The research program focused on new polymeric materials for use in reflective displays and other optoelectronic applications. It was carried out by a consortium of seven researchers from four universities (University of Rochester, Massachusetts Institute of Technology, University of Texas at Austin, and Utah State University). The cornerstone of the planned research was to design, synthesize, and characterize polymeric materials having environmentally responsive optical properties, which allows them to be switched efficiently. In recognition of the importance of studying these materials in the context of their intended application, the team included expertise in modeling, fabricating, and evaluating display devices and systems.
MEMORANDUM OF TRANSMITTAL

U.S. Army Research Office
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Research Triangle Park, NC 27709-2211

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REPORT TITLE: Tunable Optical Polymer Systems

is forwarded for your information.

SUBMITTED FOR PUBLICATION TO (applicable only if report is manuscript):

Sincerely,

Samson Jenekhe
TUNABLE OPTICAL POLYMER SYSTEMS (TOPS)
MURI CENTER PERSONNEL

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An extensive research program to investigate new polymeric materials for use in reflective displays and other optoelectronic applications is proposed by a consortium of seven researchers from four universities (University of Rochester, Massachusetts Institute of Technology, University of Texas at Austin, and Southern Illinois University). The cornerstone of the planned research is to design, synthesize, and characterize polymeric materials having environmentally responsive optical properties which allow them to be switched efficiently. In recognition of the importance of studying these materials in the context of their intended application, the team includes expertise in modeling, fabricating, and evaluating display devices and systems.

The MURI program on Tunable Optical Polymer Systems (TOPS) consists of the following coordinated activities: (1) Development of new synthetic methodology and new chromogenic materials: Three synthetic polymer chemists (Chen, Jeneikhe and Swager) have designed novel approaches to incorporation of optically and electrically active chromogenic chromophores into processable polymers suitable for conformal coatings of large areas. New classes of electrochromic conjugated polymers, photoelectrochromic polymer/organomettalic nano-composites, liquid crystalline conjugated polymers and block copolymers, electroluminescent polymers, and self-organizing polymers will be synthesized. (2) Experimental and theoretical characterization of color switching phenomena: Extensive material characterization is planned, including studies of the multifunctional optical polymers during operation in model devices. Various types of color change phenomena will be exploited including those which rely on electrochemical reaction (Bard), photoelectrochromic effects, photochromism and electroluminescence. Molecular modeling (Scheiner) of electron and proton transfer processes will accompany these studies to guide synthetic work towards more durable materials with larger chromogenic effects. (3) New paradigms for self-assembly of organized sub-wavelength and wavelength-sized supramolecular structures and nano-structures: Perhaps the most important property of organic polymer is their ability to be processed conveniently. Recently, much activity has extended this further by taking advantage of their thermodynamic or intermolecular forces driven propensity to self-organize via microphase separation. Three of the leading practitioners in this area (Chen, Hammond, Jeneikhe) are among the team members and propose several ideas for making sub-wavelength and wavelength-dimension structures which will be useful in enhancement of optical switching phenomena in polymers. (4) Design and modeling of device structures to enhance color-change phenomena: Our team includes a device physicist experienced in utilizing microcavity effects to tailor and improve the properties of optical display devices (Rothberg). Construction and characterization of microcavity geometries which enhance switching is planned, and modeling software to assist team members in designing devices which optimally take advantage of material properties will be developed. (5) Development of patterning technologies to organize these polymeric materials and devices into large arrays: Exciting new work on microcontact printing promises to revolutionize the way pixelation of displays is done. One team member has combined this work with self-assembling layers so that it is possible to make three-dimensional structures with micron dimensions and incorporate a wide variety of functional materials (Hammond). The potential for construction of large area color switchable arrays avoiding expensive and cumbersome processes such as lithography and evaporation is enormous. (6) Fabrication and testing of devices to deduce mechanism and robustness: Spectroscopic characterization of materials during device operation is planned to determine properties such as switching efficiency, speed and degradation rate (Bard). Standard measurements such as electroabsorption and electroreflectance (Rothberg) will be available. These will help to determine operation mechanism of these devices so that appropriate materials properties can be incorporated in the polymers. (7) Colorimetric evaluation of devices and assemblies from a display perspective. Finally, we plan a common facility for testing optical properties at a systems level. This will include colorimetric and contrast measurements as performed in the display industry.

The primary goal of this MURI research program is to identify promising new classes of chromogenic polymers and device structures into which they can be incorporated to produce large-area, addressable color tunable devices which are low cost and rugged. We also plan to intimately involve many graduate, undergraduate, and postdoctoral students as well as industrial and DoD collaborators in this highly interdisciplinary research with important commercial and military applications. In addition, the infrastructure for research in the areas of materials chemistry, polymer science, computational chemistry and organic devices in the participating universities will be augmented.
TOPS MURI AGENDA
Annual Review Meeting, 15-16 August 2000
Army Natick RD&E Center: Natick, MA

15 August 2000

08:40 - Introductory Remarks (10 min.) Doug Kiserow
08:50 Overview of NRDEC (25 min) Ed Crivello
09:15 - Overview of TOPS MURI Center (25 min.) Sam Jenekhe
09:40 - Break (20 min.)

