

# REPORT DOCUMENTATION PAGE

AFRL-SR-AR-TR-03-

Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for the data needed, and completing and reviewing this collection of information. Send comments regarding this burden estimate reducing this burden to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Management and Budget, Paperwork Reduction Project (0704-0188), Washington, DC 20503

maintaining  
stations for  
the Office of

0294

|   |   |  |  |  |
|---|---|--|--|--|
| <b>1. AGENCY USE ONLY (Leave blank)</b>   |   | <b>2. REPORT DATE</b><br>July 21, 2003         | <b>3. REPORT TYPE AND DATES COVERED</b><br>Final Report 12/1/99-11/30/02 |  |
| <b>4. TITLE AND SUBTITLE</b><br>Controlled Redox and Electrical Properties in Polyheterocycles  |   |  | <b>5. FUNDING NUMBERS</b><br>F49620-00-1-0047<br>2303/CX<br>61102F       |  |
| <b>6. AUTHOR(S)</b><br>John R. Reynolds   |   |  |  |  |
| <b>7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)</b><br>Department of Chemistry<br>University of Florida<br>P. O. Box 117200<br>Gainesville, FL 32611-7200   |   |  | <b>8. PERFORMING ORGANIZATION REPORT NUMBER</b><br>4.                    |  |
| <b>9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES)</b><br>AFOSR/NL<br>4015 Wilson Blvd, m Room 713<br>Arlington VA 22203-1954   |   |  | <b>10. SPONSORING / MONITORING AGENCY REPORT NUMBER</b>                  |  |
| <b>11. SUPPLEMENTARY NOTES</b><br><br><div style="text-align: center; font-size: 2em; font-weight: bold;">20030910 036</div>  |   |  |  |  |
| <b>12a. DISTRIBUTION / AVAILABILITY STATEMENT</b><br>Approve for Public Release: Distribution Unlimited   |   |  | <b>12b. DISTRIBUTION CODE</b>  |  |
| <b>13. ABSTRACT (Maximum 200 Words)</b><br>The Reynolds research group at the University of Florida has developed an extensive program for the development and application of variable gap conjugated polymers which are luminescent and semiconducting, can be doped to high levels of conductivity, and can be redox switched between charge neutral, oxidized (p-type), and reductive (n-type) states. A soluble and processable dibutyl derivative of poly(3,4-propylenedioxy-thiophene) has been synthesized directly in its neutral form by Grignard metathesis which can be switched from deep red-purple in the neutral state to highly transmissive sky blue in the oxidized state. In addition, a full series of poly(3,4-alkylenedioxy-pyrroles) (PXDOs) have been developed as electron rich electrochromic polymers where substitution in the N-position allowed us to attain the high gap/high HOMO polymers. These polymers exhibit multi-color and high contrast electrochromism. We have utilized in-situ colorimetric analysis and composite coloration efficiency to elucidate the properties of these electrochromic properties. We have applied these polymers to a series of electrochromic devices utilizing both absorption/transmission and absorption/reflection designs to attenuate electromagnetic absorption through a window or shutter, or off of a surface. By using PProDOP-NPrS as the anodically coloring layer, the contrast of the ECDs has been optimized to 68% ΔT. |   |  |  |  |
| <b>14. SUBJECT TERMS</b>  |   |  | <b>15. NUMBER OF PAGES</b>   |  |
|   |   |  | <b>16. PRICE CODE</b>  |  |
| <b>17. SECURITY CLASSIFICATION OF REPORT</b>  | <b>18. SECURITY CLASSIFICATION OF THIS PAGE</b> | <b>19. SECURITY CLASSIFICATION OF ABSTRACT</b> | <b>20. LIMITATION OF ABSTRACT</b>  |  |
|   |   |  |  |  |

***Final Report***

for

F49620-00-1-0047

**Controlled Redox and Electrical Properties in Polyheterocycles**

Reporting Period:

December 1, 1999 to November 30, 2002

John R. Reynolds  
Department of Chemistry and  
Center for Macromolecular Science and Engineering  
University of Florida  
P. O. Box 117200  
Gainesville, FL 32611-7200

## 1. Objectives

The effect of macromolecular structure and redox switching between charge states has been used to control the optoelectronic properties of conjugated polymers. Specific properties investigated include structure:property effects via model compounds, electrochromism, n-type doping, and high stability conductors, along with applying new processable systems to conducting elastomers.

## 2. Status of Effort

The Reynolds research group at the University of Florida has developed an extensive program for the development and application of variable gap conjugated polymers which are luminescent and semiconducting, can be doped to high levels of conductivity, and can be redox switched between charge neutral, oxidized (p-type), and reductive (n-type) states. The work has been directed to enhancing and controlling static electronic properties such as conductivity ( $\sigma$ ), the electronic band gap ( $E_g$ ), and redox potential. Simultaneously, we have developed materials with optimized active or dynamic properties including their redox switching rates, multi-color electrochromism, and high contrast electrochromism. We have applied these polymers to a series of electrochromic devices utilizing both absorption/transmission and absorption/reflection designs to attenuate electromagnetic absorption through a window or shutter, or off of a surface.

We have focused a significant amount of our work on new poly(3,4-alkylenedioxythiophenes) (PXDOT's) which yield enhanced conducting, switching and stability properties relative to other available electroactive and conducting polymers. Both AG Bayer and Agfa Gevaert have commercialized PEDOT/PSS and it is now an important commercially available conducting polymer with applications as an anti-static coating in photographic film, a solid electrolyte-conducting coating in high energy density tantalum capacitors, a conducting scaffold for copper deposition for feed-through holes in printed circuit boards, and as a hole transport material in organic and polymer-based LEDs. The Reynolds research group has continued interactions with Agfa and other companies (see description below in Transitions section) who are using the new polymers being developed through this AFOSR funding.

## 3. Accomplishments

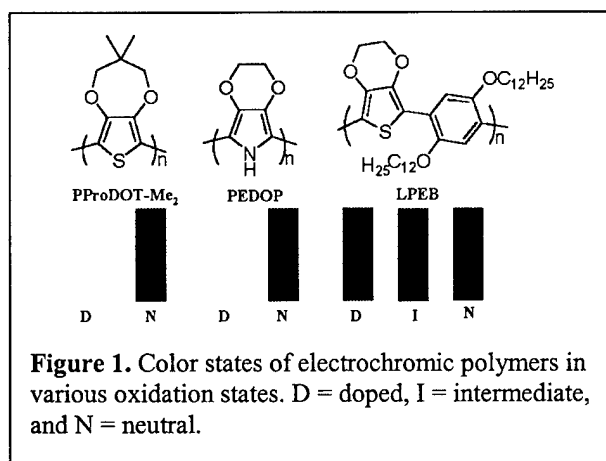
### 3.1 Electrochromic Polymers

Through the early to mid-1990's, the Reynolds group developed a large number of electrochromic polymers resulting in the ability to access many colors throughout the visible spectrum. Through this last research period we have developed methods for in-depth characterization of the color changes in these materials. Thus we have utilized *in-situ* colorimetric analysis and composite coloration efficiency to further elucidate the mechanism, process, and structural origin of color change in our electrochromic polymers.

