Final Technical Report
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SUPERCONDUCTIVE ORGANIC POLYMERS:

CONCEPTUAL DESIGN, SYNTHESIS, AND CHARACTERIZATION

Principal Investigator:
Ronald L Elsenbaumer
Ronald L. Elsenbaumer
The University of Texas at Arlington
Box 19031
Arlington, Texas 76019

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110 Duncan Avenue Suite B115
Bolling AFB DC 20332-0001

Executive Summary

Significant Findings:

- ○ Theoretical studies indicate that extended chains conisting of isomeric TTF structures have electronic properties and stabilities comparable to TTF extended structures and are therefore of considerable interest as possible polymeric organic superconductive compositions.

- ○ Synthetic stratigies were developed to prepare polymeric TTF and isomeric TTF structures.

- ○ Dramatically simplified synthetic procedures were developed to prepare TTF and ET-TTF donors in high yield and large quantities from inexpensive starting materials.

- ○ Developed new techniques to purify, characterize and grow large single crystals of TTF and ET-TTF.

- ○ Synthesized new organic conductive polymers with good electrical conductivities and processibility.

- ○ Developed new processing and doping techniques for polyalkylthiophenes to provide consistently high conductivity materials.

Personnel Involved in the Project:

Principal Investigators:

Ronald L. Elsenbaumer
Dennis S. Marynick
Martin Pomerantz
Suresh S. Sharma

Students and Post-docs

Ronald L. Meline
Seeyearl Seong
Jiping Wang

Kyle P. Starkey
Long Ngugen
Reginald C. Hyer
Rajiv G. Pethe
H. Yang
Haitao Cheng
Yueping Fu
Y. Cheng
Toshiya Yogi

Collaborators:

Richard D. McCullough
John R. Reynolds

Journal Publications (Total of 20)

Elsenbaumer, R.L.; Marynick, D.S.; Seong, S.; Meline, R.L. "Sulfur Containing Conjugated Polymers With Interesting Electronic Properties", *Mat. Res. Symp. Proc., 328* (**1994**) 221-225.

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"A New Dithiophene Fused p-Phenylene Vinylene Conducting Polymer. Synthesis and Study," M. Pomerantz, J. Wang, D.S. Marynick, S. Seong, R.L. Elsenbaumer, and S.C. Sharma, paper presented at the Materials Research Society Meeting, Boston, Massachusetts, November 29-December 3, **1993**.

"Isomeric Sulfur Containing Conjugated Polymers with Interesting Electronic Properties," D.S. Marynick, S. Seong, R.L. Meline, M. Pomerantz, R.L. Elsenbaumer, and S.C. Sharma, paper presented at the Materials Research Society Meeting, Boston, Massachusetts, November 29-December 3, **1993**.

"Synthesis and Study of New Sulfur Heterocycle Fused p-Phenylene Vinylene Conducting Polymers," M. Pomerantz, J. Wang, K.P. Starkey, L. Nguyen, D.S. Marynick, S. Seong, R.L. Elsenbaumer, and S.C. Sharma, presented at the 16th International Symposium on the Organic Chemistry of Sulfur (ISOCS 16), Meresburg, Germany, July 10-15, **1994**.

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"Temperature Dependence of the *dc* Electrical Conductivity of Poly(benzo[1,2-*b*:4,5-*b*']-dithiophene-4,8-diyl vinylene)," Hyer, R. C.; Pethe, R. G.; Sharma, S. C.; Pomerantz, M.; Wang, J.; Elsenbaumer, R. L. 209th National Meeting of The American Chemical Society, Anaheim, California, April, **1995**.

"Structure/Property Relationships in Conjugated Polymers: Oxidation Potentials, Reduction Potentials, and Band Gaps for a Series of Regiospecifically Methoxy Substituted Thiophene Vinylenes and Poly(bithiophene vinylenes), " Fu, Y.; Elsenbaumer, R.L. 209th National Meeting of The American Chemical Society, Anaheim, California, April, **1995**.

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"Preparation and Properties of Some New Low Band Gap Conductive Polymers" Elsenbaumer, R.L.; International Symposium: Polymers for Electronic and Photonic Applications, Oct. 22-23, **1996**.

"Organic Superconductors: New Methods and Materials" Meline, R. L.; Elsenbaumer, R. L.; ACS Meeting in Minature, Texas Christian University, April 19, **1997.**

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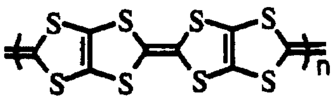
Superconductive Organic Polymers: Conceptual Design, Synthesis, and Characterization

Ronald L. Elsenbaumer, Martin Pomerantz, Dennis S. Marynick,
and Suresh C. Sharma

Departments of Chemistry, Physics, and Materials Science & Engineering
The University of Texas at Arlington
Arlington, Texas 76019

I. Introduction

As part of our long-standing program to develop new highly conjugated, multifunctional electrically conducting polymers, we attempted to design, prepare and characterize new materials that show enhanced conductivity and possibly even superconductivity at low temperature. This was anticipated to be achieved in several ways, including synthesizing materials which are more ordered on a molecular level, stretch orienting polymer chains and increasing dimensionality of the polymer array. To this end we designed and prepared systems which, in addition to the one-dimensionality of the polymer backbone, also have controlled degrees of increased dimensionality transverse to the chain axis direction. This should increase interchain electronic interactions and provide the needed two-dimensional conduction network. Our approach combined the known attributes of charge transfer complexes which contribute to their electrical conductivity, and even superconductivity, where conduction occurs along stacks of these ring systems, with the chain conduction of doped, high molecular weight conjugated polymers. These attributes include their flat, broad conjugated nature, their ability to form ordered structures and that they contain a number of large, polarizable atoms such as sulfur which allow for orbital interaction, through short intermolecular S–S distances, from one planar molecule to a nearest neighbor. We chose three classes of polymers to study that have an abundance of sulfur atoms on the periphery of the polymer backbones; the isomeric TTF polymers **1-3**, poly(benzo[1,2-*b*:4,5-*b'*]dithiophen-4,8-diyl vinylene) (**4**), and poly(1,4,6,9-tetrathiaanthra-5,10-diyl vinylene) (**5**).



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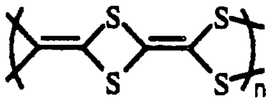

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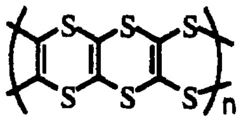

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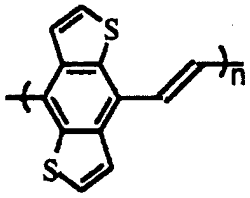

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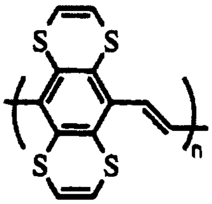

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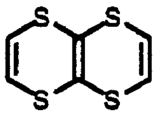
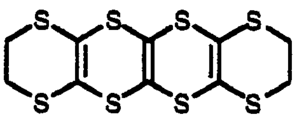
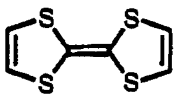
Our studies also led us to the design and synthesis of a new class of organic donors for charge transfer complexes. These are tetrathianaphthalene (TTN, **6**) and its derivatives such as ET-TTN **7**, that are isomeric structrues of TTF. Dramatically improved synthesis of TTF and ET-TTF were also developed from inexpensive starting materials.



