

Final Report

for

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Variable Gap Conjugated Polymers

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1. Objectives

Conjugated polymers having structurally controlled valence (HOMO) and conduction (LUMO) states, along with systems having specific electron donor and acceptor capabilities, have been developed as optoelectronic materials for photovoltaic, electrochromic, and charge carrier transport properties. Prototype photovoltaic and electrochromic device platforms have been developed and utilized to test and optimize these polymer properties.

2. Status of Effort

The Reynolds research group has carried out the development and application of variable gap conjugated polymers which serve as electromagnetic absorption and charge carrying components in photovoltaic materials, are electrochromic, luminescent, semiconducting, and can be doped to high levels of electronic conductivity. Photovoltaic devices having reproducible AM 1.5 efficiencies of up to 2.7% have been constructed using MDMO-PPV/PCBM with a highly conducting gold interfacial layer interjected between the ITO glass electrode and the PEDOT/PSS hole transport layer. A family of low band gap, and near IR absorbing, cyanovinylene based polymers have been synthesized utilizing dioxythiophene repeat moieties yielding materials with band gaps ranging from 1.5 to 1.8 eV. These polymers have been blended with MEH-PPV to provide multi-polymer/PCBM photovoltaic devices with a broad spectral response ranging from 750 nanometers in the NIR, through the full visible spectrum. Regio-symmetric bis-thienyl-phenylene polymers have been synthesized with mid range band gaps of 2.0 to 2.2 eV as potential replacements for vinylene linked PPV type polymers. Initial photovoltaic devices prepared in both our Florida laboratories, and the UCLA laboratory of Professor Yang Yang, demonstrate these polymers to have AM 1.5 efficiencies of 0.5%. Combined oxadiazole and phenylene vinylene linked hybrid molecules have been used as donors with PCBM for enhanced electron carrying capabilities in photovoltaic devices with efficiencies of up to 0.6%. A broad family of spray processable alkylated poly(3,4-propylene dioxythiophenes) (PProDOTs) have been tested as high contrast electrochromic materials with especially high coloration efficiencies up to $1200 \text{ cm}^2/\text{C}$. These same polymers have been used as the active material in organic polymer field effect transistors yielding mobilities of $3 \times 10^{-4} \text{ cm}^2/\text{Vs}$. Enhanced order is being introduced into the PProDOT family by the use of chiral substituents which form optically active aggregates, and the utilization of 3,4-phenylene dioxythiophene polymers which form highly planar species directed to easily stackable polymers. PProDOTs functionalized with ether, ester and alcohol functional groups have been prepared and processed. Thin film chemical saponification of the ester derivatives yield insoluble, yet electroactive, PProDOT's which can be used as both electrochromics and as the hole transport layers in light emitting diodes. Hybrid electrochromic and electroluminescent (EC/EL) devices have been pursued using new oligoether functionalized carbazole based polymers which emit blue light while simultaneously being electrochromic switching from a fully transparent and colorless neutral state to a yellow oxidized form. Highly transmissive carbon nanotube electrodes having low surface resistivities of 30 ohms per square, have been

used as the electrodes in dual doping (simultaneous n- and p-type doping) devices for modulation of both visible and infrared radiation.

The Reynolds research group has developed extensive interactions with government laboratories and multiple companies (see description below in Transitions section) who are using the new polymers being developed through this AFOSR funding.

3. Accomplishments

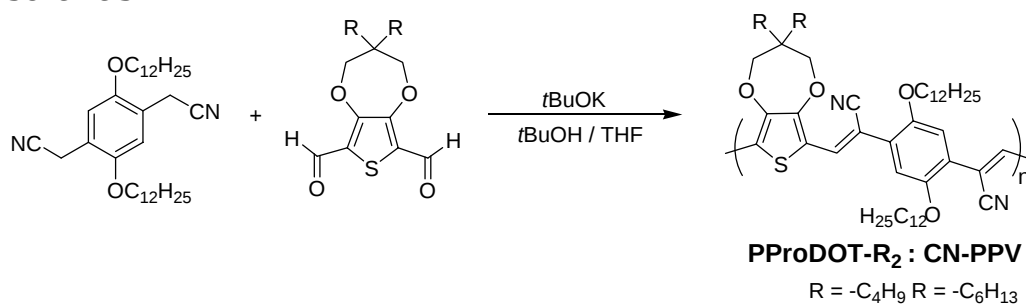
Extensive annual reports have been submitted and are available should the reader of this final report desire more details. What follows is an overview of results and approaches from our work that highlights our efforts and notes important directions.