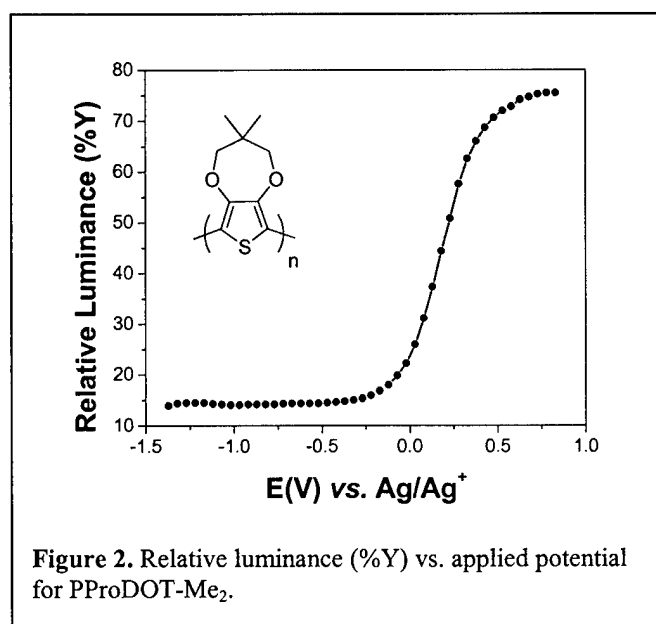
Colorimetric analysis allows for the precise measurement and understanding of color and color change, which is necessary for applications in which reproducible color states and color

matching (i.e. dynamic camouflage) are required. For this purpose, we have developed an *in-situ* method of characterization based on the CIE system of colorimetry. In this color system, all colors can be accurately described according to their hue (dominant wavelength), saturation (level of white and pure color), and luminance (brightness or transmissivity). These attributes are measured using the CIE 1931  $Y_{xy}$  or  $L^*a^*b^*$  color spaces.

In our colorimetric studies, we have examined the numerous thiophene and pyrrole based polymers synthesized in our labs. Figure 1 shows just three of these polymers; electrochemically prepared PProDOT-Me<sub>2</sub> and PEDOP, and the soluble chemically prepared LPEB which has provided us with a strong interaction with researchers at EIC Laboratories in the area of Dynamic Camouflage. Cataloguing the colors of our polymers in this manner highlights our ability to produce variable gap conjugated polymers ( $E_g$  ranging from 1.1 to 3.3eV), as the colors we have achieved in both the doped and neutral forms span the entire visible region.



full range of applied potentials on a single curve. It should be noted that this is a major step over our early single wavelength transmissivity experiments.



One major impact of colorimetric analysis is that it allows us to accurately determine the human eye perceived light transmission properties of thin polymer films. Figure 2 shows the relative luminance (%Y) of PProDOT-Me<sub>2</sub> over a full range of applied potentials. This illustrates the high contrast between the highly absorbing neutral form and the highly transmissive oxidized form. The advantage here is that relative luminance offers a method of relating information about a film's transmittance across the entire visible region as perceived by the human eye as a function of the

We have now, in collaboration with David Rauh at EIC, developed composite coloration efficiency as a practical method to measure the change in the optical density of a material relative to the amount of the injected/ejected charge. Composite coloration efficiencies were measured *via* a tandem chronoabsorbometry/chronocoulometry experiment in which  $\Delta\%T$  was monitored at  $\lambda_{max}$  while the amount of injected/ejected charge was recorded. Figure 3 shows the coloration efficiency of three dioxythiophene (PXDOT) polymers as a function of the percentage of their full attainable contrast. These studies indicate that our electrochromic polymers exhibit

high coloration efficiencies relative to most of their inorganic and other organic counterparts and that the substituted PProDOT derivative provides for a substantially high efficiency when compared to PEDOT. High coloration efficiencies are of great benefit because they indicate that very little charge is required for large color changes which would be of importance in applications where only portable or battery power is available.

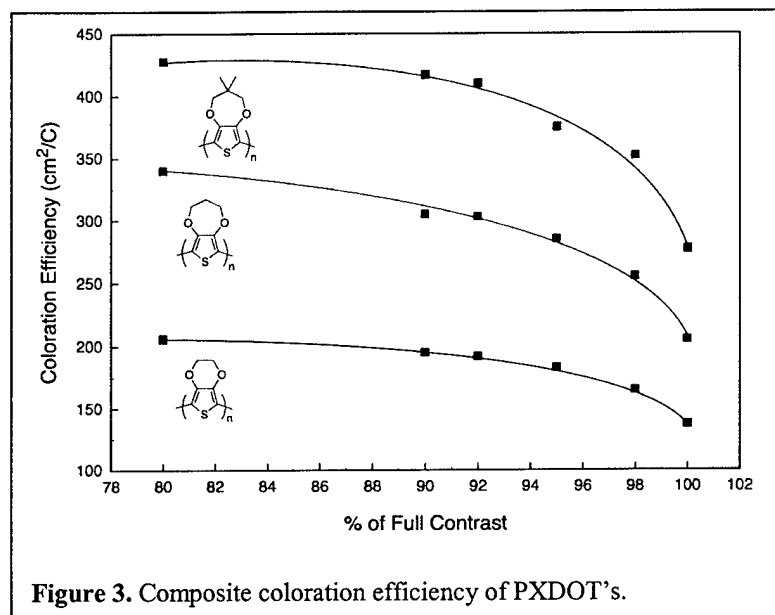
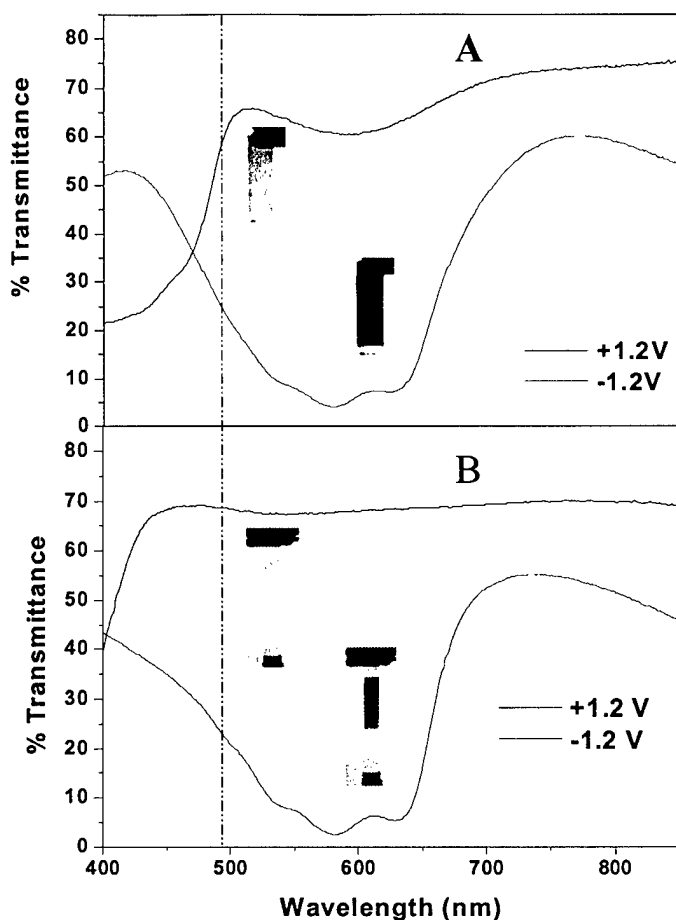


Figure 3. Composite coloration efficiency of PXDOT's.

### 3.2 Optimization of the Contrast in Electrochromic Windows.

Electrochromic devices (ECD's) in a window configuration may find applicability in protecting optical devices from external radiation, in security for doors, in dialed-tint windows (e.g., aircraft canopies), and as active camouflage. Using substituted derivatives of the PXDOT and PXDOP families, we have developed electrochromic polymer devices having the highest contrast throughout the visible region of the spectrum reported to date. The fact that these polymers switch their electromagnetic absorption and reflection properties over the visible, near infrared, mid-IR and microwave regions of the electromagnetic spectrum, suggests they can be used to alter the signature of surfaces.