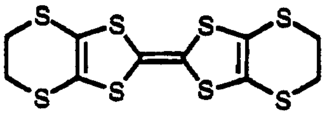
TTN 6



ET-TTN 7



TTF 8



ET-TTF 9

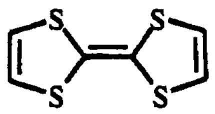
II. Approach and Results

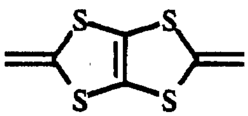
A. Conceptual Design of Candidate Systems

Although there are no known organic polymeric superconductors, there are several organic superconductive charge-transfer complexes known. A vast majority of these have been derived from tetrathiafulvalene and related electron donor molecules, such as BEDT-TTF (ET-TTF, **9**), MDT-TTF, and BEDO-TTF. It is well known that many of these superconductive materials have short S--S intermolecular contacts between molecules in adjacent stacks. These short S--S contacts provide the increased dimensionality needed for superconducting coherence. For these reasons, we have initially chosen three classes of polymers to study that have an abundance of sulfur atoms on the periphery of the polymer backbones; the isomeric TTF polymers **1**-**3**, poly(benzo[1,2-*b*:4,5-*b'*]dithiophen-4,8-diyl vinylene) (**4**), and poly(1,4,6,9-tetrathiaanthra-5,10-diyl vinylene) (**5**).

Considerable interest in the polymeric TTF isomers prompted a detailed theoretical investigation of the electronic structures of these materials. These studies have led to some interesting discoveries.

For the initial calculations on these systems, we employed the method of partial retention of diatomic differential overlap (PRDDO). Subsequently, *ab initio* MO calculations were performed with GAUSSIAN 92 on both CONVEX C-220 and CRAY Y-MP computers. STO-3G, 4-31G, and 6-31G* basis sets were used for the geometry optimization. The effect of electron correlation energy on the relative energies of the monomers was taken into account by performing second-order Møller-Plessent (MP2) perturbation calculations. To obtain the geometries of the oligomers, we first optimized the trimers of all the isomers (**1a, 1b, 2a, and 3a**) at the PRDDO level. Then the central monomer unit was taken to build up the geometry of the trimer, tetramer, pentamer, and hexamer oligomers. The 4-31G basis set was used for the energetics of the oligomers since it yielded the results closest to those obtained from MP2 calculations on the monomers. These optimized geometries were used for the band structure calculations employing extended Hückel theory since the SCF-Hartree Fock methods greatly overestimates band gaps.


1a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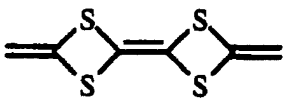
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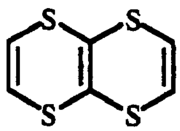

3a

The conformation of TTF determined by the PRDDO method agrees very well with the experiment. The isomer **1b** in its extended structure linked by sulfur atoms leads to the identical polymer (**1**) as that derived from the extended form of **1a**. Calculated bond lengths were essentially identical to those for TTF. As expected, monomer **3a** was found to exhibit two low energy conformations; chair and boat forms. The chair conformation in the monomer is slightly more stable than the boat form. The calculated order of monomer stability is **1a** > **3a** > **2a**.

Since the calculations on monomers have no direct bearing on the question of relative stability of polymers, we have performed calculations on the oligomers of **1**, **2**, and **3**. We used **1a** (TTF) as the reference structure and compared the stabilities between the isomers. The results are shown in the table. The energy differences are the difference between the energy of TTF and the isomers; $\Delta E = E_{TTF} - E_{isomer}$.

Table. Energy Difference per Unit Chain Length ($\Delta E/n$, n = number of repeat units) Between TTF and its Isomers and Oligomers.

Chain Length	ΔE/n (Kcal) for Monomers and Oligomers 1a	1b	2a	3-Chair	3-Boat
1	0.00	7.72	29.95	1.10	3.14
2	0.00	3.77	28.24	-2.20	1.88
3	0.00	2.51	26.98	-3.95	-0.63
4	0.00	2.01	26.35	-3.77	-0.78
5	0.00	1.88	26.35	-4.14	-1.00
6	0.00	1.76	25.73	-4.27	-1.26
∞	0.00	1.71	25.82	-4.39	-1.34

It was found that the stability order for the polymers is different than for the monomers. In particular, the polymer stability order is **3-chair > 3-boat > 1 >> 2**. The stability order regarding the monomers of **1** and **3** reverses on going to the higher oligomers and polymers. These results strongly suggest that the higher fused derivative of TTF would prefer the hexa-cyclic ring to their penta- or tetra-cyclic isomers.

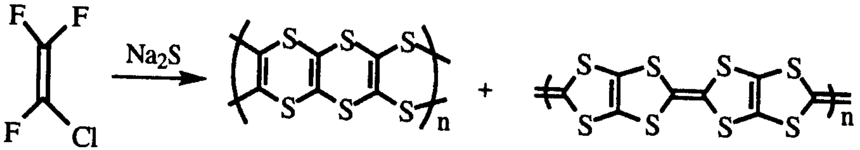
EHT band structure calculations on the three isomeric polymers **1**, **2**, and **3** were also performed. Band gaps were found to be 2.82, 2.78, and 2.74 eV, respectively. The band widths in these systems are small (0.54 - 1.03 eV). Nonetheless, polymer **3** is expected to have better electrical conductivities than **1** or **2** on oxidative doping because of its wider highest occupied valence band. Ionization potentials are considerably smaller than that of polythiophene, thus, p-type oxidative doping should be expedient.

More theoretical details are available in the published articles on this work[1,2].

B. Preparation of isomeric poly-TTF derivatives.

Initial efforts have focused on the preparation of polymers **1** and **3** by the condensation reaction outlined in scheme I.

Scheme I

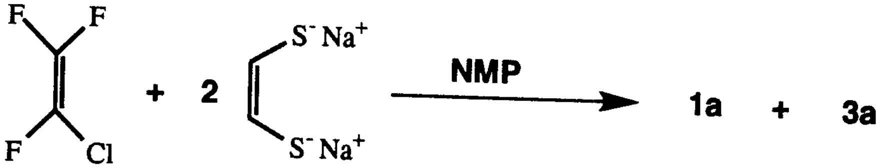


3

1

To understand what isomer might be preferentially formed by this synthesis, we looked at the model reaction system shown in scheme II. Indications are that isomer **3a** is preferred. We have not been able to detect the formation of TTF by this route. This indicates that there will be a high probability of forming polymer **3** by our proposed scheme, which incidentally is the one predicted by theoretical calculations to be of higher conductivity and stability than **1**.