3-1. Photovoltaic Polymers and Devices

Our efforts in the area of polymer photovoltaics have been focused on three major projects. First, we have developed narrow band gap polymers based on dioxothiophenes and cyanovinylenes as a route to donor-type polymers that can strongly absorb visible light. These polymers are intended for use with the C60 derivative PCBM, as it is the most efficient of the known acceptors. Second, we have developed a family of soluble donor-type polymers with variable band gaps from 1.5-2.5 eV, which can be blended with each other or with commercially available polymers (e.g. MEH-PPV, P3HT, etc.) in order to blanket the solar spectrum. Initial device results on these multi-component blends are promising. In addition, we have focused on improving device performance by controlling film morphology and have attained AM 1.5 efficiencies as high as 1.5%.

In the development of narrow band gap conjugated polymers, our primary targets are soluble donor-acceptor polymers based on cyanovinylene as the acceptors and 3,4-alkylenedioxythiophenes (XDOT's) as the donors as illustrated in Scheme 3-1. In our previous work, this donor-acceptor route to narrow band gap polymers has proven effective with the electropolymerization of XDOT donors with cyanovinylene, pyridine, and pyridopyrazine acceptors.^{1,2} As just one example PProDOT-Hx₂:CN-PPV has been synthesized in 89% yield with an M_n = 18,000 g/mol and is soluble in toluene, chloroform, dichloromethane, as well as THF.

Scheme 3-1



The solution absorption spectra of two new polymers, PProDOT-Hx₂:CN-PPV and PBProDOT-Hx₂:CNV are shown in Figure 3-1. It can be seen that both polymers

give blue solutions in toluene (low gap PEDOT blue!!) with absorption maxima at wavelengths greater than 600 nm and high extinction coefficients. Full studies including electrochemistry, electronic absorption, photoluminescence, and blending with C60 has characterized these polymers as excellent candidates for PV.

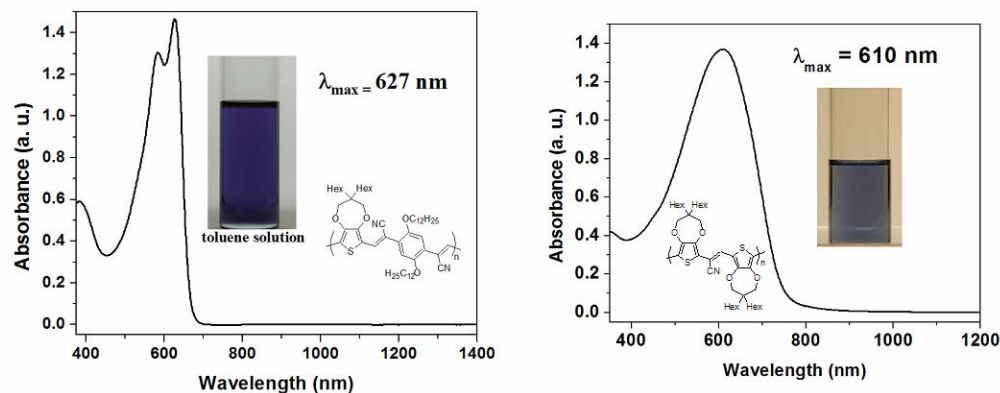


Figure 3-1. Solution absorption of PProDOT-Hx₂:CN-PPV and PBProDOT-Hx₂:CNV in toluene.

We have utilized these cyanovinylene polymers in blends with MEH-PPV ($E_g = 2.2 \text{ eV}$) as a means of achieving a broader absorption of sunlight. These two donors absorb sunlight across much of the visible region and then transfer electrons to the common PCBM acceptor as illustrated by the spectroscopic and IPCE PV device results of Figure 3-2. Interestingly, the IPCE results see in essence a summation of the response from each polymer, even though the content of each polymer is decreased by about 50% in the blends. As we move ahead, we propose to use these dioxathiophene-cyanovinylene hybrid polymers as a core structural unit for the absorption of long wavelength light (500-800 nm) not easily accessible with commercially available π -conjugated polymers.