Considering this potential utility we have focused our research on developing high contrast ECDs based on dual conducting polymers. We have constructed ECDs based on cathodically coloring dimethyl substituted poly(3,4-propylenedioxythiophene) (PProDOT-Me<sub>2</sub>) along with poly[3,6-bis(2-ethylenedioxythienyl)-N-methyl-carbazole] (PBEDOT-NMeCz) and N-propane sulfonated poly(3,4-propylenedioxythiophene) (PProDOP-NPrS) as anodically coloring polymers. These transmissive/absorptive devices operate at low applied voltages ( $\pm 1.2$ V) and switch between a highly transmissive state and a dark colored state in less than 1 second. By using PProDOP-NPrS as the anodically coloring layer, the contrast of the device at 580 nm increases by 12% (from 56% to 68%), as compared to the device comprising PBEDOT-NMeCz as illustrated in Figure 4. The long-term stability of the PProDOP-NPrS device was measured by stepping the potential between  $-1.2$  and  $+1.2$  V and was shown to retain up to 86% of its optical response after 20,000 double potential steps.



**Figure 4.** Transmittance spectra and photographs of dual polymer ECD's using PProDOT-Me<sub>2</sub> as the cathodically coloring polymer and PBEDOT-NMeCz (A) and PProDOP-NPrS (B) as the anodically coloring layers with the devices in the two extreme (colored and bleached) states.

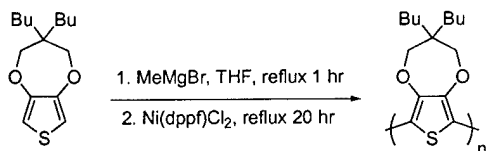
### 3.3 Regiosymmetric Poly(3,4-propylenedioxythiophenes) (PProDOT's)

Over this last research period the Reynolds group has focused effort on the transition metal mediated polymerization of soluble PProDOT derivatives. By chemical polymerization, a large amount of processable polymer can be generated and fully characterized, which is a difficult task when performing electropolymerization. Also, by using known chemical polymerization techniques such as Grignard Metathesis, the structural regularity of the polymer can be controlled, a quality electropolymerization lacks.

A soluble and processable dibutyl derivative of poly(3,4-propylenedioxythiophene) has been synthesized directly in its neutral form by Grignard metathesis as shown in Scheme 1. The structure of the monomer was chosen because of its plane of symmetry, which ultimately yields a regiosymmetric polymer which can be switched from deep red-purple in the neutral state to highly transmissive sky blue in the oxidized state. The polymer also displays a strong deep red photoluminescence in solution with moderate quantum efficiencies. Very important for the consideration of AF applications (e.g. conducting elastomers) oxidatively doped films prepared

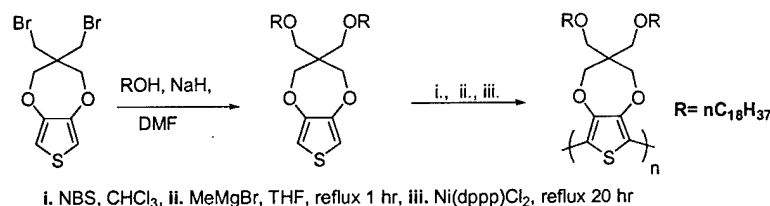
by spin casting have a conductivity of *ca.* 10 S/cm and exhibit a high level of ambient stability with little change observed over 4 months air exposure.

### Scheme 1

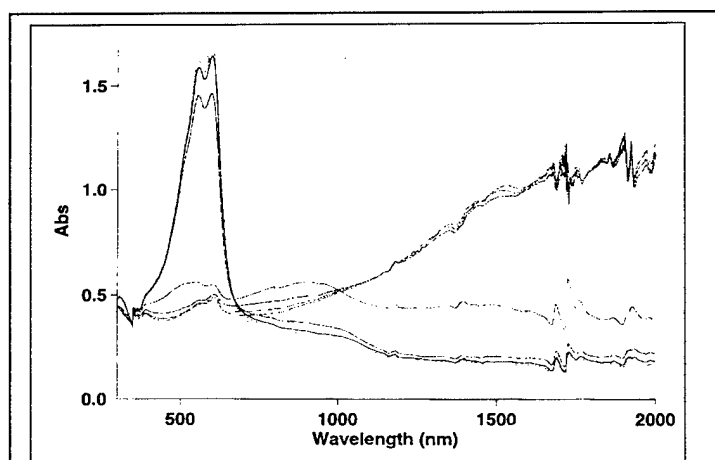


A series of alkoxy substituted ProDOT compounds were synthesized in order to obtain a crystalline monomer that could easily be purified and chemically polymerized using Grignard metathesis. By first synthesizing a bis(bromomethylated) precursor as shown in Scheme 2, alkoxy groups were subsequently incorporated into the monomer to increase solubility, induce crystallization, and to provide steric bulk to decrease interchain interactions in the polymer that can lead to luminescence quenching.

### Scheme 2



Solution cast films of PProDOT(CH<sub>2</sub>OC<sub>18</sub>H<sub>37</sub>)<sub>2</sub> show a reversible redox system with an  $E_{1/2}$  of 0.4 V vs Ag/Ag<sup>+</sup>. Spectroelectrochemistry shown in Figure 5 indicates full oxidation is easily accessible and the  $\pi$  to  $\pi^*$  transition totally bleaches as desired for a high contrast electrochromic.

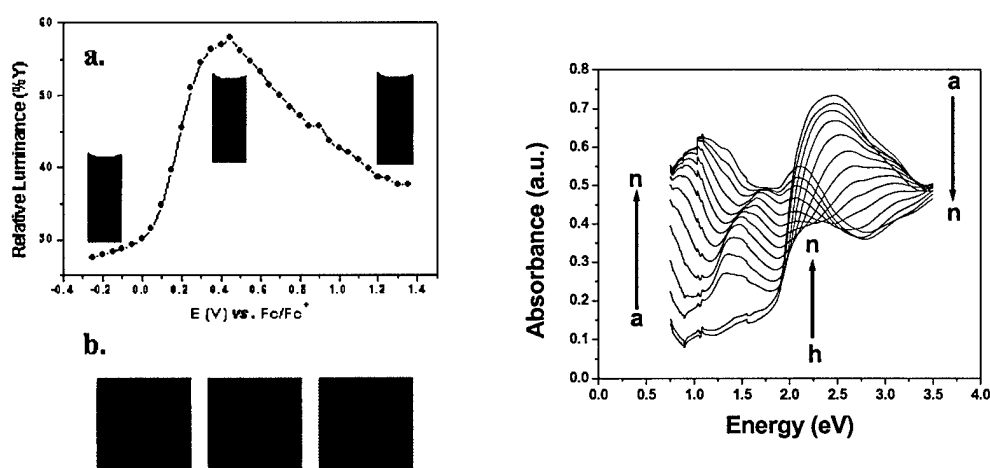
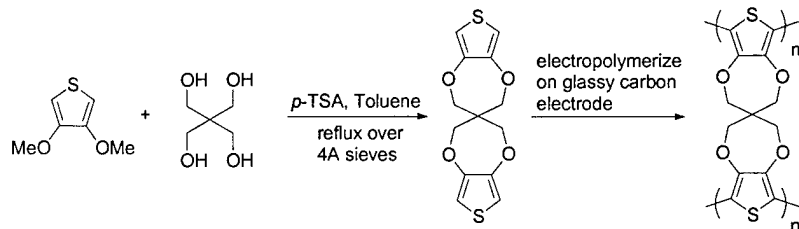


**Figure 5.** Spectroelectrochemistry of a solution cast film of ProDOT(CH<sub>2</sub>OC<sub>18</sub>H<sub>37</sub>)<sub>2</sub> on ITO glass indicating complete bleaching of the interband transition and subsequent charge carrier band formation in the near infrared.