10:00 - Tunable Reflection Systems

10:00 - Liquid Crystalline Polymers with Tunable Optical Properties (25 min.) Shaw Chen
10:25 - Liquid Crystalline Conjugated Polymers as Multifunctional Optical Materials (30 min.) Dimitris Katsis
10:55 - Chromogenic Block Copolymer Assemblies (25 min.) Paula Hammond
11:20 - TOPS Test Beds (25 min.) Lewis Rothberg
11:45 - Additional Questions and Discussions

12:00 - Lunch Break

13:00 - Posters and Device Demonstrations

14:45 - Break

15:00 - Tunable Emission Systems

15:00 - Tunable Light Emitting Polymers and Devices: Polymer/Polymer Interfaces (25 min.) Sam Jenekhe
15:25 - Tunable Electroluminescence in Conjugated Polymers (25 min.) Katie Meeker
15:50 - Aggregation Quenching in EL Polymers (25 min.) Pei Wang
16:15 - ECL and Light Emitting Devices (25 min.) Al Bard
16:40 - Additional Questions and Discussions
17:00 - TOPS TAB/EAB Executive Session

iii
16 August 2000

08:40 - Tunable Absorption Systems

08:40 - Thin Film Electrochromic Devices
(25 min.) D. DeLongchamp 159

09:05 - Electrochromic Ladder Polymers
(25 min.) Maurizio Quinto NA

09:30 - Highly Stable Polycyclic Aromatic
Conjugated Polymers Polymers
(25 min.) JD Tovar 179

09:55 - Break
(20 min)

10:15 - Computational Modeling of Chromogenic Effects
(25 min.) Steve Scheiner 193

10:40 - Synthesis of New Electrochromic Polymers
(25 min.) Tim Swager 225

11:05 - Discussions and Concluding Remarks
(15 min.) Sam Jenekhe

11:20 TOPS TAB/EAB Executive Session
(Lunch Break for MURI Center Team)

13:30 - Feedback of TAB/EAB to MURI PIs
(30 min.) Doug Kiserow

14:00 - TOPS MURI Annual Review Meeting Adjourned

*Each Speaker should plan to leave 5 minutes of allotted time for questions and change of speakers.


CHAMELEONS AND THE FUTURE OF TOPS

- Learning From Nature
- Chameleon Optoelectronics
- Chameleon Nanophotonics
- Novel Reflective Displays
- Color Switchable Wall Paper

Brookesia perarmata is the largest of the Malagasy dwarf chameleons at just over 4” (11 cm) in length.

The world's smallest chameleon — Brookesia minima on a fingernail.
ACADEMIC RESEARCH PERSONNEL

UR CHEM. ENG.
- S. A. JENEKHE
- S. H. CHEN
  - 1 POSTDOC
  - 4 GRAD STUDENTS
  - 2 UNDERGRADS

MIT CHEM. ENG.
- P.T. HAMMOND
  - 1.5 GRAD STUDENTS
- T. M. SWAGER
  - 2 GRAD STUDENTS

MIT CHEMISTRY

SIU CHEMISTRY
- S. SCHEINER
  - 2 GRAD STUDENTS

UT-AUSTIN CHEMISTRY
- A. J. BARD
  - 2 POSTDOCS

L. J. ROTHBERG
- 1 POSTDOC
- 1 GRAD STUDENT
- 1 UNDERGRAD

S. A. JENEKHE
ARO TOPS MURI
I. Design, synthesis, characterization and processing of new generation of chromogenic polymers for optoelectronic and photonic applications
   - Structural design at the electronic, molecular, supramolecular, nanostructure and macroscopic levels
   - New synthetic methodologies
   - New paradigms for self-assembly of nanostructures and for polymer processing
   - Enhanced chromogenic effects
   - Lower switching energies
   - Improved durability and switching speeds

II. Fundamental understanding of the physical/chemical mechanisms of chromogenic phenomena in polymers
   - Chemistry and photophysics of color switching
   - Dynamics of color-switching processes
   - What factors influence lifetime (# of cycles)
   - Learn from chromogenic phenomena in nature (biology)

III. Construction and evaluation of model devices/displays using the new chromogenic polymers
TUNABLE REFLECTION SYSTEMS

Research Team
• Shaw Chen - LC Polymers with Tunable Optical Properties
• Paula Hammond - Chromogenic Block Copolymer Assemblies
• Sam Jenekhe - Self-Organizing Photonic Band Gap Materials
• Lewis Rothberg - TOPS Test Beds

Relationship to DoD
Reflective Displays; Self-Aseembly for Nanotechnology; Intelligent Sensors/ Detectors; Materials for Photonics; Optical Filters; Photoresponsive Transducers

Interactions with Army
• CRADA with ARDEC, Picatinny Arsenal
• Many Planned

MURI Funding Level: $350 K/yr.

Personnel
• Graduate Students: 3
• Postdocs: 1
• Undergraduate Students: 1
TUNABLE EMISSION SYSTEMS

Research Team
• Al Bard - Electrochemiluminescent Systems
• Paula Hammond - 3-D Array Patterning by Self-Assembly
• Sam Jenekhe - Tunable Electroluminescent Polymers and Devices
• Lewis Rothberg - Microcavity Design for Emissive Displays

Relationship to DoD
Addressable Color Tunable Devices; Large Area Displays; Nanofunctional Devices; Smart/Interactive Clothing; Low Cost Rugged Flexible Displays.

Interactions with Army
• Many Planned

MURI Funding Level: $270 K/yr.

Personnel
• Graduate Students: 1
• Postdocs: 2.5
• Undergraduate Students: 1
TUNABLE ABSORPTION SYSTEMS

Research Team
• Al Bard - Electrochromic Ladder Polymers
• Paula Hammond - Electrochromic Thin Film Devices
• Steve Scheiner - Computational Modeling of Chromogenic Effects
• Tim Swager - Synthesis of New Electrochromic Polymers
• Lewis Rothberg - Electrochromic Test Beds

Relationship to DoD
Large Area Displays; Color-Tunable Clothing/Wall Papers/Coatings; Environmentally Responsive Materials; Smart Materials

Interactions with Army
• Many Planned

MURI Funding Level: $380 K/yr.