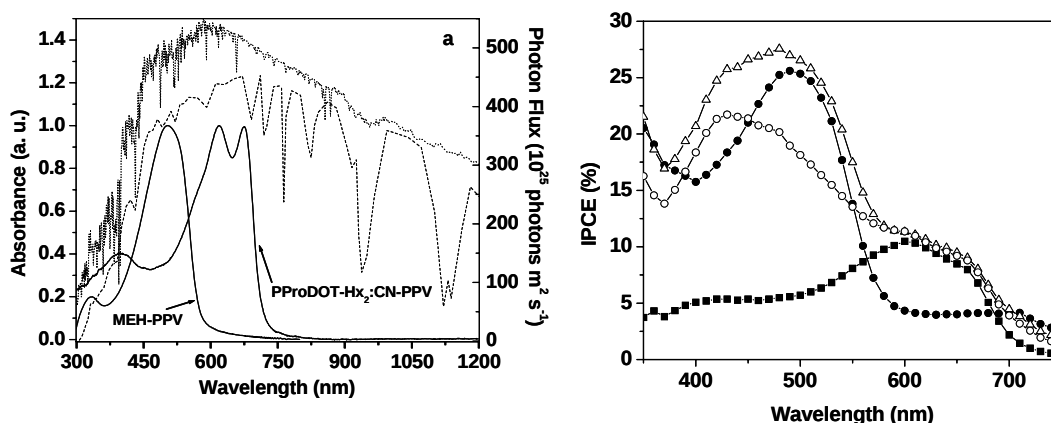
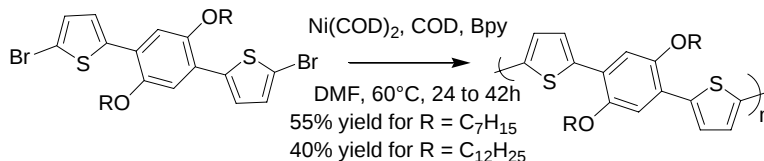


Figure 3-2: Left - Solar spectrum related absorption spectra for MEH-PPV and PProDOT-Hx₂:CN-PPV. Right - IPCE data for blends consisting of MEH-PPV, **PProDOT-Hx₂:CN-PPV**, and PCBM. **PProDOT-Hx₂:CN-PPV** / PCBM (1/4) (■), MEH-PPV / PCBM (1/4) (●), MEH-PPV / **PProDOT-Hx₂:CN-PPV** / PCBM (0.5 / 0.5 / 4) (Δ), and MEH-PPV / **PProDOT-Hx₂:CN-PPV** / PCBM (0.1 / 0.9 / 4) (○).

As a second approach to using variable band gap polymers for organic electronic and photovoltaic applications, we have synthesized several bis(2-heterocycle)phenylene polymers. Two families currently being investigated: PBT-B(OR)₂ (illustrated in Scheme 3-2) and PBEDOT-B(OR)₂ with R = OC₇H₁₅ and R = OC₁₂H₂₅ are prepared using the Yamamoto coupling reaction of Br₂-BT-B(OR)₂ monomers with the zerovalent nickel reagent, bis(1,5-cyclooctadiene)nickel(0) (Ni(COD)₂).

Scheme 3-2



Solar cells were fabricated using PBTB(OC₁₂H₂₅)₂/PCBM photoactive films which contained 20 wt% of the polymer in PCBM. The AM1.5 power conversion efficiency of these cells was found to be 0.5 % with short circuit current density of 1.6 mA/cm². The open circuit voltages (V_{oc}) and fill factor of the solar cells were 0.76 V and 0.4, respectively. A typical I-V curve is shown in Figure 3-3.