Demonstrating some of the power of the transesterification methodology we have developed for synthesizing dioxythiophenes, poly(spiroBiProDOT) has been prepared as outlined in Scheme 3 where the monomer is formed by linking two ProDOT molecules together at the 2-position of the propylene bridge. Due to the increased functionality, the resulting molecule has the ability to cross-link during oxidative polymerization. The luminance change results of Figure 6 show poly(spiroBiProDOT) to exhibit three color states. The luminance increases at low potentials as the film

changes from dark red to light gray-green, followed by formation of a dark blue color at higher potential. This unique anodically coloring ability of the polymer is attributed to a peak at 2.1 eV observed by spectroelectrochemistry (Figure 6) which begins to grow in at 0.55 V.

### Scheme 3



**Figure 6.** Potential dependence of the luminance and spectroelectrochemical response of poly(spiroBiProDOT).

Recently our group, in collaboration with AGFA-Gevaert, has developed a new mild and rapid route to XDOTs and XDOPs which employs standard Mitsunobu conditions (diethyl azodicarboxylate (DEAD), PPh<sub>3</sub>, and THF) to couple dihydroxyheteroaromatics with diols. With this technique in hand, we have synthesized XDOT derivatives with a high degree of steric congestion around the alkylendioxy bridge—molecules that were difficult to synthesize using traditional Williamson ether or transesterification methodologies. As we move into the next phase of our AF supported Variable Gap Conjugated Polymer research, having expertise in multiple methods of dioxyheterocycle syntheses gives us the ability to prepare polymers where we can more fully tune the optoelectronic and redox properties.

### 3.4 Donor-Acceptor Conjugated Polymers

As we continue to develop electroactive polymer systems for the Air Force capable of use in application such as color changing electrochromic devices, electrical charge storage devices (especially super-capacitors), photovoltaic devices, and light-emitting devices, the ability to prepare materials which are capable of attaining reductively (n-doped) states has become more and more important. This can prove to be quite difficult due to the instability of the anionic charge carriers to ambient conditions (water and oxygen). Development of materials in which

both the p- and n-doped states can be accessed will open up entirely new areas in electrochemical, optical, and transport properties and applications.

Within our AF supported research program, we have developed four families of oxidatively polymerizable bis(2-heterocycle)arylenes utilizing the electron rich donor EDOT or EDOP as the electropolymerizable moiety and an electron-poor acceptor as the core unit. Within this model, the donor repeat units provide the HOMO energy levels, while the acceptor repeat units provide the LUMO energy levels. To this end, we have used four types of acceptors: the cyanovinylenes, the fluorenones, the pyridines, and the thienopyrazines.

### 3.4.a Cyanovinylenes

Donor-Acceptor-Donor (D-A-D) polymers, having the structures shown in Figure 7 and linked *via* a cyanovinylene acceptor, have been efficiently synthesized using a Knoevenagel condensation. Using spectroelectrochemistry and combining this information with the onsets of the redox processes in electrochemical energy space, we have examined the structure-property relationships of these systems. This polymer family has relatively low band gaps ranging from 1.1 eV to 1.6 eV and can be reversibly p-doped quite easily at relatively low potentials. The polymers tend to switch between a dark blue to a blue highly transmissive film upon oxidation, but displays no color changes upon reduction. This lack of color change upon reduction can be explained by pinning of the anionic state on the electron accepting pendant cyano group. Examination of the effect of the donor on the D-A system has shown that dioxythiophenes offer the best combination of electrochemistry and optical properties in addition to ease of synthesis when compared to the dioxypyrroles.

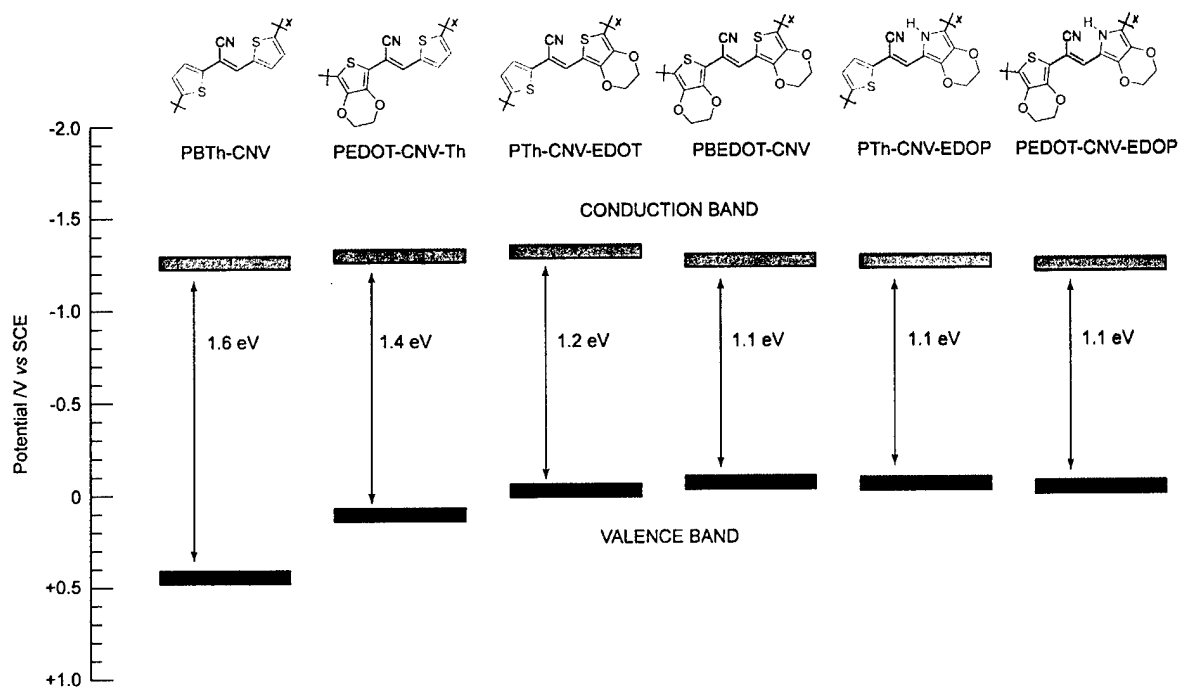
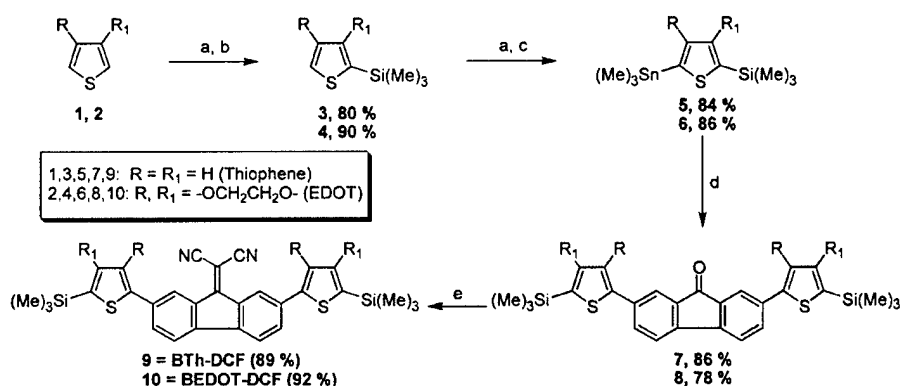


Figure 7. Relative energy plot of the cyanovinylene-family of acceptors

### 3.4.b Fluorenones

Two fluorenone-based acceptor systems have been developed as illustrated by Scheme 4. These systems have been prepared *via* a Stille-type coupling with dibromofluorenone. After the coupling reaction, the dicyanomethylidene acceptor is added to the system using Doebner modified conditions of the Knoevenagel condensation. Poly(BEDOT-DCF) has a band gap of 1.9 eV and exhibits two reductions; one with an onset of -0.6 V and the other with an onset of -1.2 V. While this low reduction potential was of initial high interest, the fact that the process occurs in the mid-gap leads us to believe that the reduction occurs on the pendant cyano groups and poly(BEDOT-DCF) does not exhibit true n-type doping.