Scheme II

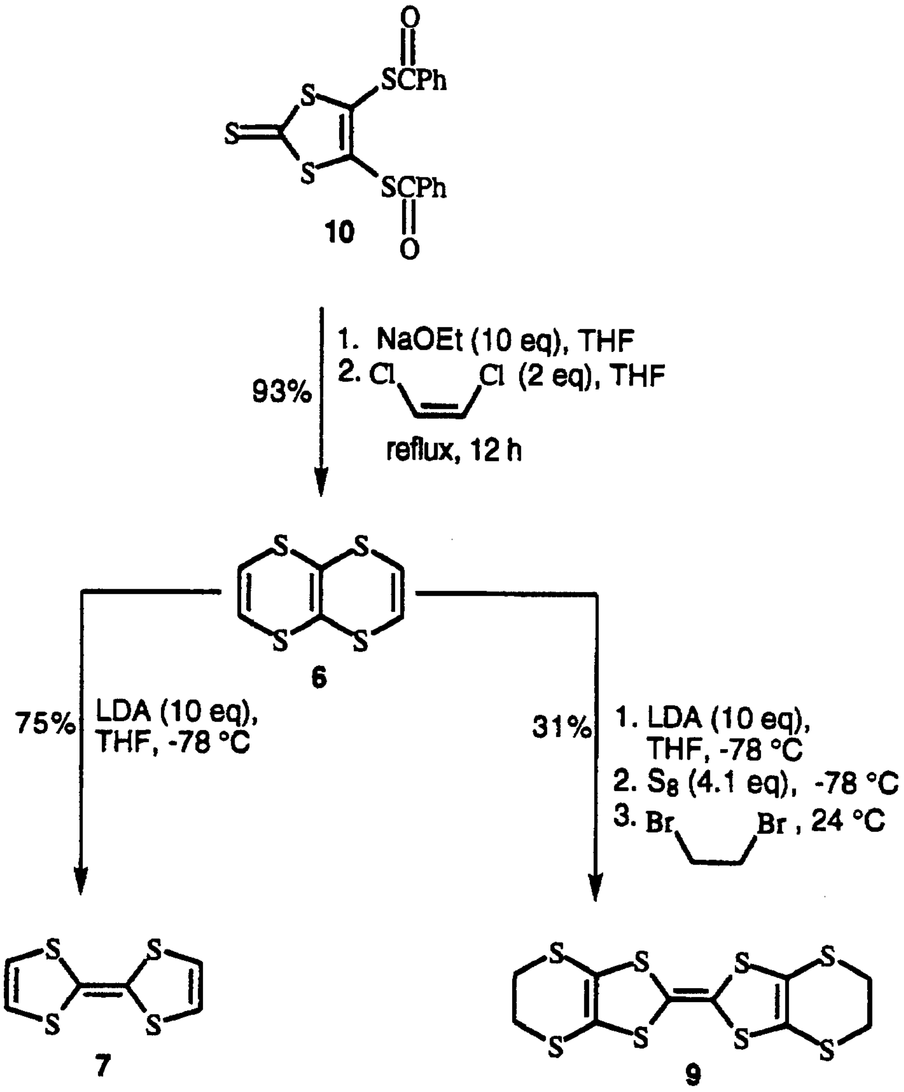


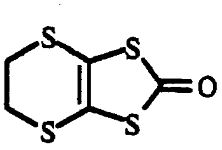
C. Improved syntheses of TTF and ET-TTF

BEDT-TTF (2,2'-bi-5,6-dihydro-1,3-dithiolo[4,5-b][1,4]dithiinylidene) (ET-TTF, 9) has been used in the preparation of at least 20 superconductors, thereby comprising the bulk of known organic superconducting molecular solids.[3,4] The most common syntheses of BEDT-TTF involve the multistep formation of 2-oxo-5,6-dihydro-1,3-dithiolo[4,5-b][1,4]dithiin (5), which is coupled by refluxing in trialkylphosphite/solvent.[5-8] Recently, Becher has reported a method whereby the precursor is coupled and then functionalized in order to yield BEDT-TTF.[9] In each case, a multistep procedure involving coupling is implemented. Alternative synthetic methods could facilitate the syntheses of known donors like BEDT-TTF or lead to the production of new materials sensitive to the coupling procedure.

Here we describe syntheses of TTF and BEDT-TTF which offer the following advantages: (i) easily attainable from inexpensive starting materials; (ii) short number of reaction steps; (iii) a precursor that is easily rearranged into TTF or BEDT-TTF.[10,11]

Scheme III

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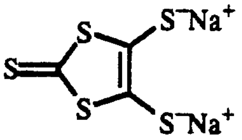

12

The syntheses of TTN and BEDT-TTF are outlined in scheme III. 4,5-Bis(benzoylthio)-1,3-dithiole-2-thione (**10**) was prepared according to published procedures.[12] TTN was originally synthesized by Cava, involving a multistep procedure starting with disodium 1,3-dithiole-2-thione-4,5-dithiolate (**12**) derived from the alkoxide ester cleavage of

(**10**), and culminating in a chromatographic separation.[13] More recently, TTN was prepared from (**12**) by refluxing with cis-dichloroethylene.[14] (**12**) was precipitated from a large volume of ether and was filtered using the schlenk technique being stable under Ar in the dark for only a few days.[12] Our synthesis comprises the coaddition of (**10**) and cis-dichloroethylene into gently refluxing THF containing dissolved excess sodium ethoxide. Presumablly, (**10**) is cleaved at the thioester linkages, and the 1,3-dithiole-2-thione ring is ring opened to give by-products $PhCO_2Et$ and $(EtO)_2C(S)$ respectively as well as the reactive tetrasodium salt of ethylenetetrathiolate. The ethylenetetrathiolate is nucleophilic enough to add cis-dichloroethylene 'side-on' to give a high yield of TTN. It should be noted that the other apparant isomer available upon addition (**9**; tetrathiafulvalene) is not detected by TLC or upon workup (NMR). The reaction provides a high yield (93%) of TTN in a one step reaction eliminating the need for air sensitive schlenk techniques.

TTN is a very useful starting material for other organic metals. Yoshida et al. reported that TTN could be electrochemically oxidized into tetrathiafulvalene.[15] More recently, Anzai et al. stated that TTN could be converted into tetrathiafulvalene in 70% yield via reaction with lithium diisopropylamide (LDA, >4eq.).[16] We have subsequently verified the Anzai reaction and demonstrate that tetralithiated TTN can also be used to prepare BEDT-TTF. Upon tetralithiation of TTN with LDA at -78°C in THF under N_2, elemental sulfur (sublimed, 4.1 eq.) was added to the reaction flask and warmed slowly to room temperature. The addition of excess 1,2-dibromoethane produced polymeric ethyl bridged tetrathiafulvalenetetrathiolate polymers/oligomers as well as BEDT-TTF. Simple soxhlet extraction with carbon disulfide provided pure BEDT-TTF. The conversion of TTN into BEDT-TTF is less an alternative synthesis of BEDT-TTF than a demonstration that inexpensive/easily attainable TTN can be used to synthesize tetrasubstituted tetrathiafulvalenes. This reaction scheme follows a number of studies on the reactivity of tetralithiated tetrathiafulvalene.[17-22] Chalcogen insertion into tetralithiated TTF can often give tetrachalcogenolato-TTF's, which can be alkylated with alkyl halides to give functionalized TTF tetrathioles. Alkylation of tetrakis(chalcogeno)TTF's with alkyldihalides to obtain BEDT-TTF and mixed chalcogen analogues was found not to be possible except for the modified synthesis of BEDSe-TTF[21] or when protecting groups were employed for chalcogen analogues of BEDT-TTF.[19]

The purification of BEDT-TTF also has been explored in this synthesis. BEDT-TTF is insoluble or poorly soluble in common solvents but it has been recrystallized from large volumes of chloroform or chlorobenzene.[5-8] We have found that homogeneous crystals (rods, 0.5 X 0.1mm) can be obtained upon cooling from hot sulfolane (100°C). Much larger homogeneous crystals (rods, 1.4 X 0.2mm) were sequestered from hot thiophene upon slow cooling.