These interesting results show that we were able to obtain a strong photovoltaic response with short chain polymers and that the regiosymmetry of the molecules might play an important role on the photovoltaic efficiencies. Single crystals X-ray studies showed high π -stacking of the symmetrically derivatized monomers. This feature confers a high degree of order in the polymeric materials, which was confirmed by polymer film X rays studies as well as DSC measurements. We have carried out a collaboration with Professor Yang Yang from UCLA to investigate this in detail. Annealing studies will be

performed on these bis-heterocycle-phenylene polymers by his group in order to elucidate how a higher ordering might lead to higher power conversion efficiencies.

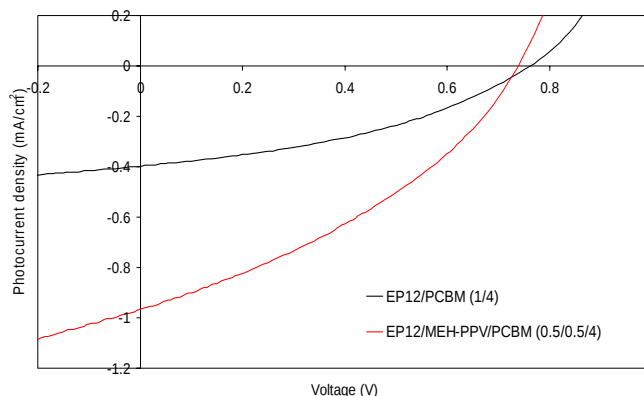
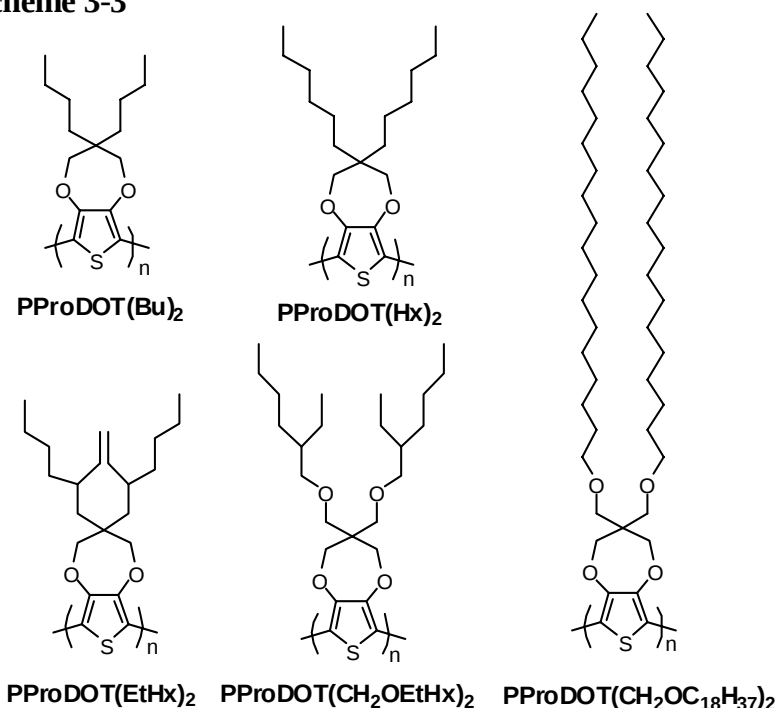


Figure 3-3: Photovoltaic results for devices incorporating PBTB(OC₁₂H₂₅)₂ alone with PCBM and as a blend with MEH-PPV and PCBM. The values for each device are an average of the values of three measured pixels.

3-2. Spray Processable PProDOT Derivatives.

Soluble, spray-processable and spin-coatable disubstituted poly(3,4-propylenedioxythiophenes) (see structures in Scheme 3-3) have been synthesized via Grignard metathesis polymerization to form regiosymmetric polymers by utilizing the C₂ symmetry of the propylenedioxythiophene monomer.^{3,4} As the propylenedioxy ring functions as a spacer to separate the alkyl chains from the polymer backbone, there is a minimal effect on the extent of conjugation while allowing increased solubility in organic solvents.

