ = 0) and coupling constants are reported in Hz. Electronic spectra were recorded as toluene solutions with a Perkin-Elmer Lambda-19 UV/VIS/NIR spectrometer. Photoreactions were carried out in precision 1-cm square quartz cells placed in at the center of a Rayonet Photochemical Reactor equipped with 350 nm bulbs.

3'-Bromo-2:2'-5':2''-terthiophene was prepared by the NiCl₂(dppp) catalyzed coupling of 2-thiophenylmagnesium bromide and 2,3,5-tribromothiophene by the method described by Kumada for related compounds.⁴

3'-Cyano-2:2'-5':2''-terthiophene. Zinc dust (0.10 g, 1.53 mmol) was added to a 45 °C solution of NiCl₂·1.5H₂O (0.07 g, 0.45 mmol) and triphenylphosphine (0.48 g, 1.83 mmol) in 30 mL anhy. acetonitrile under argon. After ca. 45 min., the dark red-yellow solution was treated with 3'-Bromo-2:2'-5':2''-terthiophene (1.50 g, 4.58 mmol) and NaCN (0.24 g, 4.90 mmol). After 60 hours, 50 mL of ether was added, the solution was filtered, washed twice with water (50 mL), and dried over anhy. MgSO₄. The oil obtained after filtering and evaporating this solution was chromatographed on silica using a 95/5 solution of hexane/ether to yield 3'-cyano-2:2'-5':2''-terthiophene (0.32 g, 1.17 mmol, 26% yield) as a bright yellow solid.

3'-Acetyl-2:2'-5':2''-terthiophene. Methylmagnesium bromide (3M in ether, 3.60 mmol) was added via syringe to a solution (25 mL benzene + 1 mL ether) of 3'-cyano-2:2'-5':2''-terthiophene (0.50 g, 1.83 mmol) under argon. After refluxing for 4 hours conversion to the ketimine salt appeared to be quantitative by TLC. After cooling to room temperature, 4 mL of

H₂O followed by 4 mL of 6 N HCl were cautiously added and the solution returned to reflux for 5 additional hours. The aqueous layer was separated and extracted twice with 25 mL of ether. The organic layers were combined and washed with 20 mL of sat. NaHCO₃. The aqueous layer was separated and extracted once with 25 mL of ether. The organic layers were combined, dried over anhy. MgSO₄, filtered, and evaporated to give 3'-acetyl-2:2'-5':2''-terthiophene in quantitative yield.

3'-Fulgide-2:2'-5':2''-terthiophene (1) was prepared from 3'-acetyl-2:2'-5':2''-terthiophene by the Stobbe condensation followed by hydrolysis and dehydration reactions in a manner analogous to that used by Heller to prepare monothienyl fulgides from 2-acetyl and 3-acetyl thiophenes.⁵ *E*- and *Z*-isomers were separated on silica using a 60/40 solution of hexane/ether.