Because of the poor solubility of BEDT-TTF, solution NMR studies have been restricted to the proton site. We have been able to obtain solution ^{13}C-NMR pertinant to our isomerization dependant synthesis using deuterated nitrobenzene as a lock solvent. At 80°C, enough BEDT-TTF dissolves in $C_6D_5NO_2$ to obtain a singlet at 30.62 ppm corresponding to the 4 equivalent ethyl carbons. Although differentiation between TTN and TTF required a 50 second delay between pulses to observe the central quaternary carbon peaks (assignments confirmed from undecoupled spectra), a 100 second relaxation delay failed to reveal any quaternary peaks in BEDT-TTF. The addition of chromium(III) acetylacetonate (5 mg) to a saturated BEDT-TTF/deutero nitrobenzene solution in a 5mm tube (80°C) revealed the 2 central quaternary carbon's peak at 114.41 ppm using only a 5 second delay between pulses. The other 4 equivalent quaternary carbon's signal is buried in the lock solvent peaks as determined by solids NMR studies of related alkyl substituted tetrathiafulvalene tetrathioles.[23]

In Summary, herein we have shown a simple synthesis of 1,4,5,8-tetrathianaphthalene: a valuable precursor that can be easily converted into tetrathiafulvalene or bis(ethylenedithio)tetrathiafulvalene. The utility of this method may be explored for the isomerization of other tetrachalcogenonaphthalenes.[20,24]

Melting points were obtained from Mel-Temp 2 apparatus and are uncorrected. NMR spectra were recorded on a Bruker MSL 300 spectrometer. Mass spectra were obtained from a Finnegan Mat TSQ 70. IR spectra were recorded with a BioRad 40S spectrometer. THF was distilled over sodium/benzophenone prior to use.

1,4,5,8-Tetrathianaphthalene (**6**):

Fresh sodium (9.2g, 400 mmol) was added to a 3-necked 2000 mL round flask equiped with a stirbar, two 250 mL pressure equalizing funnels and a reflux column all under N_2. 200 mL of ethanol was added to the sodium through one of the addition funnels. After all of the sodium had reacted, 500 mL of THF were charged into the flask. 4,5-bis(benzoylthio)-1,3-dithiole-2-thione (**10**) (16.24g, 40 mmol) was dissolved in 250 mL of THF and added to one addition funnel, and *cis*-1,2-dichloroethylene (6.4 mL, 84 mmol) was dissolved in 250 mL of THF and added to the remaining dropping funnel. The two solutions were simultaneously added dropwise over a 4 hr period to the sodium ethoxide solution under gentle reflux with stirring. (**10**) turned red upon reaction with the alkoxide solution, and the whole reaction mixture turned yellow accompanied by a large amount of precipitate after allowing the reaction to reflux gently overnight. After cooling, 200 mL of water was added to the flask, dissolving the precipitate and turning the solution a purple color. The THF (and some of the water) was then removed by rotoevaporation to give a light brown-yellow solid. The solid was collected by vacuum filtration through a glass sintered funnel and washed with copius amounts of water. The product was recrystallized from cyclohexane/hexane (5:3) to give yellow/orange crystals. 7.60g (93%); mp 125-127^{o}C.

^{1}H-NMR ($CDCL_3$/TMS): s = 6.45 (s, 4H)

^{13}C-NMR($CDCL_3$/TMS): s = 118.70 (s, int. C=C); 125.39 (s, ext. C=C)

MS: m/e = 204(M+)

Tetrathiafulvalene (**7**)

BuLi (80 mL of a 2.5m solution in hexanes, 200 mmol) was syringed (glass w/teflon plunger) through a rubber septum into a solution of diisopropylamine (30 mL, 214 mmol) in dry THF (100 mL) in a 1000 mL round bottom flask with a stir bar at -78°C (dry ice/isopropanol) under nitrogen (purge through the rubber septum). After stirring the solution for 1 hr, TTN (**6**) (4g, 19.6 mmol) was dissolved in dry THF (400 mL) and added to a pressure equalizing 500 ml funnel and placed on top of the flask. Nitrogen was then transferred to the top of the funnel. The TTN was then added dropwise over a 4 hour period to the LDA solution whereupon a brilliant yellow color persisted. The solution was stirred at -78°C for 3 hours and was then allowed to warm to 24°C. After 30 minutes, 20 mL of water were slowly added into the flask turning the mixture a yellow/amber color. The THF (and some of the water) was then removed by rotoevaporation to give an orange/brown solid. The solid was collected by vacuum filtration through a glass sintered funnel and washed with copius amounts of water. The product was recrystallized from cyclohexane/hexane (5:3) to afford orange/yellow crystals 2.98g (75%); mp 118-120°C.

^{1}H-NMR (CDCL$_3$/TMS): s = 6.32 (s, 4H)

^{13}C-NMR (CDCL$_3$/TMS): s = 110.10 (s, int. C=C); 119.06 (s, ext. C=C)

MS: m/e = 204(M+)

Bis(ethylenedithio)tetrathiafulvalene (**9**)

4g of TTN was tetralithiated exactly as described for the synthesis of (**7**). After the solution of tetralithiated TTN was stirred at -78°C for 3 hrs, the addition funnel was removed, and the nitrogen (purge through a septum) was placed back on the round bottom flask. Sublimed sulfur (2.6g, 81 mmol) was then added to the flask in one portion. (Occasionally sulfur insertion can be difficult. If encountered, the sulfur can be dissolved in a minimal volume of CS$_2$ and then added to the reaction mixture.) The resultant brown solution (solid materials) was stirred at -78°C for 1 hr and slowly allowed to warm to 24°C overnight (Dewar kept in place w/o Dry Ice replenishment). The following day, hexamethylphosphoramide (HMPA, 50mL) was syringed into the flask at 24°C.[21] One hour after HMPA addition, 1,2-dibromoethane (18 mL, 209 mmol) was slowly syringed (2 hr) into the reaction flask quenching the reactive intermediates. Stirring was maintained for one day, whereupon the round bottom flask was condensed, and the solid orange-brown residue was soxhlet extracted with carbon disulfide (300 mL) to give an orange solution, which was subsequently rotoevaporated to give a bright red solid. BEDT-TTF was fully recrystallized from sulfolane (small crystals) or from thiophene (large crystals).