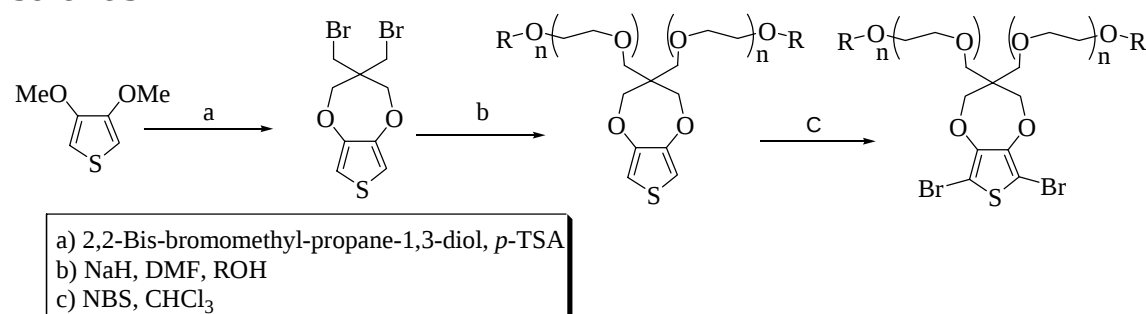
Scheme 3-3



GPC results gave number average molecular weights ranging from 33,000 to 47,000 g mol⁻¹ and weight average molecular weights between 47,000 and 75,000 g mol⁻¹ with polydispersities ranging from 1.4 to 1.7 after fractionation. These high molecular weights do not likely affect the optical or electronic properties of these polymers,⁵ but do enhance film forming ability, leading to easier processing.

Disubstituted poly(3,4-propylenedioxythiophenes) containing polar oligoether substituents have been prepared as our first attempt to synthesize dioxythiophenes which can be processed from industrially favorable alcohol and ester solvents while being insoluble in the lower polarity solvents normally used to spin films of conjugated polymers. Here our goal is to prepare hole transport and optoelectronically active polymers that can be sequentially solution processed with the second polymer deposition not disturbing the morphological, optical, or electrical characteristics of the first polymer deposited. In the synthesis of the oligoether ProDOT derivatives, a Williamson etherification reaction was used as shown for the monomer synthesis in Scheme 3-4 where $n = 1-4$. Bromination of the two and five position was carried out by exposure to NBS. To date, oxidative polymerization of the non-halogenated derivatives has been successful, and we now look to focus on the better controlled dibrominated monomers.

Scheme 3-4



Branched alkyl derivatives allow for the introduction of chirality in the PProDOT polymers. In the case of **PProDOT(EtHx)₂** and **PProDOT(CH₂OEtHx)₂**, the reagents used were racemic and led to a random distribution of R and S chiral centers. Obtaining chiral polymers is of great interest because of the ability of these polymers to self-assemble into organized structures in the aggregate state. This could lead to enhanced electronic and optical properties such as conductivity and charge transport compared to the racemic analogues, while maintaining their solution processability in organic solvents. In preliminary experiments we have synthesized PProDOT-((2S)-methylbutyl)₂ and examined the thermochromism and solvatochromism of these polymers by circular dichroism in order to examine how these polymers order upon aggregation. These results demonstrate that PProDOT-((2S)-methylbutyl)₂ forms highly ordered chiral aggregates at low temperatures or in poor solvents mixtures, as evidenced by a strong CD signal (Figure 3-4). The CD spectrum is similar to the spectrum obtained from aggregated chiral poly(thiophene)s derivatives, implying that PProDOT-((2S)-methylbutyl)₂ also forms one-handed chiral aggregates.⁶