Personnel
• Graduate Students: 6
• Postdocs: 1
• Undergraduate Students: 1
FIRST YEAR HIGHLIGHTS

TUNABLE REFLECTION

• Developed Chiral-Nematic Poly(p-phenylene)s Having Tunable Selective Reflection (IR to UV) (Dimitris Katsis)
• High Degree of Circular Polarization Demonstrated (Dimitris Katsis)
• Micropatterning of Chromogenic Polymers Demonstrated (Paula Hammond)

TUNABLE EMISSION

• Tris(bipyridine)ruthenium (II) Complexes (Al Bard)
  - Efficient Bright Red LEDs Developed (Al Bard)
  - Tunable Multicolor PPV/Ru(bpy)$_3^{2+}$ LEDs (Katie Meeker)
• Understanding of Polymer/Polymer Interfaces in Optoelectronic Devices (Sam Jenekhe)
• Developed a New Calorimetric Instrument for Measuring Absolute Fluorescence Quantum Yields (Lewis Rothberg)

TUNABLE ABSORPTION

• New Approaches to Electrochromic Thin Film Devices (Dean DeLongchamp)
• Electrochromic BBL and BBB Ladder Polymers Demonstrated (Maurizio Quinto)
• New Electroactive Conjugated Polymers Synthesized (Tim Swager)

S.A. JENEKHE
ARO TOPS MURI
TUNABLE REFLECTION SYSTEMS

Research Team
- Shaw Chen — LC Polymers and glasses with Tunable Optical Properties
- Paula Hammond — Chromogenic Block Copolymer Assemblies
- Sam Jenekhe — Self-Organizing Photonic Band Gap Materials
- Lewis Rothberg — Reflective Display Devices and TOPS Test Beds

Personnel
- Graduate Students: 3
- Postdocs: 1
- Undergraduate Students: 3

Relationship to DoD
- Reflective Displays; Optical Notch Filters; Self-Assembly for Nanotechnology; Intelligent Sensors and Detectors; Materials for Photonics; Photoresponsive Transducers

Interactions with Army
- CRADA with ARDEC, Picatinny Arsenal
- Others Planned

S. H. Chen, University of Rochester ARO MURI
Background and Introduction

- **Nature of coloration**
  - pigmented colors due to absorption
  - structural colors due to interference, diffraction or scattering
  - emissive colors due to photo- or electroluminescence
  - structural colors tend to be brilliant, iridescent, and long lasting

- **Stimuli to induce color change**
  - thermal, electric, magnetic
  - photochemical, electrochemical
  - proton transfer, pH

- **Mechanisms of color crypsis**
  - spontaneous response to external stimuli ⇒ “smart skins”
  - nervous control of color change ⇒ “intelligent skins”

- **Bio-inspired synthetic materials as an ultimate goal**
Research Overview: Shaw H. Chen, U. Rochester

- **Research Projects**
  - Multifunctional liquid crystalline conjugated polymers (presentation by Dr. Katsis)
  - Poly(fluorene)s for electroluminescence: stability, efficiency, color tunability, morphology and polarization control
  - Tuning reflective, emissive, and absorptive colors in fluid, gel, melt, and solid films

- **Objectives**
  - Conjugated polymers for coloration by selective reflection, emission and absorption
  - Helically stacked or coiled conjugated systems for efficient emission of polarized light
  - Color tunability by external stimuli: photochemical, thermal, electric, magnetic, etc.

- **MURI Collaborators**
  - Lewis Rothberg, Samson Jenekhe, Paula Hammond

- **Publications**
Liquid Crystalline Conjugated Polymers as Multifunctional Optical Materials

D. Katsis, H. P. Chen, J. C. Mastrangelo*, and S. H. Chen

Department of Chemical Engineering, Materials Science Program
Laboratory for Laser Energetics, Room 1210, COI, University of Rochester

*Now at Naval Research Laboratory, Washington, D.C.

TOPS MURI Review Meeting, 15-16 August 2000, Natick, MA
Four Types of Liquid Crystalline Order

Nematic

Smectic

Cholesteric

Columnar
Characteristic Textures of Liquid Crystals
Observed with Polarizing Optical Microscopy

Nematic

Smectic

Cholesteric

Columnar
Four Types of Liquid Crystalline Order

- **Nematic**
- **Smectic**
- **Cholesteric**
- **Columnar**
Characteristic Textures of Liquid Crystals Observed with Polarizing Optical Microscopy
Coloration via Selective Reflection

- Chiral-nematic liquid crystalline film as a helical stack of quasinematic layers, illustrated below with a LH structure:

Case 1: \( \lambda \neq \lambda_R = p\bar{n} \), complete transmission
Case 2: \( \lambda = \lambda_R \), LHCP reflected and RHCP transmitted
A Concept of Tunable Reflection via Electrochemical Doping with Chiral Salts

Undoped

Doped with $C_R^*$
Pitch Tightening

Doped with $C_S^*$
Pitch Loosening
Existing Chiral-Nematic Materials

- Low viscosity fluids, polymer melts
- Lyotropic polymers, ‘chaotropic effect’
- Polymer/LC composites, anisotropic gels
- Thermotropic polymers
- Low-molar-mass vitrifiable LCs

All these are nonconjugated systems with tunable reflection color by various means
Multifunctional LC Polymers

- Amorphous or crystalline conjugated polymers capable of tunable absorption and emission
- Chiral-nematic nonconjugated polymers capable of tunable reflection
- A new challenge: chiral-nematic conjugated polymers for multiple modes of tunability

\[
\begin{align*}
\text{Non-LC } \pi\text{-conjugated backbone} & \quad \text{Nematic } \pi\text{-conjugated backbone} \\
\text{Ch}_x & \quad \text{achiral}_{1-x}
\end{align*}
\]
Synthetic Scheme for Chiral-Nematic Poly(\(p\)-phenylene)s
Absorption and Emission Spectra in Dilute Solution

![Absorption and Emission Spectra Graph]

- Absorption and emission spectra for a dilute solution of 10^{-5} M in CH_2Cl_2.
- The excitation wavelength is 350 nm.