Yield: 2.30g (31%); mp 241-244°C (dec.)

^{1}H-NMR (CDCL$_3$/TMS): s = 3.28 (s, 8H, CH2)

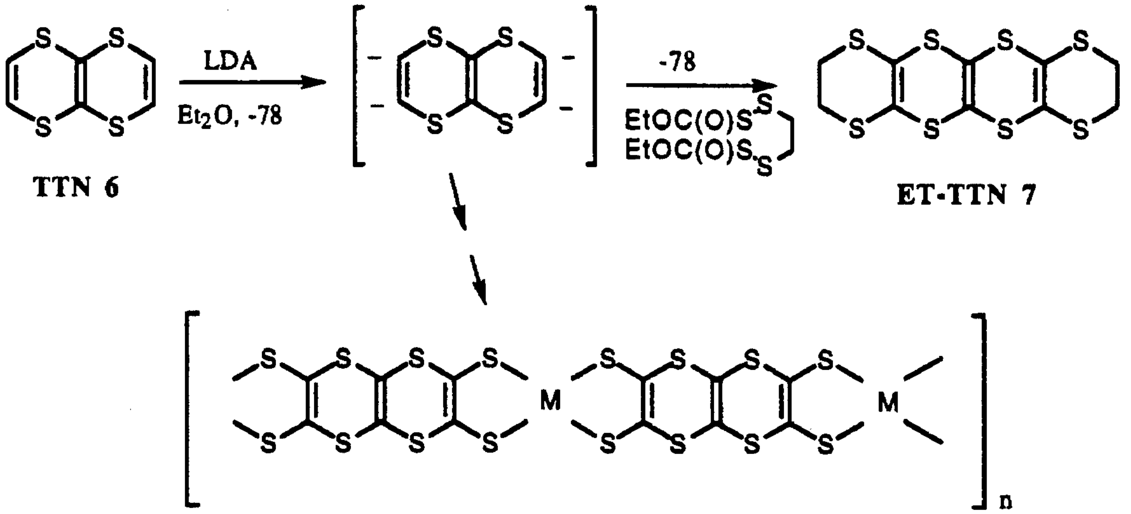
13C-NMR ($C_6D_5NO_2$): s = 30.62 (s, ext. CH_2CH_2); 114.41 (s, int. C=C); ext. C=C not visible (solvent)

MS m/e = 384(M+), 296, 268, 236, 208

IR (KBR) : Identical with a known sample

D. Synthesis of New Isomeric ET-TTF Donors

The synthetic work outlined above has also led to the preparation of the isomeric ET-TTF structrure ET-TTN, **7**. Surprisingly, this simple TTF analog has not been prepared and thus, neither have any charge-transfer complexes been prepared or studied for superconductivity. We have prepared ET-TTN in small yield and as yet not pure by the scheme shown below. We have also begun to develop methodologies for preparing all the analog donors to those of TTF. Especially interesting will be the polymeric metal complexes that are analogs of DMIT.

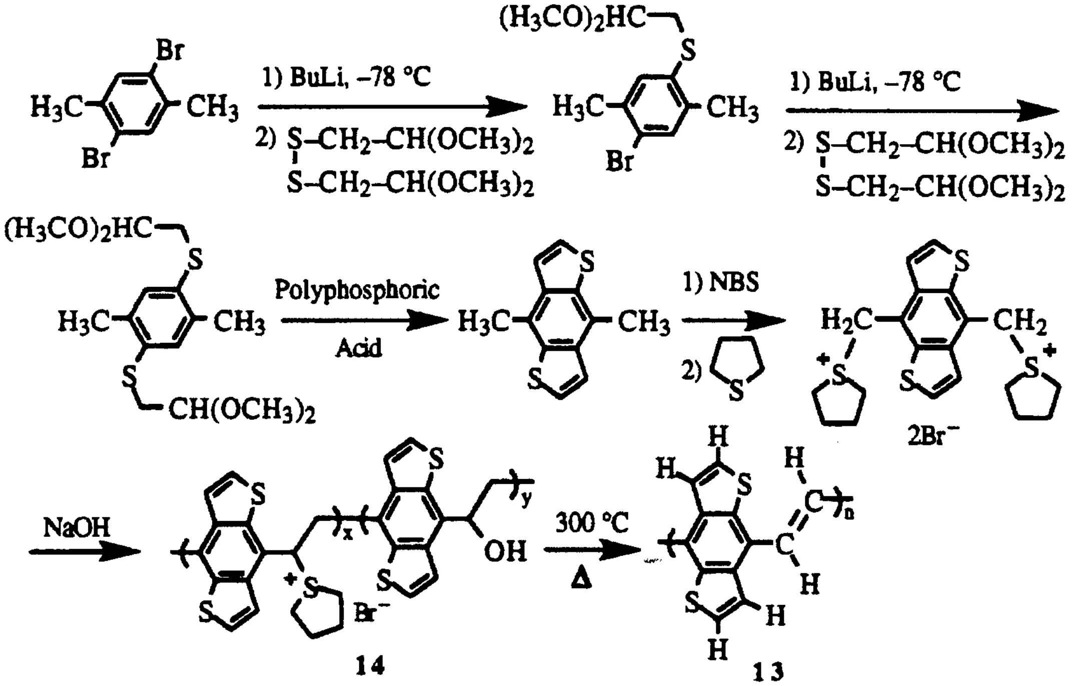


E. Synthesis and Characterization of New Conjugated Polymers

1. Preparation of Poly(benzo[1,2-b:4,5-b']dithiophen-4,8-diylvinylene)(13)

The new sulfur containing conductive polymer **13** has been prepared. The synthetic scheme involved the preparation of a soluble precursor polymer **14** as shown in scheme III. the precursor polymer **14** was found to contain about 33% sulfonium groups and 67% hydroxyl groups. Spectral studies indicated that elimination temperatures of at least 300°C are required to cause complete conversion of **14** to **13**. A film of polymer **13** exhibited a UV-vis spectral maximum at 501 nm and a band-gap (band edge) of 1.92 eV. Thermogravimetric analysis (N_2) showed the onset of decomposition to occur at 380°C with about 10% weight loss at 585°C and 20% at 700°C. Upon oxidative doping the polymer film became electrically conductive and turned from burgundy to light bluish-green in color. With ferric chloride as dopant, the polymer exhibited a conductivity of 15 S/cm. The original absorption peak at 501 nm decreased while two new NIR absorptions at 860 and 1860 nm appeared with doping. Low temperature measurements have been performed.