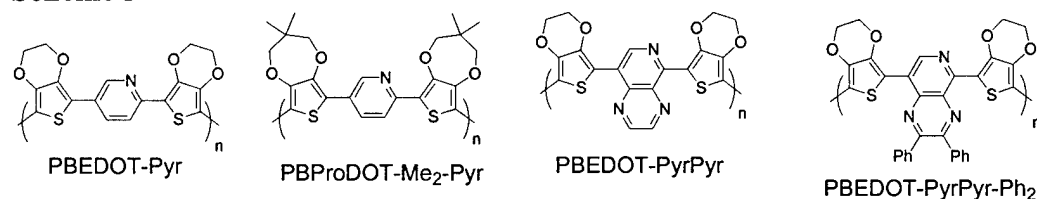
#### Scheme 4



### 3.4.c. Pyridines

In earlier work, we had found that polymers prepared from bis(EDOT)pyridine (BEDOT-Pyr) exhibit the desired properties for multi-color electrochromism due to a the low LUMO level of the electron poor pyridine unit. This system not only displays p-type doping from a red neutral form to a dark navy blue oxidized form, but also n-type doping to a transmissive sky blue. Capitalizing on this, we have investigated a number of pyridine-based D-A-D polymers as illustrated in Scheme 5. Replacement of the bi-EDOT linkage with a bi-ProDOT-Me<sub>2</sub> group leads to more transmissive doped states as expected. This polymer switches from a red neutral state to a transmissive purple oxidized form and upon reduction to an almost totally transmissive blue form. By further substitution of the pyridine ring, we have begun to work with the pyridopyrazines. The poly(BEDOT-PyrPyr-Ph<sub>2</sub>) system is of great interest as it is capable of achieving four colored states: a lime green neutral, a light gray oxidized, a burgundy n-doped, and a dark gray/black upon a second reduction.

#### Scheme 5



Conductivity experiments performed on poly(BEDOT-Pyr) and poly(BEDOT-PyrPyr-Ph<sub>2</sub>) shown in Figure 8 have allowed us to elaborate on the n-type doping process and compare it to p-doping. The upper red trace is a plot of the p-type doping conductances using tetrabutylammonium perchlorate (TBAP) as the electrolyte. The multi-colored traces on the upper left are of the reductive doping conductances using tetrabutylammonium (TBA<sup>+</sup>), tetraethylammonium (TEA<sup>+</sup>), sodium (Na<sup>+</sup>), and lithium (Li<sup>+</sup>) as the counterions. Examination of the lower set of conductance traces during reduction at higher sensitivity show the conductivities to peak near the reduction potential for the polymers as would be expected for a redox type charge-hopping transport mechanism. While the overall conductances are approximately a factor of 30 lower than that of p-type doping, to the best of our knowledge, this is the smallest p-type/n-type conductivity ratio reported for a polyheterocycle of this type. In addition to displaying interesting conductance behavior, BEDOT-Pyr, BProDOT-Me<sub>2</sub>-Pyr, and BEDOT-PyrPyr-Ph<sub>2</sub> polymerize smoothly and form films very efficiently with little or no over-oxidation and both the p-doped and n-doped states can be accessed many times.

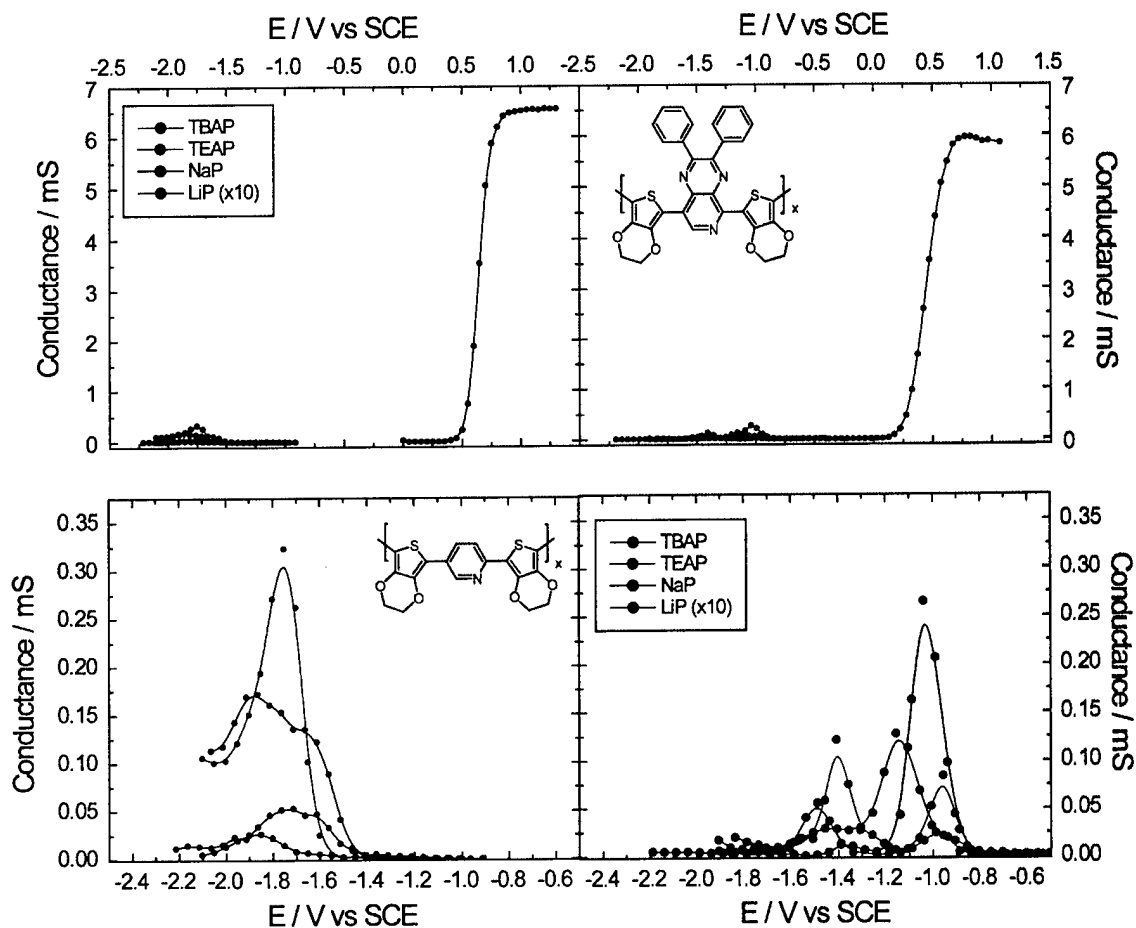
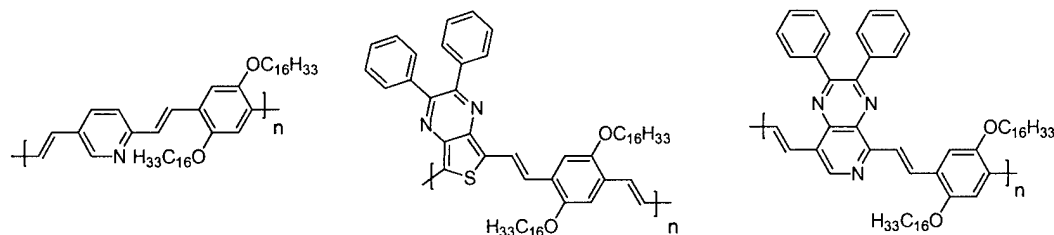


Figure 8. *In-situ* conductance results for poly(BEDOT-Pyr) and poly(BEDOT-PyrPyr-Ph<sub>2</sub>).