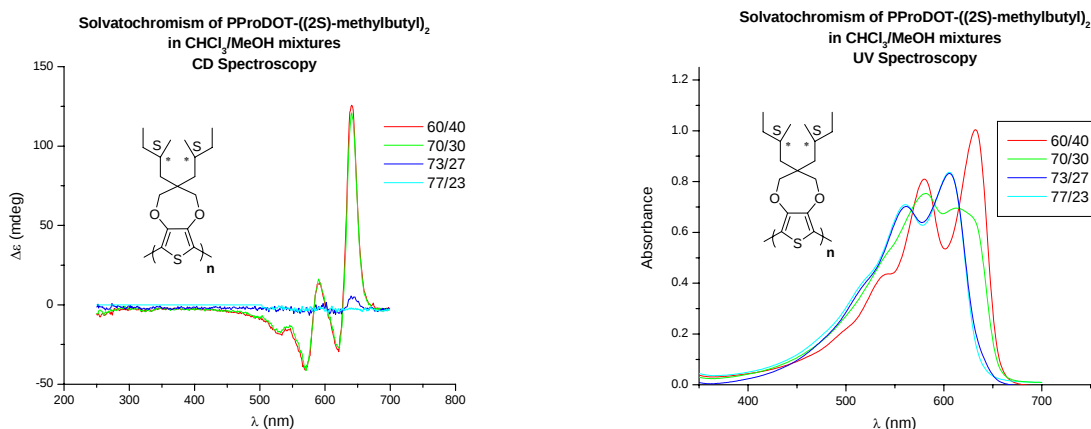


Figure 3-4: CD and UV-Vis spectroscopy of PProDOT-((2S)-methylbutyl)₂ in a solvatochromism experiment

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Peer Reviewed Publications:

1. Sönmez, G., Schwendeman, I., Schottland, P., Zong, K., Reynolds, J. R.
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12. Aubert, P. H., Argun, A. A., Cirpan, A., Tanner, D. B., and Reynolds, J. R.
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13. Argun, A. A., Aubert, P.-H., Thompson, B. C., Schwendeman, I., Gaupp, C. L., Hwang, J., Pinto, N. J., Tanner, D. B., MacDiarmid, A. G., and Reynolds, J. R.
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19. Mortimer, R. J., Reynolds, J. R.
J. Mater. Chem., **15**, 2226-2233 (2005).
“In Situ Colorimetric and Composite Coloration Efficiency Measurements for Electrochromic Prussian Blue”
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22. Witker, D., Reynolds, J. R.
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AFOSR Funded Publications In Press as of 11-05:

1. Kim, Y. G., Thompson, B. C., Ananthakrishnan, N., Padmanaban, G., Ramakrishnan, S., Reynolds, J. R.
J. Mater. Res., Special Issue: Energy and the Environment, accepted for publication
“Variable Band Gap Conjugated Polymers for Optoelectronic and Redox Applications”
2. Walczak, R., Cowart, J. S., Khalil, A., Reynolds, J. R.
Chem. Mater., accepted for publication
“Conformational Locking for Band Gap Control in 3,4-Propylenedioxythiophene Based Conjugated Polymers”

AFOSR Funded Patents

1. Reynolds, J. R., Zong, L., Schwendeman, I., Sonmez, G., Schottland, P., Argun, A. A., Aubert, P. H.
U. S. Patent 6,791,738, Issued Sept. 14, 2004
“Electrochromic Polymers and Polymer Electrochromic Devices”
2. Reynolds, J. R., Argun, A., Berard, M., Aubert, P.
U. S. Provisional Patent Application, UF #11335, subgrant #0160-G-AC859
“A Method to Contact Patterned Electrodes on Porous Substrates and Devices Thereby”

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. We are utilizing four external interactions detailed below as routes with which to attain a higher level of materials properties characterization, along with device construction and testing. The Reynolds group has formed important liaisons with multiple companies that also impacts this work through collaboration or materials development for commercialization. These include **Ciba Specialty Chemicals**, **SRI International**, **Crosslink**, and **Agfa**; all involved in electroactive and electronic materials.