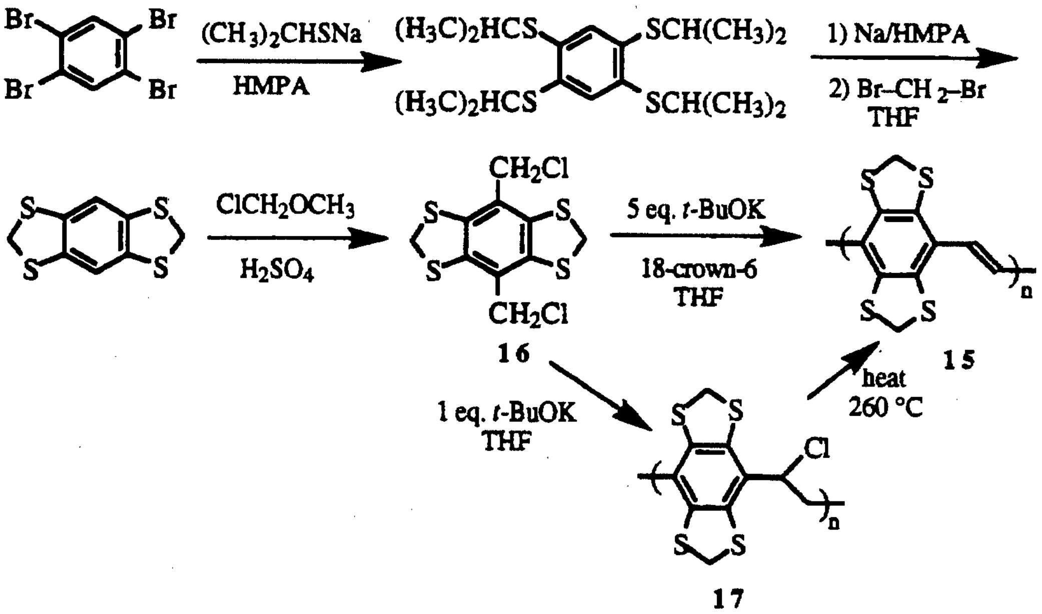
Scheme IV



2. **Poly{benzo[1,2-*d*:4,5-*d'*]bis(1,3-dithiole)-4,8-diylvinylene} (15)**

Poly{benzo[1,2-*d*:4,5-*d'*]bis(1,3-dithiole)-4,8-diylvinylene} (**15**) was synthesized by the sequence of reactions shown in Scheme 1, after numerous other synthetic attempts had failed. Monomer **16** could be[Boger, 1984 #293] polymerized to the polymer **15** using an excess of KO-*t*-Bu in the presence

Scheme V

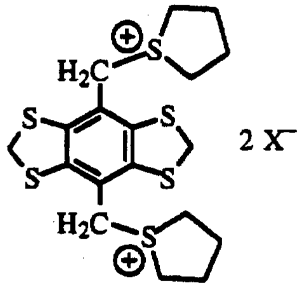


of a crown ether or, with one equivalent of base the soluble precursor chloro-polymer **17** could be obtained. This, in turn, could be eliminated at elevated temperature to produce **15**. Unsuccessful routes involved monomers such as **18** and **19** and attempts to prepare precursor polymers or **15** from these.

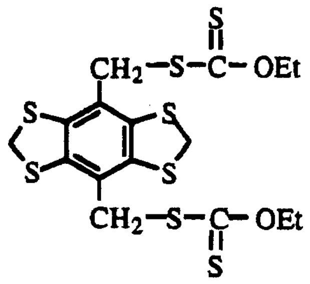
Precursor polymer **17** also had some of the chlorine groups substituted by hydroxyl as shown by a broad peak at about 3400 cm^{-1} in the FTIR spectrum. After thermal elimination in a vacuum oven at 260 °C for 2 hours, a new peak appeared at 961 cm^{-1} which is indicative of the formation of trans vinylene groups in polymer **15**. Polymer **15** obtained directly by polymerization of **16** showed a trans vinylene IR peak at 964 cm^{-1}. Thermogravimetric analysis (TGA) of **15** showed a slow weight loss of about 12% from 100 to 320 °C and then a relatively quick weight loss of an additional 19% up to 470 °C, another gradual weight loss of about 17% to about 660°C and finally a slightly more rapid loss to 720 °C giving a total weight loss of 59%.

The electrical conductivities of pressed pellets of polymer **15** (made directly from **16**) doped with iodine gave a maximum conductivity of 1.4 x 10^{-3} S cm^{-1} after 4 days of doping. No significant conductivity increase was observed upon doping with $FeCl_3$.

In an attempt to prepare **18**, X = Cl, by reaction of **20** with tetrahydrothiophene in DMSO solvent, a dark red powder was obtained, which was partly soluble in DMSO and insoluble in $CHCl_3$ and methanol. The weight average molecular weight of the DMSO soluble part was 1200 g/mol, determined by GPC using polystyrene standards. Interestingly, the conductivity of the film made from the DMSO solution was 0.3 S cm^{-1} when doped with I_2.



18; X = Br, Cl



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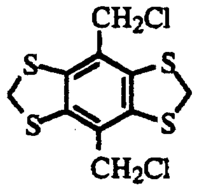

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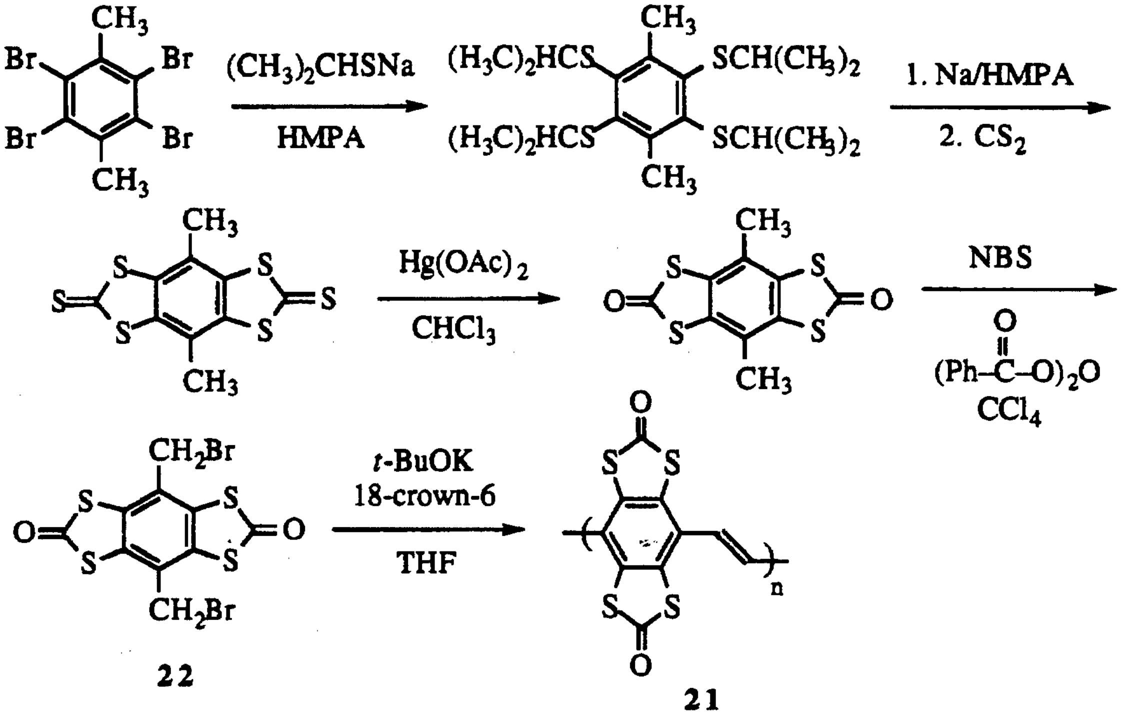
Another polymer, poly{benzo[1,2-*d*:4,5-*d'*]bis(1,3-dithiole-2-one)-4,8-diyl vinylene} (**21**), was synthesized by the sequence of reactions shown in Scheme 2, this also after several other attempts were unsuccessful. The polymerization of 4,8-dibromomethylbenzo[1,2-*d*:4,5-*d'*]bis(1,3-dithiole-2-one) (**22**) was carried out in THF with excess KO-*t*-Bu and a small amount of 18-crown-6 at 60-65 °C. The grass-green polymer was formed in an almost quantitative yield. The FTIR spectrum showed a strong peak at 1674 cm^{-1} for the carbonyl groups and at 975 cm^{-1} for the *trans* vinylene groups. TGA on polymer **21** showed a 12% weight loss up to 280 °C, followed by a rapid weight loss of an additional 65% by 475 °C at which point it leveled off to a total weight loss of 80% by 750 °C.