![Graph Details]

- The graph shows the absorbance (10^{-4} ε, M^{-1} cm^{-1}) and emission intensities (PL, a.u.) as a function of wavelength (λ, nm).
- Two sets of spectra are plotted, labeled as (1-1) and (III-0.00).
Optical Set-Up for Characterization of LPPL

- Excitation Beam
- Lens
- UV Linear Polarizer (UV LP) effective @ 275-750nm
- UG11 Band Pass Filter < 400nm
- Nematic Sample
- UV Linear Polarizer (UV LP) effective @ 275-750nm
- To Analyzer
- Lens
- Al Mirror
Characterization of the Alignment of Conjugated Backbones and Nematic Pendants

(III - 0.00), 4 μm film
λ_ex = 350 nm, S = 0.62

Il excitation:
- Il emission
- - - - - emission

Il excitation:
- - - - - emission
- - - - - emission

O.D.

λ, nm

PL, a.u.

v, cm⁻¹

A Il

A⊥
Supramolecular Structure of Chiral-Nematic Poly(p-phenylene)s

Chemical structure and molecular arrangement diagram showing the director and half-pitch.
Absorption and Selective Reflection of Thin Films

Absorption (O.D.) and Reflectance (R) spectra for 4 μm films.

Optical density (O.D.) and absorbance (α) as a function of wavelength (λ).

The graph shows the variation of O.D. and α with wavelength, with distinct peaks and valleys indicating absorption and reflectance properties of the thin films.

Wavelength (nm) ranges from 400 to 1000 on the x-axis for O.D. and from 250 to 450 on the x-axis for α. The y-axis for O.D. ranges from 0 to 0.4 and for α from 0 to 16.

Key points:
- (III - 0.17)
- (III - 0.12)
- (III - 0.07)
- Optical Density values for different wavelengths.
- Absorbance values for different wavelengths.

Legend:
- 4 μm films
- Spin-coated 0.27 μm film
- Sandwiched 4 μm film

The graph illustrates the selective reflection and absorption properties of thin films at various wavelengths, highlighting the regions of maximum absorption and reflection.
Transmission of Circularly Polarized Light

(III - 0.12), 4 µm film
Optical Set-Up for Characterization of CPPL

\[ g_e = 2 \frac{I_L - I_R}{I_L + I_R} \]

Unpolarized Excitation @ 370 nm

Lens

UG11 Band Pass Filter < 400 nm

Chiral Nematic Sample

Zero Order Quarter Waveplate centered @ 425 nm

UV Linear Polarizer effective between 275-750 nm

To Detector
Spectra of Circularly Polarized Photoluminescence from Thin Films

(\( \text{III} - 0.07 \), 4 \( \mu \text{m} \) film, \( \lambda_{ex} = 350 \text{ nm} \))

(\( \text{III} - 0.17 \)/ \( \text{III} - 0.23 \)) = 79/21 by weight

2 \( \mu \text{m} \) film, \( \lambda_{ex} = 350 \text{ nm} \)
Effect of Film Thickness on Degree of Circular Polarization

$$\frac{(III - 0.17)}{(III - 0.23)} = \frac{79}{21} \text{ by weight}$$
solid films, $\lambda_{\text{exc}} = 350$ nm

![Graph showing effect of film thickness on degree of circular polarization]
Optical Set-Up for Characterization of Viewing Angle Dependence

[Diagram of optical set-up with labels: Xe lamp, monochromator, lens, PMA-11 polarizer, sample, 45° angle, and other optical components]
Viewing Angle Dependence Of CPPL

\[ \lambda_{em} = 400 \text{ nm} \]

\[ \lambda_{em} = 425 \text{ nm} \]

\[ \lambda_{em} = 450 \text{ nm} \]

\[ \lambda_{em} = 475 \text{ nm} \]
Glass-Forming Chiral-Nematic Liquid Crystals

- Ease of processing into large area, monodomain, vitrified films
- Environmental durability
- Availability of both enantiomers
- Selective reflection tunable from UV to IR depending on ratio (I)/(II)
Material Synthesis

\[ \text{HOOC} \overset{1) (CH_3CO)_2O / reflux}{\longrightarrow} \overset{2) \text{SOCl}_2 / reflux}{\longrightarrow} \overset{53\%}{\longrightarrow} \]

\[ \text{HOOC} \rightarrow \overset{\text{NOH / DMAP / Et}_3\text{N}}{\longrightarrow} \overset{52\%}{\longrightarrow} \]

\[ \text{HOOC} \rightarrow \overset{(S)-ChOH}{\longrightarrow} \overset{52\%}{\longrightarrow} \]

\[ \text{HOOC} \rightarrow \overset{(R)-ChOH}{\longrightarrow} \overset{52\%}{\longrightarrow} \]

\[ N = -(\text{CH}_2)_3O- \begin{array}{c} \text{CN} \\ \end{array} \]

\[ Ch = -(\text{CH}_2)_2O- \begin{array}{c} \text{COO} \\ \overset{*}{\text{CONHCH}} \\ \text{CH}_3 \end{array} \]

\[ \text{DMAP: 4-(dimethylamino)pyridine; DEADC: diethyl azodicarboxylate; PPh}_3: \text{triphenylphosphine} \]
Transmission of Circularly Polarized Light through Glassy Chiral-Nematic Films

(\(I - S\)) / (\(I\)) at 42 / 58 mass ratio
8 \(\mu\)m film

(\(I - R\)) / (\(II\)) at 42 / 58 mass ratio
8 \(\mu\)m film
High-Performance Reflector and Notch Filter

![Graph showing the performance of a high-performance reflector and notch filter across different wavelengths (nm). The x-axis represents wavelength (nm) ranging from 400 to 800, and the y-axis represents O.D. (Optical Density). The graph highlights the reflectance characteristics at specific wavelengths, indicating high reflectance peaks at certain points.]
Conclusions