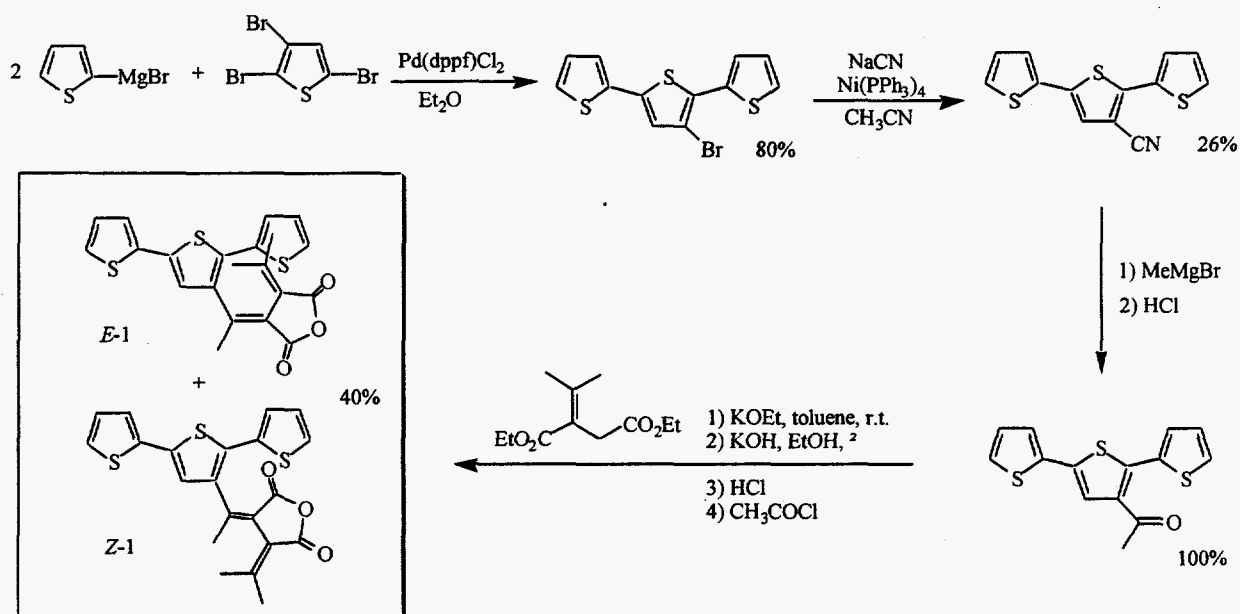
RESULTS AND DISCUSSION

SYNTHESIS

We envisioned the synthesis of **1** as being quite facile, adapting the synthesis detailed by Heller⁵ for monothienyl fulgides to the novel ketone 3'-acetyl-2:2'-5':2''-terthiophene, in turn derived from 3'-bromo-2:2'-5':2''-terthiophene⁶ following its cyanation and subsequent conversion to the ketone with methylmagnesium bromide (Scheme 1). Indeed, the synthesis of the target fulgide proceeds by the standard Stobbe condensation, hydrolysis, and dehydration sequence used by Heller to prepare a number of thienyl fulgides.

The fulgide is produced as a 2:1 mixture of *Z*- and *E*-isomers. We have been able to partially separate this mixture by column chromatography, obtaining pure *E*-fulgide and a mixture highly enriched in the *Z*-isomer (90%). Our assignment of the isomers is consistent with the well-established ¹H-NMR chemical shifts observed in related compounds in which shielding and deshielding effects of the aryl ring and carbonyls, respectively, are important, i.e.

substituents *cis* to a carbonyl group are deshielded while those underlying aryl rings *trans* to a carbonyl group are shielded.⁷ In the *E*-isomer, Me_b and Me_c (Figure 1) are both shielded by the thiophene ring and appear at higher field; however, there is a competitive deshielding effect from the carbonyl *cis* to Me_c. Me_a is likewise deshielded and appears at lowest field. In the *Z*-isomer, only deshielding from the carbonyl *cis* to Me_c is important; resonances from Me_a and Me_b appear at normal positions while Me_c appears further downfield. The methyl groups in our assigned isomers closely parallel those published by Heller for thienyl fulgides (Table 1).⁵



Scheme 1. Synthesis of 3'-fulgide-2:2'-5':2''-terthiophene (1).

Table 1. Methyl Group $^1\text{H-NMR}$ Chemical Shifts (δ).^a

	Obsd.	Ref. 4	Obsd.	Ref. 4	Obsd.	Ref. 4
Z-isomer	2.45	2.49	2.15	2.49	2.10	2.33
E-isomer	2.65	2.66	2.17	2.34	1.46	1.31

^a $^1\text{H-NMR}$ (300 MHz), **1**: δ 7.33 (dd, $J=1.2, 5.1$ Hz, 1H); 7.28 (dd, $J=1.1, 5.0$ Hz, 1H); 7.19 (dd, $J=1.1, 3.7$ Hz, 1H); 7.05 (dd, $J=3.7, 5.0$ Hz, 1H); 7.03 (dd, $J=3.6, 5.0$ Hz, 1H); 7.01 (s, 1H); 6.98 (dd, $J=1.2, 3.6$ Hz, 1H); 2.65 (s, 3H); 2.34 (s, 3H); 1.46 (s, 3H).