1. a) Reynolds/Florida, b) Conjugated polymers for photovoltaics c) Michael Durstock (michael.durstock@wpafb.af.mil) d) John Reynolds provided information on use of conjugated polymers in solid state photovoltaic devices, advised AFRL researchers on the use of poly(thienylene vinylene) in PV devices, and served to link AFRL researchers with Crosslink Polymer Research Inc for development of screen printable large area dye sensitized solar cells.
2. a) Reynolds/Florida, b) electroactive star polymers for photovoltaics (F49620-03-C-0020), c) Drs. David Rauh and Fei Wang, EIC Laboratories (781-769-9450), d) We are supplying new electron rich EDOT-based, and electron poor pyridine-based, monomers and polymers as arms for the stars and also provide characterization in the form of electrochemistry, spectroelectrochemistry, and photovoltaic device testing.
3. a) Reynolds/Florida, b) high mobility polymer dyes for dye sensitized solar cells (FA9453-04-M-0283), c) Dr. David Rauh, EIC Laboratories (781-769-9450), d) We are synthesizing hyperbranched triphenylamine polymers having ruthenium complexes pendantly attached as dyes to be adsorbed on nanoporous TiO₂ for DSSCs.
4. a) Reynolds/Florida, b) crosslinkable conjugated oligomers for organic electronics, c) Dr. David Rauh, EIC Laboratories (781-769-9450), d) We are supplying end functionalized thiophene oligomers which can be crosslinked to provide enhanced thermal stability while providing order via liquid crystallinity .
5. a) Reynolds/Florida, b) Conjugated polymers for organic electronics c) Prof. Rod Devine, University of New Mexico (devine@chtm.unm.edu) and Lt. Gregory Theriot, Kirtland AFB (departed project) d) Provided interaction on use of conjugated polymers in organic electronics; specifically field effect transistors.
6. a) Reynolds/Florida, b) PProDOTs for Conducting Elastomers c) Pat Valentino (pat.valentino@afrl.af.mil), Rob Mantz (robert.mantz@wpafb.af.mil)]. d) Application of soluble PProDOT derivatives in polymer blends directed to forming conducting elastomers.

7. a) Reynolds/Florida, b) Surface Reactive PProDOTs for Conducting Elastomers (F49620-03-C-0066) c) John Lennhoff, Physical Science Inc. (978-738-8156). d) PProDOTs having reactive pendant functional groups were developed for adsorption onto metal coated micro and nano fibers as conductivity interface modifiers.

8. a) Reynolds/Florida, b) Redox switchable conducting polymers for modulating infrared reflectivity from metals, c) Dr. Marc Ullrich 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.

9. 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. NOTE: Field effect transistors have been made this year at Xerox using our PProDOT-(CH₂OC₁₈H₃₇)₂ which demonstrate the material to have a mobility of 10⁻³ cm² V⁻¹ s⁻¹.

10. a) Reynolds/Florida, b) 3,4-Alkylendioxythiophene 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. NOTE: This work led to 2 Agfa patent applications in new synthetic methods and fluorinated dioxythiophene molecules.

11. 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.

12. a) Reynolds/Florida, b) Conducting Polymer Obscurants c) Susan T. P. Gardner, 978-738-8231 d) Use of biodegradable dioxythiophene based copolymers as electromagnetic obscurants (chaff).

13. 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

14. 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. NOTE: Spray coatable formulations of PProDOTs are being used at SRI in their device development.

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

University of Florida, Research Foundation Fellowship 1999

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- ¹ (a) Sotzing, G. A.; Thomas, C. A.; Reynolds, J. R.; Steel, P. J. *Macromolecules* **1998**, *31*, 3750.
(b) Thomas, C. A.; Zong, K.; Abboud, K. A.; Steel, P. J.; Reynolds, J. R. *J. Am. Chem. Soc.* **2004**, *126*, 16440.
(c) Thompson, B. C., Kim, Y-G., Reynolds, J. R., *Macromolecules*, in press.
- ² (a) Dubois, C. J.; Reynolds, J. R. *Adv. Mat.* **2002**, *14*, 1844. (b) DuBois, C. J.; Abboud, K. A.; Reynolds, J. R. *J. Phys. Chem. B* **2004**, *108*, 8550.
- ³ Welsh, D. M.; Kloeppner, L. J.; Madrigal, L.; Pinto, M. R.; Thompson, B. C.; Schanze, K. S.; Abboud, K. A.; Powell, D.; Reynolds, J. R. *Macromolecules*, **2002**, *35*, 6517.
- ⁴ Reeves, B. D.; Grenier, C. R. G.; Argun, A. A.; Cirpan, A.; McCarley, T. D.; Reynolds, J. R. *Macromolecules*, **2004**, *37*, 7559.
- ⁵ *Electronic Materials: The Oligomer Approach*; Mullen, K., Wegner, G., Eds.; Wiley-VCH: Weinheim, 1998.
- ⁶ Langeveld-Voss B. M. W., Janssen R. A. J., Meijer E. W., *Journal of Molecular Structure* **2000**, *521*, 285.