- Chiral-nematic poly(p-phenylene)s were shown to self-assemble into helically stacked \( \pi \)-conjugated systems
- With increasing chiral content, selective reflection of neat films was tunable from the infrared, through the visible, and down to the ultraviolet region
- Unpolarized excitation at 350 nm was found to induce emission predominantly from the polymer backbone with no evidence of excimer formation
- A high degree of circular polarization was observed with chiral-nematic films when emission occurred in the resonance region
- High-performance reflectors were prepared with glass-forming LCs having identical chemical structure except opposite chirality
Current and Future Research

- Tuning reflection colors via reversible isomerization of photoresponsive dopants in vitrified chiral-nematic films
- Design, synthesis, characterization and molecular dynamics simulation of helically coiled conjugated polymers in addition to helically stacked systems
- Electroluminescent poly(fluorene)s: optimized structure for efficient and stable electroluminescence, color tunability via copolymerization or blending, and polarization control
- Potential of helically arranged conjugated polymers for tunable absorption and reflection colors via electrochemical doping with chiral salts
- Synergy between two or three modes of color tunability
- Color patterning via spatially modulated thermal and photochemical film processing
Tunable Optical Polymer Systems: Mesostructured Chromogenic Polymer Assemblies

ARO MURI - TOPS
Co-PI: Paula T. Hammond
Dept. of Chemical Engineering, MIT
1) Layer-by-Layer Polydye Microstructures
2) Block Copolymer Chromogenic Materials
3D Array Patterning by Self Assembly

Research Team
• Paula T. Hammond  Patterned Deposition Techniques/Chromic Thin Films
• Alan Bard  Electrochemical Analysis/Adsorption Studies
• Lewis Rothberg  Electrochemically Assisted Microfabrication

Goals
• New Solid State Medium for Electro and Photochromic Systems
• Opportunity for Device Fabrication

Interactions with Army
• Potential Contact with Natick Labs on Thin Films

MURI Funding Level: $50 K/yr.

Personnel
• P.T. Hammond
• Dean Delongchamp

P.T. Hammond  ARO MURI
TOPS Objectives - Mesostructured Polymers Layer-by-Layer Films

- Use ionic layer-by-layer technique to develop new electro- and photochromic, reversible, polymer-dye layered composite films (with Swager/Jenekhe lab).
- Create functional microstructures for chromogenic display applications based on expertise in selective deposition.
- Characterize electron transfer processes of complex multilayered systems using spectroelectrochemistry and spectroscopy (with Bard and Rothberg labs).
Layer-by-Layer Ionic Assembly

- Step-wise deposition of molecular scale layers
- Can incorporate a number of functional dyes
- Use layer-by-layer to tailor redox properties
- Vary electron transfer to different regions with layer position
Comparison of Photolithography to Chemistry-templated Multilayer Assembly

<table>
<thead>
<tr>
<th>Photolithography</th>
<th>Chemistry-templated assembly</th>
</tr>
</thead>
<tbody>
<tr>
<td>• expensive both in capital and operating cost</td>
<td>• little capital investment, procedurally simple</td>
</tr>
<tr>
<td>• not suitable for patterning non-planar surface</td>
<td>• access to new types of surfaces, optical structures, sensors and prototype devices etc.</td>
</tr>
<tr>
<td>• ineffective in generating 3-D structures</td>
<td>• not subject to the limitations set by optical diffraction and optical transparency</td>
</tr>
<tr>
<td>• difficult for introducing specific chemical functionality</td>
<td></td>
</tr>
</tbody>
</table>
Self-Assembled Monolayers (SAMs) and Micro-contact Printing (μCP)

- COOH SAM promotes adsorption
- Oligoethylene glycol (EG) SAM resists adsorption of polyions.
Luminescent dyes

Ru(Phen*)₃⁻⁺

poly(p-phenylene) anion

O(CH₂)₃SO₃Na⁺

poly(p-phenylene) cation

O(CH₂)₃SO₃Na⁺

absorbance max. 470nm
emission max. 628nm (red)

(supplied by Rubner group at MIT)

absorbance max. 350nm
emission max. 420nm (blue)
Microscopy of Patterned Ru Dye Multilayers

Ten bilayers of Ru/LPEI on five bilayers of PAA/LPEI adsorbed at pH 4.8.
Patterning Ru dye with different polyamine ---- fluorescence micrographs

(PAH/PAA)$_5$(PAH/Ru)$_{10}$, pH4.8

(LPEI/PAA)$_5$(LPEI/Ru)$_{10}$, pH4.8
Combination of two dyes into patterned thin film

(PAH/Ru)$_{10}$ under Fluorescence Microscope using red filter

(PDAC/PPP(-))$_{10}$ under Fluorescence Microscope using DAPI filter

Hammond et al., 2000
Motivation
---Multicolor Flat Panel Display

Advantages of using fluorescent dyes in organic electroluminescent devices:
- an emission in wide visible spectral range
- large area flat panel displays driven at low voltage

Old:
- vapor deposition, spin coating
- color variability is controlled by polarity and strength of E field based on stacking multilayer of fluorescent dyes

New:
- layer by layer assembly
- color image is controlled by site addressing and E field variation based on multicolor pixel array
Multilevel Patterning

- Pattern with COOH/EG
- Polyion multilayers
- Stamping functional resist
- Polyion multilayers

Idea: stamping resist on underneath multilayer

Model resist:
Multilevel pattern containing Ru dye - AFM

1. Adsorb multilayer system A (vertical)
2. EO-MAL stamp (horizontal)
3. Adsorb multilayer system B
EO-MAL patterning on Polystyrene Substrate (dot stamp)

1. (BPEI/PAA)\textsubscript{4}BPEI at pH5
2. Stamp EO-MAL 1hr (EO-MAL is stamped outside dots)
3. (PAA/LPEI)\textsubscript{12} at pH5
Chromogenic Block Copolymer Assemblies

Research Team
• Paula T. Hammond  Block Copolymer Synthesis and Characterization
• Shaw Chen  Collaborative design of chiral nematic copolymer systems
• Lewis Rothberg  Characterization of chromic and spectroscopic prop.
• Sam Jenekhe  Synthesis of Chromogenic Dyes for Functionalization

Goals
• New reflective and absorptive displays utilizing Block Copolymer Morphology

Interactions with Army
• Possible interaction with LC/Displays groups

MURI Funding Level: $50 K/yr.