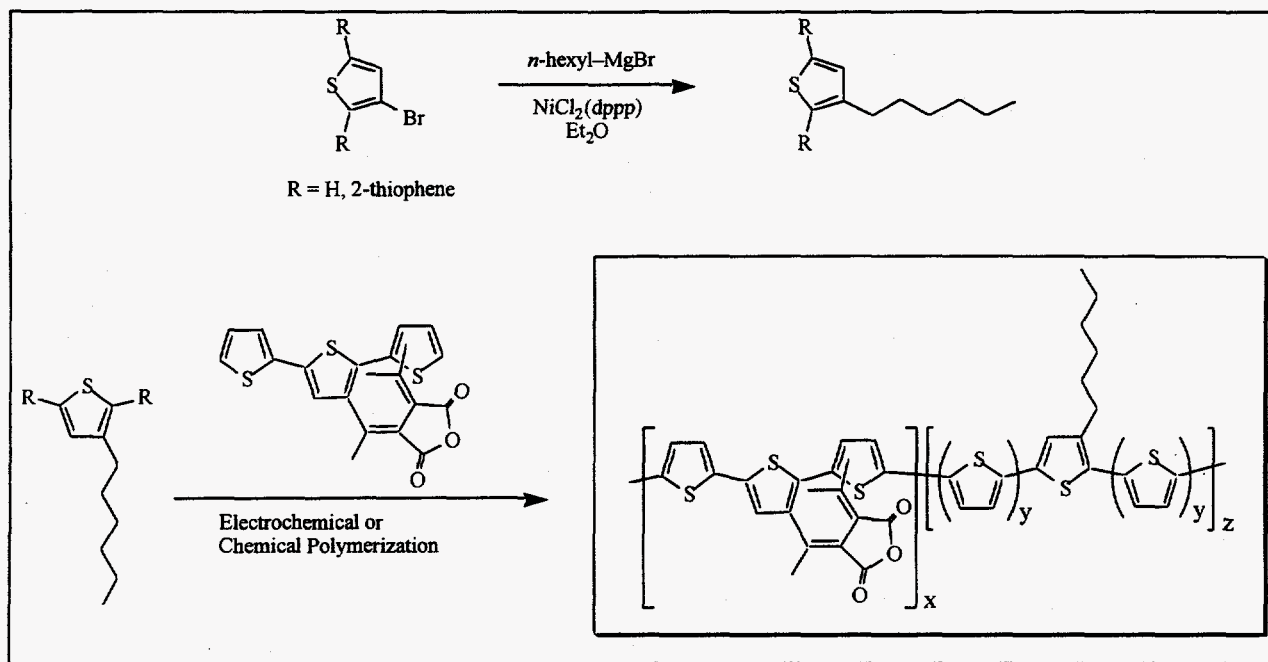
POLYMER PREPARATION

Historically, thiophene oligomers and polymers have been prepared by several methods;⁸ the three most prevalent are:

- 1) transition metal catalyzed grignard polycondensation of 2,5-dibromothiophenes;⁹
- 2) transition metal catalyzed oxidative polymerization;¹⁰
- 3) electrochemical polymerization.¹¹

Of these three popular methodologies, we have found the latter two to be applicable for the preparation of poly(**1**), however, this material is intractable and has not yet been thoroughly characterized. Based on the observation that soluble polythiophenes can be prepared from 3-alkylthiophene monomers,⁸ we believe that copolymerization of 3'-fulgide-terthiophene with alkyl-substituted thiophenes will allow us to tune the physical properties of the polymers as well as maintain their photoswitching ability. In this regard, we have prepared 3-hexylthiophene and

3'-hexylterthiophene and are currently investigating the conductivities and physical properties of the various homopolymers and copolymers which can be derived from them and **1** (Scheme 2).



Scheme 2. Homopolymer and copolymer syntheses.

Photochemical Experiments

When irradiated with a wide variety of sources of UV light, including handheld laboratory lamps, low-power arc lamps, and a Rayonet Photochemical Reactor equipped with 350 nm bulbs (~100 W of UV light!), solutions of **1** change rapidly from yellow to deep red in color. ¹H-NMR experiments show that *E*-**1** undergoes both *E,Z*-isomerization *and* cyclization to the 7,7a-DHBT. The photochemical reaction to give **2** is faster by the pure *E*-isomer than with the mixture that is predominantly *Z* (Figure 3). This is expected because the *Z*-isomer must first undergo *E,Z*-isomerization before it can form **2**. Future synthetic efforts will be directed toward suppressing the double bond isomerization pathway for the *E*-form.