### 3.4.d Soluble Donor-Acceptor Polymers

Above we illustrate how we have used electropolymerization to develop the structure property relationships for the D-A-D family of polymers. With this information in hand, and as we move to using these polymer types in photovoltaic devices and laterally configured ECD's, access to soluble polymers becomes important. Towards this end, an initial family of vinylene-linked donor-acceptor polymers has been synthesized with the goals of producing materials with reduced electronic band gaps and easily accessible oxidative and reductive states. The Heck reaction was used to synthesize poly(2,5-pyridyl vinylene-1,4-hexadecyloxy-phenylene vinylene), poly(2,3-diphenyl[3,4-*b*]-pyridopyrazine vinylene-1,4-hexadecyloxy phenylene vinylene), and poly(ProDOT-MeOC<sub>16</sub>H<sub>33</sub> vinylene-1,4-pyridyl vinylene) having the structures shown in Scheme 6.

Scheme 6



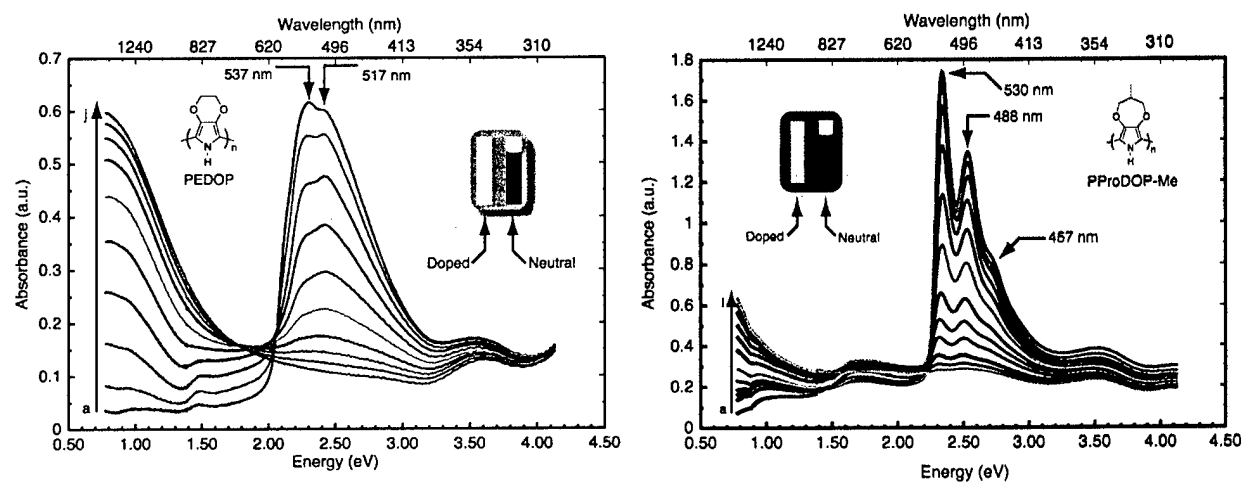
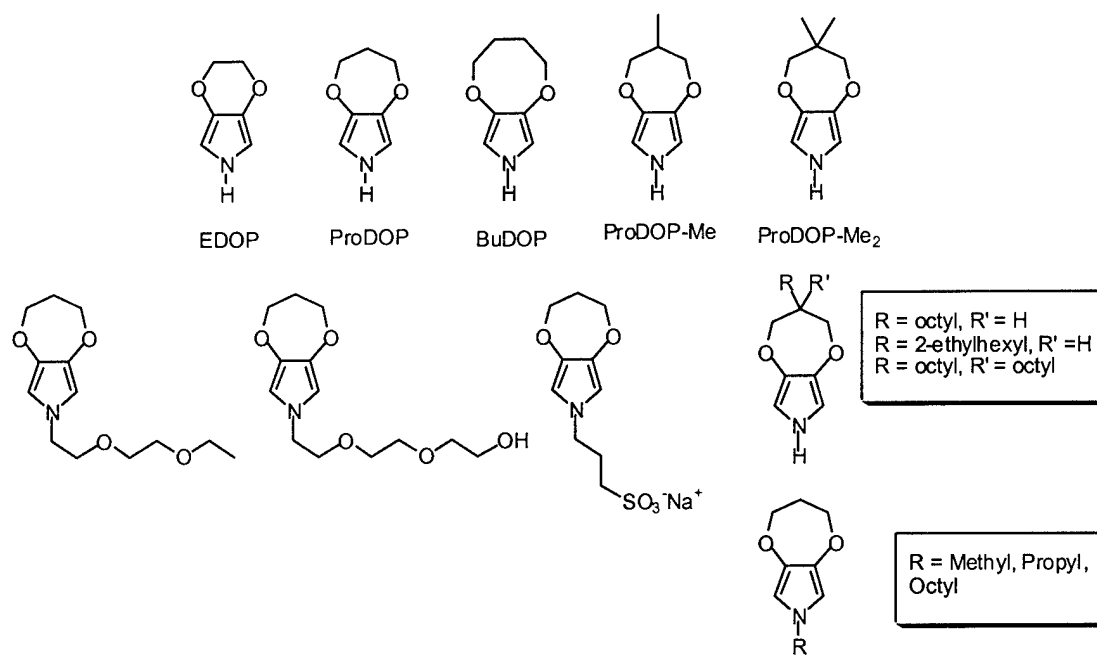
These polymers exhibit band gaps of 2.4, 2.0, and 2.4 eV respectively and weight average molecular weights that range from 8,700 to 33,000 g/mol as determined by GPC vs polystyrene standards. The polymers are luminescent and doping of the polymers with antimony pentachloride shows the formation of new red-shifted optical absorption bands characteristic of charge transfer species.

### 3.5 Poly(3,4-Alkylenedioxyppyroles): Stable Electrochromic Conducting Polymers

A full series of poly(3,4-alkylenedioxyppyroles) (PXDOPs) have been developed as electron rich electrochromic materials as illustrated by the monomer structures shown in Scheme 7. Substitution in the N-position allowed us to attain the high gap/high HOMO polymers that were instrumental in optimizing the contrast in the window-type ECD's.

We have demonstrated that the PXDOPs can be electrosynthesized in either aqueous or organic media to form smooth, redox active films on a variety of conducting substrates (Pt, gold on mylar, ITO-coated glass, glassy carbon). The PXDOPs are highly transmissive sky blue in their oxidized (doped) state switching to either a red (PEDOP) or orange (PProDOPs, P Bu DOP) reduced (neutral) state and have electronic band gaps between 2.0 and 2.2 eV as illustrated in Figure 9. PProDOP-NPS (N-propylsulfonate) is a water soluble and self-dopable polymer which can be electrostatically deposited onto conducting substrates to form multilayer systems.

### Scheme 7



**Figure 9.** (Left) Spectroelectrochemistry of a  $\sim 0.1 \mu\text{m}$  thick ( $50 \text{ mC/cm}^2$ ) PEDOP (Left) film in  $0.1 \text{ M LiClO}_4/\text{PC}$  at applied potentials of  $-0.87$  to  $-0.37 \text{ V}$  vs.  $\text{Ag}/\text{Ag}^+$ : (a)  $-0.87$ , (b)  $-0.82$ , (c)  $-0.77$ , (d)  $-0.72$ , (e)  $-0.67$ , (f)  $-0.62$ , (g)  $-0.57$ , (h)  $-0.52$ , (i)  $-0.47$ , (j)  $-0.37 \text{ V}$  and PProDOP-Me (Right) film at applied potentials of  $-1.07$  to  $-0.37 \text{ V}$  vs.  $\text{Ag}/\text{Ag}^+$ : (a)  $-1.07$ , (b)  $-0.97$ , (c)  $-0.87$ , (d)  $-0.77$ , (e)  $-0.72$ , (f)  $-0.67$ , (g)  $-0.62$ , (h)  $-0.57$ , (i)  $-0.52$ , (j)  $-0.47$ , (k)  $-0.42$ , (l)  $-0.37 \text{ V}$ .