Personnel
• P.T. Hammond
• Aaron Moment
• P.T. Hammond
Design:
- Flexible "soft" block - chromophore attached as side group
- Spacer unit - decouples chromophore from main chain
- Glassy rigid block - mechanical properties, transparent medium

Most rigid chromophores would act as LC systems:
- can orient block copolymer continuous morphologies for anisotropic chromic behavior
Advantages of Block Copolymers

- Ability to use thermoplastic processing, obtain uniform films
- Nanoscale morphology presents potential
- Films with high mechanical integrity
- Can utilize a low Tg block to obtain “fluid” matrix
  Increased kinetics for coloration, switching
TOPS Objectives - Mesostructured Polymers: Side Chain LC Block Copolymers

- Attach known LC’s/chromophores of interest to polystyrene-vinyl siloxane backbone
  - Cholesteric LC’s (reflective)
  - Merocyanine dyes
  - Salicylidenes
  - Substituted azobenzenes
- Examine chromic and spectroscopic behavior in oriented block copolymers as function of structure (Rothberg)
- Explore potential for reflective systems via layered photonic arrays or chiral nematics (Shen)
Investigating Interplay between LC order and Morphological Order

• Discovered BlockCopolymer Order-Disorder as well as Order-Order transitions can be induced by liquid crystal phase changes.

• Established LC orientation w/in blocks can be controlled by molecular structure.

Spacer length = 6

Spacer length = 10

Can use oriented blocks to obtain highly ordered, switchable chromophores
TEM images of Mesogen B polymers

PS 12 - LCPB 8
TEM 155Å, SAXS 186Å

PS 14 - LCPB 94
TEM 257Å, SAXS 294Å
OM images of PS14K-LCP57K (A) elastomeric material on stretching

Mesogen A:

![Chemical structure of Mesogen A]

Free standing film, 25 C

500um

stretch → release

~ 8% strain, 1mm stretch
Summary of liquid crystalline transitions and SAXS data for block copolymers

Mesogen A:

<table>
<thead>
<tr>
<th>Wt% PS</th>
<th>Mn PS Block</th>
<th>Mn LC Block</th>
<th>S-L C</th>
<th>Smectic d, Å</th>
<th>Morphology d, Å</th>
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<tr>
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<td>34,000</td>
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<td>26</td>
<td>13,000</td>
<td>38,000</td>
<td>66.3</td>
<td>36</td>
<td>PS cylinders</td>
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<tr>
<td>20</td>
<td>14,000</td>
<td>57,057</td>
<td>79.4</td>
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<td>PS cylinders</td>
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<td>66</td>
<td>40,000</td>
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<td>42.6</td>
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<td>327/lamellar</td>
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TOPS MURI Review

August 2000
Natick Meeting

Lewis Rothberg

L. Rothberg, Rochester  ARO MURI
Overview

• Absolute luminescence quantum yields in films: Development and applications of a new calorimetric technique (Lisa Marshall)

• Origin of luminescence quenching in the solid state: dynamical studies that implicate interchain excitation (Pei Wang)

• Molecular weight dependence of conjugated polymer optical properties (Jui-Hung Hsu)

• Aggregation studies of MEH-PPV trimers (Jui-Hung Hsu)

• Patterned electrostatic self-assembly (with Hammond)

• Devices based on conjugated polymers in vitrified liquid crystal (with Chen)

• Testbeds
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L. Rothberg, Rochester

ARO MURI
Motivation

• Luminescence efficiency is an important factor in organic light-emitting diodes
  – theory predicts that EL proportional to PL

• Direct measurement of emitted light out per absorbed energy is difficult due to surface roughness, self-absorption and waveguiding
  – no reliable standards available
  – many calibrations required for integrating sphere measurements
Idea: calorimetric measurement

• Measure the heat in and assume that what does not come out as heat must come out as light
  – premises:
    • No photochemistry
    • No “irreversible” charge generation

• KEY TRICK: No standard required. Use internal calibration of the amount of heat based on Kasha’s Rule

L. Rothberg, Rochester

ARO MURI
Heat per absorbed energy vs. Wavelength

Spectrometer and lamp

Mechanical chopper

Phase sensitive detector

Sample

L. Rothberg, Rochester
**Procedure**

Heat will be proportional not only to the fraction of energy going into heat but also to the total energy deposited. This depends on the lamp intensity at the given wavelength and the absorption of the sample at that wavelength. Therefore, the first things we do are:

1) Measure the absorption spectrum of the sample (standard UV-vis)
2) Measure the emission spectrum of the lamp and spectrometer (by using a black absorber in the heat deposition setup)

These are used to correct the observed signal and turn it into heat yield. Obtaining quantum yield from that is described on the next viewgraph. It also involves knowing the PL spectrum.
Analysis

We assume that luminescence quantum yield is excitation wavelength independent (Kasha’s rule)

Energy out as heat = Total energy - Energy out as light

where the latter term is not dependent on excitation wavelength

Heat per absorbed photon = $\frac{hc}{\lambda_{exc}} - \phi_{PL}(\frac{hc}{\lambda_{em}})$

L. Rothberg, Rochester
Predicted Behavior

Heat per absorbed energy ($\phi_H$)

Intercept at $\phi_H = 1$

Slope proportional to PL yield $-\phi_{PL}$

Intercept at $\lambda_{em}/\phi_{PL}$

$\lambda_{exc}$

L. Rothberg, Rochester

ARO MURI
PhiiH
Linear Fit of R4_PhiH

rl4_25a3, .04, l2 = 593
3.30362 (+-.67014) - .00493 (+-.00127) X
.8842 +/- .2278

<= ugly spike

---

rabssld3, .04, l2 = 593
4.35483 (+-.56226) - .00688 (+-.00107) X
.93685 +/- .1457

<= ugly dip in abs
\(\psi_H = 2.63\)

\[\begin{align*}
\text{o1_abs1} & : 3.145 (+- 0.06619) - 0.0033a (+- 1.4648E-4)x \\
\text{(abs error is greatest diff between abs1,2,3)}
\end{align*}\]

\[\begin{align*}
\text{o1_abs2} & : 3.2503 (+- 0.08549) - 0.00351 (+- 1.89399E-4)x \\
\text{(abs error is greatest diff between abs1,2,3)}
\end{align*}\]
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L. Rothberg, Rochester

ARO MURI
D00-PPV

Absorption (normalized)

Wavelength (nm)

Intensity (a.u.)