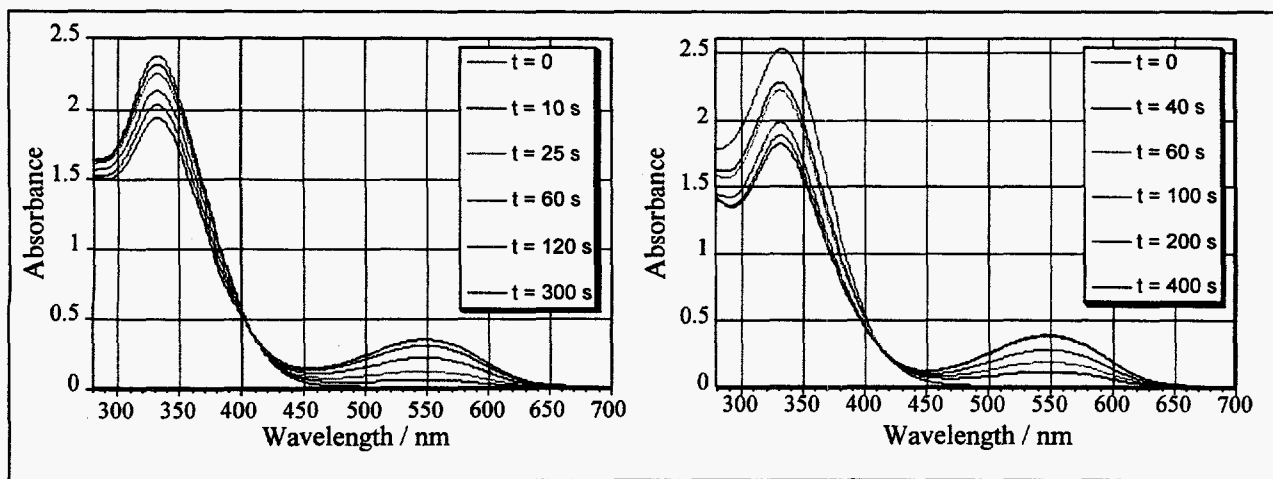


Figure 3. Time evolution of the electronic spectra of *E*-1 (left) and *Z*-1 (right) with irradiation in a Rayonet Photochemical Reactor.

Upon exposure to light of wavelength λ 500 nm, the red color of **2** is bleached back to the original yellow color of **1**. This process is slow under ambient fluorescent lighting conditions but is rapid with a low-power arc lamp/color filter combination. We have not yet characterized the photoreversal process in detail. The photochromic process also occurs in thin films of **1**.

Calculations Related To Photochromic Behavior

It is not obvious that **1** and similar molecules should photoswitch. One could easily imagine that all of the energy involved in the switching transition might funnel into the thiophene backbone of **1** and give rise to fluorescence or nonradiative decay. For this reason, we turned to the INDO/1 parameterization of ZINDO¹² as implemented in the CAChe WorkSystem suite of programs in order to model the electronic states of **1**. The basis orbitals of the thiophene trimer clearly form the HOMO and LUMO orbitals (Figure 4), however, examination of the HOMO-1 and LUMO+1 orbitals reveal that these are strongly *localized on the fulgide portion of the molecule* and are mostly decoupled from the terthiophene system (Figure 5). The calculated electronic spectra show that the absorptions associated with electronic transitions between these

orbitals have comparable oscillator strengths. These results are significant not only for 1, but also for the general case, suggesting that even longer oligomers and polymers may have localized transitions associated with forward and reverse photochromic behavior. For the reverse reaction, the model suggests that the HOMO-LUMO transition should result in a photochemically allowed ring opening, although the calculated absorption maximum does not agree with the experimental value.