## **Personnel Supported:**

### Principal Investigator:

John Reynolds

### Postdoctoral Fellows:

Pierre Henri Aubert  
Charlotte Cutler  
Youngkwan Lee

### Graduate Students:

Avni Argun  
Charles J. DuBois  
Carl Gaupp  
Jeong-Hae Han  
Benjamin Reeves  
Christopher Thomas  
Dean Welsh

### Visiting Scientists:

Selmiye Alkan

## **Peer Reviewed Publications:**

1. Thomas, C. A., Zong, K., Schottland, P., Reynolds, J. R.  
*Adv. Mater.*, **12**, 222-225 (2000).  
“Poly(3,4-alkylenedioxyppyroles) as Aqueous Compatible Conducting Polymers for Biomedical Applications”
2. Gaupp, C. L., Zong, K., Schottland, P., Thompson, B. L., Reynolds, J. R.  
*Macromolecules*, **33**, 1132-1133 (2000).  
“Poly(3,4-ethylenedioxyppyrole): Organic Electrochemistry of a Highly Stable Electrochromic Polymer”
3. Wang, F., Wilson, M. S., Rauh, R. D., Schottland, P., Thompson, B. C., Reynolds, J. R.  
*Macromolecules*, **33**, 2083-2091 (2000).  
“Electrochromic Linear and Star Branched Poly(3,4-Ethylenedioxythiophene-Didodecyloxybenzene) Polymers”

4. Thompson, B. C., Schottland, P., Zong, K., Reynolds, J. R.  
*Chem. Mater.*, **12**, 1563-1571 (2000).  
"In-Situ Colorimetric Analysis of Electrochromic Polymers and Devices"
5. Harrison, B. S., Ramey, M. B., Reynolds, J. R., Schanze, K. S.  
*J. Am. Chem. Soc.*, **122**, 8561-8562 (2000).  
"Catalytic Fluorescence Quenching of a Poly(*p*-phenylene)-Based Cationic Polyelectrolyte"
6. Schottland, P., Zong, K., Gaupp, C. L., Thompson, B. C., Thomas, C. A., Giurgiu, F., Hickman, R. H., Abboud, K., Reynolds, J. R.  
*Macromolecules*, **33**, 7051-7061 (2000).  
"Poly(3,4-alkylenedioxy pyrrole)s: Highly Stable Electronically Conducting and Electrochromic Polymers"
7. Groenendaal, L. B., Jonas, F., Freitag, D., Pielartzik, H., Reynolds, J. R.  
*Adv. Mater.*, **12**, 481-494 (2000).  
"Poly(3,4-Ethylenedioxythiophene) and Its Derivatives: Past, Present and Future"
8. Hopkins, A. R., Reynolds, J. R.  
*Macromolecules*, **33**, 5221-5226 (2000).  
"Crystallization Driven Formation of Conducting Polymer Networks in Polymer Blends"  
(Funding via AFOSR/BMDO sub-contract from Gemfire Corp.)
9. Sonmez, G., Schottland, P., Zong, K., Reynolds, J. R.  
*J. Mater. Chem.*, **11**, 289-294 (2001).  
"Highly Transmissive and Conductive Poly(3,4-alkylenedioxy pyrrole) (PXDOP) Films Prepared by Air or Transition Metal Catalyzed Chemical Oxidation"
10. Irvin, J. A., Schwendeman, I., Lee, Y., Abboud, K. A., Reynolds, J. R.  
*J. Polym. Sci., Polym. Chem.*, **39**, 2164-2178 (2001).  
"Low Oxidation Potential Conducting Polymers Derived from 3,4-Ethylenedioxythiophene and Dialkoxybenzenes"
11. Lee, Y., Sadki, S., Tsuie, B., Reynolds, J. R.  
*Chem. Mater.*, **13**, 2234-2236 (2001).  
"A New Narrow Band Gap Electroactive Polymer: Poly[2,5-bis-(2-{3,4-ethylenedioxy}thienyl)silole]"
12. Reynolds, J. R., Epstein, A. J.  
*Adv. Mater.*, **12**, 1565-1570 (2000).  
"ICSM 2000: Over Twenty-Five Years of Synthetic Metals"

13. Giurgiu, I, Reynolds, J. R., Lee, W.-P., Brenneman, K. R., Sapargin, A. V., Epstein, A. J., Hwang, J., Tanner, D. B.  
*Syn. Met.*, **119**, 405-406 (2001).  
"Dioxypyrrole and Dioxythiophene Based Conducting Polymers: Properties and Applications"
14. Thompson, B. C., Schottland, P., Sonmez, G., Reynolds, J. R.  
*Syn. Met.*, **119**, 333-334 (2001).  
"In Situ Colorimetric Analysis of Electrochromic Polymer Films and Devices"
15. DuBois, C. J., Jr., Larmat, F., Irvin, D. J., Reynolds, J. R.  
*Syn. Met.*, **119**, 321-322 (2001)  
"Multi-colored Electrochromic Polymers Based on BEDOT-Pyridines"
16. Zong, K., Reynolds, J. R.  
*J. Org. Chem.*, **66**, 6873-6882 (2001).  
"3,4-Alkylenedioxypyrroles: Functionalized Derivatives as Monomers for New Electron-Rich Conducting and Electroactive Polymers"
17. Harrison, B. S., Foley, T. J., Shim, J., Bouguettaya, M., Boncella, J. M., Holloway, P.H., Ramakrishnan, S., Reynolds, J. R., Schanze, K. S.  
*Appl. Phys. Lett.*, **79**, 3770-3772 (2001).  
"Near-Infrared Electroluminescence from MEH-PPV/Ln(TPP)acac Blends"
18. Pernaut, J.-M., Zong, K., Reynolds, J. R.  
*Synth. Met.*, **130**, 1-8 (2002).  
"A Crown Ether Derivatized Polydioxypyrrole as a Potential Lithium Sensor Material"
19. Welsh, D. M., Kloeppner, L. J., Madrigal, L., Pinto, M. R., Schanze, K. S., Abboud, K. A., Powell, D., and Reynolds, J. R.  
*Macromolecules*, **35**, 6517-6525 (2002).  
"Regiosymmetric Dibutyl-Substituted Poly(3,4-propylenedioxythiophene)s as Highly Electron-Rich Electroactive and Luminescent Polymers"
20. Cutler, C. A., Bouguettaya, M., Reynolds, J. R.  
*Adv. Mater.*, **14**, 684-688 (2002).  
"PEDOT Polyelectrolyte Based Electrochromic Films via Electrostatic Adsorption"
21. Schwendeman, I., Hickman, R., Sonmez, G., Schottland, P., Zong, K., Welsh, D. M., and Reynolds, J. R.  
*Chem. Mater.*, **14**, 3118-3122 (2002).  
"Enhanced Contrast Dual Polymer Electrochromic Devices"
22. Reeves, B. D., Thompson, B. C., Abboud, K. A., Smart, B. E., Reynolds, J. R.  
*Adv. Mater.*, **14**, 717-719 (2002).  
"Polymer Based on a Spiro Bipropylendioxythiophene [(Poly(spiroBiProDOT))]"

23. Brzezinski, J. Z., Reynolds, J. R.  
*Synthesis*, 1053-1056 (2002).  
"A New, Improved and Convenient Synthesis of 4*H*-Cyclopenta[2,1-*b*:3,4-*b'*]dithiophen-4-one"
24. Gaupp, C. L., Welsh, D. M., Rauh, D. R., Reynolds, J. R.  
*Chem. Mater.*, **14**, 3964-3970 (2002).  
"Composite Coloration Efficiency Measurements of Electrochromic Polymers Based on 3,4-Alkylenedioxythiophenes"