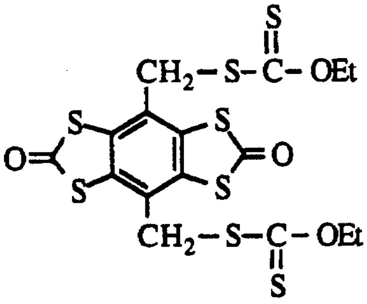
The electrical conductivity of a pressed pellet doped with iodine for 66 hours was 2.6×10^{-5} S cm^{-1}. No significant conductivity increase was observed upon doping with $FeCl_3$ and doping with concentrated H_2SO_4 gave a conductivity of 3.1×10^{-2} S cm^{-1}. The H_2SO_4 doping may have involved protonation of the carbonyl groups of the polymer.

The unsuccessful routes to polymer **21** involved monomers such as **23** and **24** and attempts to prepare precursor polymers or polymer **21** from these.

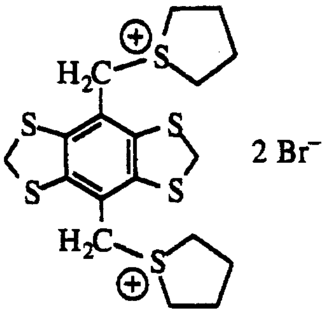
Scheme VI



Further work on these polymers is required since it is clear that they are not very pure and homogeneous and their properties, particularly electrical conductivities must be improved.



23



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F. New Processing Methods for Polythiophenes

We discovered that regioregular poly(3-dodecylthiophene) samples obtained from Richard McCullough showed variable conductivity when films were cast from solvents such as chloroform, toluene, xylene, and the like. We rationalized that if better solvents could be found for this and similar polymers, then more extended chain conformations should result on casting that should lead to better conductivities. Indeed, this was found to be the case. Typical films of poly(3-dodecylthiophene) cast from toluene or xylene exhibited electrical conductivities on the order of 0.1 S/cm on doping with $FeCl_3$ or $NOBF_4$. When films of the same material were cast from thiophene or 3-methylthiophene solutions, conductivities were consistently higher with the same dopants, falling in the range of 20-80 S/cm. This points out the benefits of using better solvents for casting and processing conjugated polymers.

G. Low Temperature Conductivity Studies

In our earlier work, we had investigated the temperature dependencies of σ and microscopic structure of poly(pyrrole tosylate) and poly(pyrrole fluoride).[25] These early data had provided useful information about what appeared to be a difficulty in applying the variable range hopping (VRH) model to $\sigma(T)$ data in poly(pyrrole tosylate) and poly(pyrrole fluoride). Specifically, the temperature dependence of σ in both of these conducting polymers could not be explained satisfactorily by the VRH model. For example, a fit of the VRH model to the temperature dependence of the conductivity had provided results for the bipolaron localization lengths of 0.02 Å and 6×10^{-8} Å for poly(pyrrole tosylate) and poly(pyrrole fluoride), respectively. The results for the density of states at the Fermi energy from this VRH fit were 1×10^{27} and 3×10^{29} eV^{-1} cm^{-3}, respectively. Obviously, these values of $N(E_F)$ and α^{-1} have no physical significance. Similar results have also been reported by others.[26-29] For example, in the cases of oxidized and substituted poly(pyrrole), α^{-1}, has been determined to fall within a range from 10^{-4} Å to 3×10^{-9} Å. The corresponding values for $N(E_F)$ in these materials range from 7×10^{33} to 3×10^{46} eV^{-1} cm^{-3}. Possible reasons for obtaining such anomalous results have been discussed and they may be related to the use of single-phonon theories to calculate υ_0 and dimensionality of the film. The $\sigma(T)$ data presented here for polymer **13** (PBDV) and poly(pyrrole) provide at least a clue to part of this anomaly. In our early experiments, we were able to measure σ of poly(pyrrole tosylate) and poly(pyrrole fluoride) down to only about 90 K. We have now extended σ measurements in poly(pyrrole) and poly(benzo[1,2-*b*:4,5-*b'*]dithiophene-4,8-diyl Vinylene) (PBDV) down to 10 K. These new data over a much wider range of temperatures clearly show a transition at around 125 K in PBDV. The VRH model with one set of parameters, $N(E_F)$ and α^{-1}, does not represent satisfactorily observed temperature dependence of the $\sigma(T)$ results. To a first approximation, the temperature dependence of σ from 295 K down to 10 K can be represented by considering competing VRH of the bipolarons with different values for $N(E_F)$ and α^{-1} above and below this transition temperature.

The *dc* conductivity measurements were made by using the *four-probe* technique with a Displex closed-cycle helium cryostat. The temperature of the samples was computer controlled with an uncertainty ≤ 1 K and was varied over a range of 10 - 295 K.. A Keithly Model 236 Source Measure Unit (SMU), interfaced to PC, was used to collect the current-voltage (I-V) data by operating the SMU in the *Source-Current and Measure-Voltage* mode in the *four-probe* configuration. The I-V data exhibited Ohmic behavior for currents between 100 - 500 μA at temperatures > 175 K and for currents in the range 10 - 90 μA at lower temperatures. The *dc* electrical conductivity was calculated by using the thin film approximation,

$$\rho = \sigma^{-1} = (\pi t / \ln 2)(V / I),$$

where ρ is the resistivity (Ω-cm) and t is the thickness of the film (t < < *four-probe* spacing).

The *dc* electrical conductivities of $FeCl_3$ doped PBDV are shown as functions of temperature in the figure below. Over the range of temperatures studied from 10 to 295 K the conductivity of PBDV increases with temperature by almost three orders of magnitude.