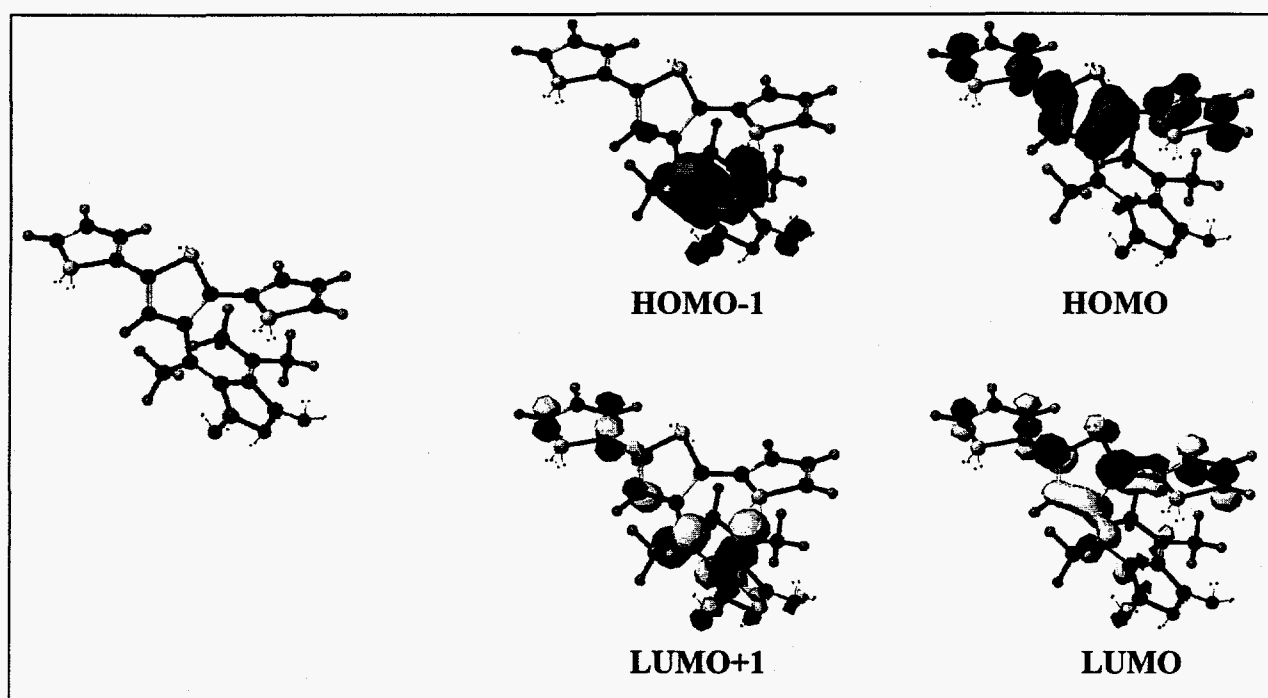


Figure 4. Representations of the frontier molecular orbitals of *E*-3'-fulgide terthiophene (*E*-1).

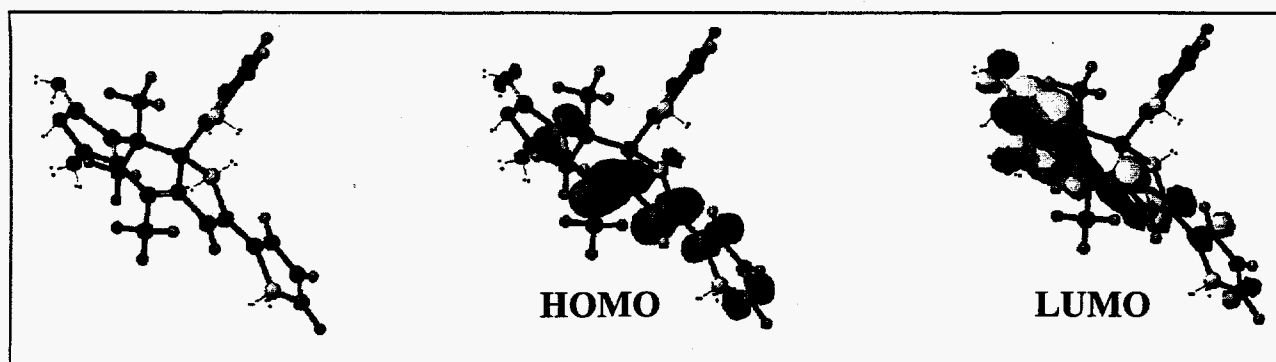


Figure 5. Representations of the HOMO and LUMO of 7,7a-dihydrobenzothiophene (**2**).

CONCLUSIONS AND FUTURE WORK

We have synthesized terthienyl fulgide **1** and shown that it undergoes photochemically induced ring closure to 7,7a-DHBT **2**, which may be converted back to **1** by irradiation with visible light, both in solution and in the solid state. Our calculations suggest that since the transition is localized on the fulgide moiety, the forward photochemical reaction occurs despite being associated with a relatively high energy absorption. Additionally, we have prepared a series of thiophene polymers incorporating these photochromic building blocks. While the utilization of these and related materials in active electronic devices has not yet been demonstrated, this research topic remains relevant and interesting. It is anticipated that molecular based electronic components will continue to be an area of active research and development.

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