#### **AFOSR Funded Publications In Press and Submitted as of 11-30-02:**

1. Sonmez, G., Schwendeman, I., Schottland, P., Zong, K., Reynolds, J. R.  
*Macromolecules*, submitted for publication  
"N-Substituted Poly(3,4-propylenedioxyppyrrrole)s: High Gap and Low Redox Potential Switching Electroactive and Electrochromic Polymers"
2. DuBois, C. J., Reynolds, J. R.  
*Adv. Mater.*, accepted for publication  
"3,4-Ethylenedioxythiophene-Pyridine Based Polymers: Redox or n-Type Electronic Conductivity?"
3. Hwang, J., Tanner, D. B., Schwendeman, I., Reynolds, J. R.  
*Phys. Rev. B.*, submitted for publication  
"Optical Properties of Non-degenerate Ground State Polymers: PEDOT, PProDOT and PProDOT-Me<sub>2</sub>"
4. Alkan, S., Cutler, C. A., Reynolds, J. R.  
*Chem. Mater.*, submitted for publication  
"High Quality Electrochromic Polythiophenes via BF<sub>3</sub> • Et<sub>2</sub> Electropolymerization"
5. Gaupp, C. L., Welsh, D. M., Reynolds, J. R.  
*Macromol. Rapid Commun.*, accepted for publication  
"Poly(ProDOT-Et<sub>2</sub>): A High Contrast, High Coloration Efficiency Electrochromic Polymer"

#### **TRANSITIONS**

An important element of our research effort has been to develop external interactions with government, industrial, and other academic researchers in order to more fully explore the properties of our conducting and electroactive polymers and to develop possible applications. As our research has led to the development of a broad family of new redox active electroactive

polymers, they have generated significant interest from outside laboratories. The examples listed below illustrate how AFOSR funding has served as a catalyst for these interactions.

### Transitions during 2001-2002

1. a) Reynolds/Florida, b) PProDOTs for Conducting Elastomers c) Pat Valentino (pat.valentino@afrl.af.mil), Max Alexander (max.alexander@wpafb.af.mil)]. d) Application of soluble PProDOT derivatives in polymer blends directed to forming conducting elastomers.
2. a) Reynolds/Florida, b) electroactive star polymers for photovoltaics (#F49620-01-C-0043) c) Drs. David Rauh and Fei Wang, EIC Laboratories (781-769-9450), d) We have supplied new electron rich EDOT-based, and electron poor pyridine-based, monomers and polymers as arms for the stars and also provided extensive characterization in the form of electrochemistry, spectroelectrochemistry, and electrochromic switching.
3. a) Reynolds/Florida, b) "Multi-color Electrochromic Camouflage", Contract #DACA41-01-C-011. c) Drs. David Rauh and Fei Wang, EIC Laboratories (781-769-9450), d) A variety of the electrochromic systems developed by the Reynolds group are being applied to ECDs.
4. a) Reynolds/Florida, b) Printable conducting polymers, c) Dr. Danielle Boils, Xerox Company (905-823-7145, ext. 309), d) Xerox is investigating soluble PProDOTs as potentially ink jet printable conducting polymers.
5. a) Reynolds/Florida, b) 3,4-Alkylenedioxythiophene polymers, c) Bert Groenendaal, Agfa Gaevert, Belgium (32 3 444 32 24), d) Agfa is developing, in collaboration with the Reynolds group, new routes to 3,4-ethylenedioxythiophene and related polymers.
6. a) Reynolds/Florida, b) Redox switchable conducting polymers for microwave devices, c) John Lennhoff at Physical Sciences (978-738-8156) and Jennifer Irvin at NAWC (760-939-6655). d) Transitioned our soluble PProDOT's to PSI who are using ink jet printing methods for the formation of electrochemically switched electromagnetic shutters.
7. a) Reynolds/Florida, b) Redox switchable conducting polymers for modulating infrared reflectivity from metals, c) Dr. Jack Rowe at ARO (919-549-4332), ARO/IR MURI, d) Electrochromic polymers developed in AF funded program demonstrate excellent contrast and switching properties in reflective devices for controlling IR reflectivity off of a metallic surface. Application to controlled emissivity surfaces and camouflage.
8. a) Reynolds/Florida, b) Conducting Polymer Obscurants c) Susan T. P. Gardner, 978-738-8231 d) Use of biodegradable dioxothiophene based polymers as electromagnetic obscurants (chaff).
9. a) Reynolds/Florida, b) Near infrared emitting PLED's c) Len Buckley, 703-696-2288, d) Conjugated polymers are being synthesized in our laboratory and applied in the development of near infrared emitting PLED's and conjugated polyelectrolyte sensors.

10. a) Reynolds/Florida, b) Reflective electrochromic devices, c) Dr. Heyward Robinson, SRI International (650-859-3867), d) EC devices prepared by the Reynolds group have been supplied to SRI for analysis of mid- to far-IR modulation of reflectivity off a metal surface.

**Additional transitions during 2000-2001**

11. a) Reynolds/Florida, b) High contrast, broad band electrochromic devices, c) Dr. Tim Bunning (AFRL/MLPJ, timothy.bunning@wpafb.af.mil), d) Laminate film electrochromic device results have been supplied to AFRL with interests in broadband absorption.

12. a) Reynolds/Florida, b) Water soluble PEDOTs for electrostatic adsorption processing, c) Dr. Jeff Baur and Michael Durstock, AFRL/MLBP ([Michael.durstock@afri.af.mil](mailto:Michael.durstock@afri.af.mil), 937-255-9208), d) Polymers for photovoltaic devices. Successful development of polymer-based PV devices require donor and acceptor polymers with controlled band states. Electron rich water soluble PEDOTs have been supplied for ESA processing and use as electron donor components in photovoltaic devices.

**Additional transitions during 1999-2000**

13. a) Reynolds/Florida, b) multi-color carbazole based electrochromic polymers which switch between yellow, green and blue colored states, c) Dr. Bert Groenendaal, AG Bayer, Krefeld, Germany (32 3 444 3224), d) Bayer researchers have investigated the electrochromic properties of some of our functionalized BEDOT-Cz based polymers for EC displays which may prove useful in camouflage and other commercial applications (signs/large area displays).

14. a) Reynolds/Florida, b) conducting hyperbranched and dendrimer polymers, c) Drs. David Rauh and Fei Wang, EIC Laboratories (781-769-9450), d) "Processible Conductive Resin for High Temperature Applications", F33615-97-C-5090. The UF group supplies synthetic and electrochemical expertise to EIC. A full spectroscopic and colorimetric analysis of conducting star polymers prepared at EIC was accomplished. These star polymers are potentially useful in EC displays which may prove useful in camouflage and other commercial applications (signs/large area displays).

15. a) Reynolds/Florida, b) conductive cladding materials using redox doped conducting polymers with controlled electrical and optical properties, c) Dr. Hilary Lackritz, Gemfire, Inc. (650-849-6800), d) advanced displays. A set of PANI and PEDOT blends in amorphous and crystalline hosts has been investigated as potential electrode materials. These can be applied as cladding layers on non-linear optical polymers in advanced displays.

16. a) Reynolds/Florida, b) transport studies of conducting polymer free-standing films, c) Prof. Art Epstein, Ohio State (614-292-1133), d) Metallic conductors. Using multiple methods of DC transport, AC transport, EPR, and microwave studies the electronic properties of a series of poly(3,4-alkylenedioxythiophenes) have shown that some polymers have electrical properties on the metallic side of the insulator:metal transition. In order for polymers to ultimately be used as current carrying components in wires and electronic circuits (printed) metallic conductivity will be required.

**Awards and Honors received by the PI (life-time received):**

University of Florida, Research Foundation Fellowship 1999