Molecular weight (g/mole)

A (Mn=3.2K)
B (Mn=5.6K)
C (Mn=8.2K)
D (Mn=11K)
E (Mn ~ 2M)
MEH-PPV

Intensity (a.u.)

Molecular weight

Absorption (a.u.)

Wavelength (nm)

- 400 nm
- 470 nm
- 520 nm
Mn=2M
Mw=3M
Overview

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  L.Rothberg, Rochester  ARO MURI
Solvent Effect Studies in the $^1$H-NMR Spectroscopy

100% Methanol

90% Methanol:10% water

Figure 9: $^1$H-NMR spectra of the Trimer of MEH-PPV in 100% methanol and 90% methanol-10% water.

Table 2: $^1$H-NMR assignment of the Trimer of MEH-PPV and its intensity in both mixtures.

<table>
<thead>
<tr>
<th>Chemical shift (ppm)</th>
<th>Assignments</th>
<th>Integral (100% MeOH)</th>
<th>Integral (90% MeOH)</th>
</tr>
</thead>
<tbody>
<tr>
<td>6.7-7.5</td>
<td>ring, vinylene $^1$H</td>
<td>0.15</td>
<td>0.075</td>
</tr>
<tr>
<td>3.6-4.0</td>
<td>O-C-H $^1$H</td>
<td>0.18</td>
<td>0.09</td>
</tr>
<tr>
<td>2.3-0.8</td>
<td>ethylhexoxy $^1$H</td>
<td>1</td>
<td>1</td>
</tr>
</tbody>
</table>
Status

- **Luminescence yield**
  - ready for ARO MURI use
  - publish and apply to conjugated polymer processing methods
  - AC thin-film EL materials with Dave Morton

- **Aggregation quenching**
  - preparing manuscripts for MEH-PPV and trimer
  - study trimer dynamics

- **Molecular weight dependence of optical properties**
  - working to understand the issues

- **Patterned electrostatic self-assembly**
  - dipping instrument working, Swager materials available soon
  - ellipsometer purchased
  - sending student to Hammond lab to learn printing and assembly

- **Testbeds**
  - I-V setup, PL yield complete
  - TSC with ARL (Forsythe and Morton) for charge mobility
TUNABLE EMISSION SYSTEMS

Research Team
• Al Bard - Electrochemiluminescent Systems
• Paula Hammond - 3-D Array Patterning by Self-Assembly
• Sam Jenekhe - Tunable Electroluminescent Polymers and Devices
• Lewis Rothberg - Microcavity Design for Emissive Displays

Relationship to DoD
Addressable Color Tunable Devices; Large Area Displays; Nanofunctional Devices; Smart/Interactive Clothing; Low Cost Rugged Flexible Displays.

Interactions with Army
• Many Planned

MURI Funding Level: $270 K/yr.

Personnel
• Graduate Students: 1
• Postdocs: 2.5
• Undergraduate Students: 1
TUNABLE MULTICOLOR EL POLYMERS AND DEVICES

CONCEPT

POSSIBLE APPROACHES

A. Bilayer/Multilayer EL polymers

B. Phase-Separated EL Polymer Blends

C. Microphase-Separated Block Copolymers

CHALLENGES

• Design of Multicomponent EL Polymers
  — Availability of R, G, B EL Polymers
  — Energy Transfer
  — Exciplex Formation
  — Photoinduced Electron Transfer
• Processing and Control of Nanophase Multicomponent EL Polymer Systems
  — Insolubility in Common Solvents
  — Solubility in Common Solvents
  — Control of Scale of Phase Separation
• Synthesis of Emissive n-Type Polymers
  — Red, Blue, Green EL
VOLTAGE-TUNABLE MULTICOLOR POLYMER LEDs

PPQ/PPV 7 V

PPQ/PPV 9 V

PPQ/PPV 12 V

New n-Type Light-emitting Polymers

BPQ-MCZ
BPQ-PTZ
BPQ-P

PCZPQ
PFPQ
PBPQ
PPTZPQ
1,2-PPPQ
1,3-PPPQ

PCZPQ-co-PFPQ

ARQ TOPS MURI
1.2, 1.0, 0.8, 0.6, 0.4, 0.2, 0.0

BuM-PPQ, PDMPQ, Bu-PPQ, PPPQ, PTPQ

EL Intensity (arb. units)

Wavelength (nm)

350 400 450 500 550 600 650 700 750

AI
Polyquinoline
TAPC/PS
ITO
POLYMER/POLYMER INTERFACES IN DEVICES

Light-Emitting Diodes/Lasers

Photodetectors/Photovoltaic Cells

- Role of Polymer/Polymer Interface
  - $(\Delta IP, \Delta EA)$
  - Charge Depletion (Space Charge) Region?
  - Built-In Potential (Field)
  - Energy Transfer
  - Exciplex Formation
  - Photoinduced Charge Transfer
    - $IP = \text{Ionization Potential (eV)}$
    - $EA = \text{Electron Affinity (eV)}$

- Finite Size Effects
- Electrode/Polymer Interfaces
  - Charge Injection Barriers
    - $(EA, IP$ Values)
Polymer/Polymer Heterojunction LEDs

**p-Type (Hole Transport)**

1. \[ \text{PPV} \]
2. \[ \text{PPQ} \]
3. \[ \text{PPPQ} \]
4. \[ \text{PBAPA} \]
5. \[ \text{PBAPQ} \]
6. \[ \text{PBTPV} \]

**n-Type (Electron Transport)**

a. \[ \text{PPDA} \]
b. \[ \text{PBDA} \]
c. \[ \text{PBADA} \]
d. \[ \text{PBSDA} \]
e. \[ \text{PPyBT} \]
f. \[ \text{PDMDA} \]
g. \[ \text{PTDA} \]
h. \[ \text{BBL} \]
POLYMER/POLYMER INTERFACES IN HETEROJUNCTION LEDS

Zhang and Jenekhe, 
*Molecular Crystals and Liquid Crystals Science and Technology* **B** 2000, 33, 2069.