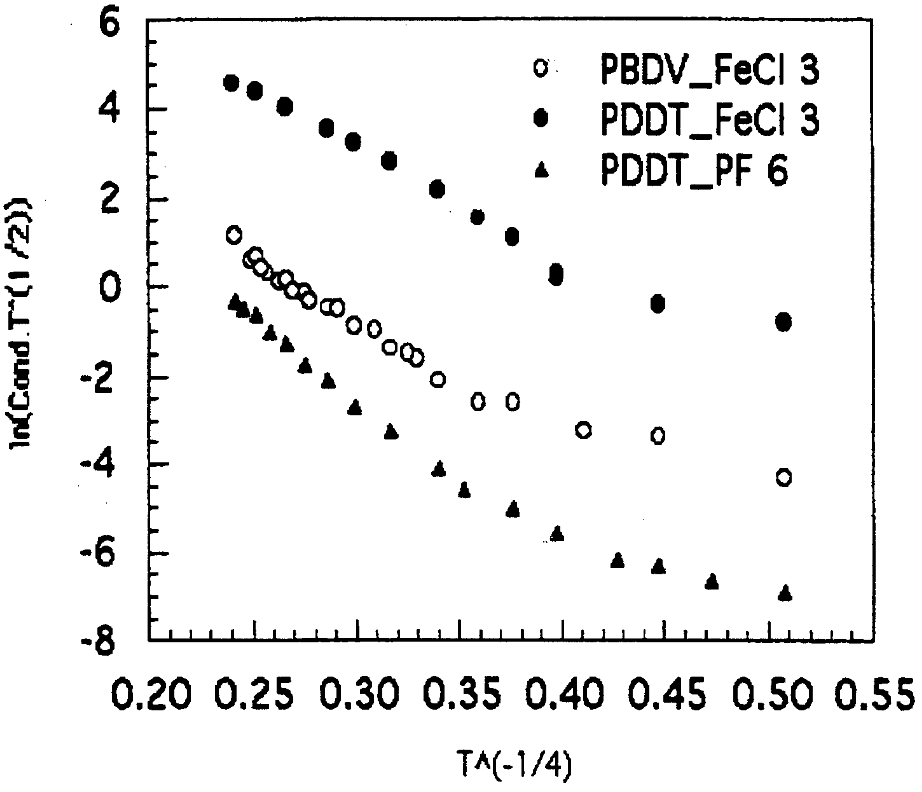
For PBDV, we measure $\sigma = 0.32$ and 0.0014 ohm^{-1} cm^{-1} at 295 K and 10 K, respectively. In spite of differences in the doping of the poly(pyrrole) films, the temperature dependence of the *dc* conductivity between 295 and 90 K is in good agreement with that seen in our earlier data.[25] The $\sigma(T)$ data for poly(pyrrole) at temperatures below 90 K are new and they vary with temperature in a manner that is similar to what is seen in the case of the $\sigma(T)$ data for PBDV. The conductivities of both polymers exhibit a transition temperature.

The temperature dependence of three-dimensional conductivity in the VRH model is given by

$$\sigma = \sigma_0 \exp(-A/T^{1/4}), \qquad (1)$$

$$\text{where } \sigma_0 = e^2 v_0 [N(E_F)/32\pi\alpha kT]^{1/2}, \qquad (2)$$

$$\text{and } A = 2.1[\alpha^3/kN(E_F)]^{1/4}. \qquad (3)$$



A cursory examination shows that all three (1D, 2D, and 3D VRH models) seem to provide an almost equally good representation for our data. It is, therefore, not possible to decide whether the $\sigma(T)$ data favor electron hopping in one, two, or three dimensions. Realizing that the film thickness is much larger than reasonably expected values of α^{-1}, we choose 3D VRH model to represent our measurements. Since the $\sigma(T)$ data exhibit a transition temperature (T^*), we analyze the temperature dependence of $\sigma(T)$ by

$$\sigma = e^2 v_0 [N(E_F)/32\pi\alpha_1 kT]^{1/2} \exp(-A_1/T^{1/4}) + e^2 v_0 [N(E_F)/32\pi\alpha_2 kT]^{1/2} \exp(-A_2/T^{1/4}) \quad (4)$$

The results obtained for $N(E_F)$ and α^{-1} from non linear least-squires fitting of equations (4)-(8) are summarized in Table 1.

TABLE 1

Model	α^{-1} (Å)	$N(E_F)$ (eV^{-1} cm^{-3})
3D VRH $T < T^*$	200	10^{17}
3D VRH $T > T^*$	0.03	10^{27}

We have also examined whether the $\sigma(T)$ data can be understood in terms of thermally activated process. The data are, at least, consistent with an activation process with a change in the activation energy occurring at the transition temperature. We obtain activation energies ranging from 0.003 eV to 0.076 eV. These results are similar to those obtained by Glenis et. al. in polyfuran.[30] Our results on the temperature dependence of the *dc* conductivity of PBDV and their analysis in terms of different models should be published in the near future.[31]

We are investigating if other models could provide a more realistic fit for the temperature dependence of the *dc* conductivity of polymeric materials. One of these models is based on the fluctuation-induced tunneling of the electrons. In applying the VRH model to $\sigma(T)$ data, it is assumed that transport occurs along a continuous chain of the polymer. However, this may be an over simplification in films in which the growth conditions yield a structure consisting of conducting islands. Under these conditions, the conductivity may be better described as resulting from the hopping of electrons between islands embedded among insulating barriers. Sheng has also developed a mechanism for conduction in disordered materials.[32] This mechanism is based on fluctuation-induced tunneling in which thermally activated voltage fluctuations across insulating gaps in a disordered material play an important role in determining the temperature and field dependencies of the conductivity. Since the electrons tend to tunnel between conducting regions at points of their closest approach, the tunnel junctions are small in size and are therefore subject to large (thermally activated) voltage fluctuations. These voltage fluctuations modulate the potential barrier seen by the tunneling electrons and introduce a characteristic temperature variation in the tunneling probability and hence in σ(T). The fluctuation-induced tunneling model provides good agreement with experimental data on the temperature dependencies of the conductivities in carbon-polyvinyl chloride, heavily-doped GaAs, and doped polyacetylene. We are currently investigating how well the fluctuation-induced tunneling model fits our data.

H. Summary and Future Work

This work has led to several new conductive polymers as well as a whole new class of organic donors. Especially interesting are the new TTN donors that are isomers of TTF. As yet unexplored, new derivatives of TTN are promising candidates for superconductive organic charge transfer complexes. We anticipate these to be exciting new materials worthy of considerable study.

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R. L. Elsenbaumer
D.S. Marynick, M. Pomerantz, and S.C. Sharma

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This work resulted in the following significant findings:

Extended chains of isomeric TTF structures have electronic properties and stabilities comparable to TTF Extended chains and are of interest for possible superconductive polymers

Synthetic strategies were developed to prepare TTF and isomeric TTF structures

Developed simplified synthesis of TTF and ET-TTF in high yield and from inexpensive starting materials

Developed simple techniques to pruify and grow large crystals of ET-TTF

Synthesized new organic conductive polymers with good electrical conductivities and processibility

Developed new processing and doping techniques for polyalkylthiophenes to provide consistenly high conductivity materials.

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Superconductive Organic Polymers, TTF, ET-TTF, Isomeric TTF.

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