![Diagram of polymer/polymer interfaces in heterojunction LEDs](image)

\[ \begin{array}{c|c|c|c}
\text{Anode} & \h^+ & \text{Cathode} \\
\text{ITO} & \text{p-Type Polymer} & \text{n-Type Polymer} & \text{(Al)} \\
\end{array} \]

\[ \Phi_a \Delta E_h \rightarrow \Delta E_A \rightarrow \Phi_c \]

\[ \Delta E_c \]

\[ \Delta \Phi \]

\[ \Delta \Phi_l \]

(a)

\[ \begin{array}{c}
\phi_{EL} (%) \\
\Delta \Phi_l (eV) \end{array} \]

(b)

\[ \begin{array}{c}
\text{Luminance (cd/m}^2) \\
\Delta \Phi_l (eV) \end{array} \]
Efficient LEDs From Polymer/Polymer Heterojuctions

POLYMER/POLYMER INTERFACES IN DEVICES

- Can Be More Important than Injection Barriers at Electrodes
- $\Delta EA$ and $\Delta IP$ Control EL Efficiency and Luminance
- Charge Transfer at Interface Coupled to Finite Size Effects
- Single-Color versus Multicolor LEDs
- Insights for Design and Synthesis of Next Generation EL Polymers ($\phi_{PL}$, $\Delta EA$, $\Delta IP$)

VOLTAGE TUNABLE MULTICOLOR LEDs

- Simple Polymer Heterojunction Diodes
- Continuous Tunability in CIE Color Space
- Easy Pixelation for Full Color Displays
- Efficient (1-3%) and Bright (820 cd/m²) Devices
- Mechanism: Mixing of p-Type and n-Type EL Spectra
- Polyquinolines — Excellent n-Type EL Polymers
Investigate the Photophysical and Charge transfer Processes of Novel Donor/Acceptor Heterojunctions of $\pi$-conjugated Polymers

--- Photophysical and Charge Transfer Processes at Polymer/Polymer Interfaces play a Critical Role in the Efficiency and Performance of LEDs.

--- Charge Transfer and Separation at Polymer/Polymer Interfaces are Key to Efficient Photovoltaic Devices.

Probe of Polymer/Polymer Interfaces using both Steady-State Photoluminescence (PL) Spectroscopy and Picosecond Time-Resolved PL Decay Dynamics:

--- Photoinduced Electron Transfer
--- Exciplex Formation
--- Energy Transfer

Donor Polymer (p-type)  
Accepter Polymer (n-type)  
Glass  

Glass  
Accepter Polymer (n-type)  
Donor Polymer (p-type)  

1) Front Face Geometry  
2) Inverted Face Geometry
Electroluminescent Conjugated Polymers

**Acceptor Polymers**

- **PPQ**: poly(2,6-(4-phenylquinoline))
- **PBPQ**: poly(2,2’-(p,p’-biphenylene)-6,6’-bis(4-phenylquinoline))
- **BBL**: poly(benzimidazobenzo phenanthroline ladder)

**Donor Polymers**

- **PHT**: poly(3-hexylthiophene)
- **POT**: poly(3-octylthiophene)
- **PPV**: poly(p-phenylene vinylene)
- **MEH-PPV**: poly(2-methoxy-5-(2’ethylhexyloxy)-1,4-phenylene vinylene)

**ARO TOPS MURI**

S. A. JENKHE
Photoinduced Charge Transfer in Polyquinoline/Polythiophene Heterojunctions

![Diagram of PPQ and PHT with charge transfer](image)

### Energy Level Table

<table>
<thead>
<tr>
<th>Energy Level</th>
<th>3.0 eV</th>
<th>3.0 eV</th>
<th>5.2 eV</th>
</tr>
</thead>
<tbody>
<tr>
<td>PPQ</td>
<td></td>
<td></td>
<td>5.8 eV</td>
</tr>
<tr>
<td>PHT</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

### Film Thickness (PPQ/PHT)

- 1) 13/0 nm
- 2) /3.2 nm
- 3) /5.0 nm
- 4) /9.5 nm
- 5) /15 nm
- 6) 0/15 nm

### Absorbance (Rel. Intensity) vs. Wavelength (nm)

- λ_ex = 420 nm

### Relative PL Intensity vs. Wavelength (nm)

- λ_ex = 420 nm
Effect of Film Thickness

Exciton Diffusion Length estimated to be 15 - 20 nm for Polyquinolines

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S. A. JENEKHE
Photoinduced Charge Transfer in Polyquinoline/Polythiophene Heterojunctions

Film Thickness (PPQ/PHT)

- $\lambda_{ex} = 420$ nm
- $\lambda_{PL} = 600$ nm

1) 130 nm
2) 3.2 nm
3) 5.0 nm
4) 9.5 nm
5) 15 nm
6) laser response

$e^-$

$\text{PPQ Thin Film}$
PL Lifetime, $\tau = 4.4$ ns

$\text{PPQ/PHT (13/15 nm) bilayer}$
PL lifetime, $\tau = 29$ ps.

$\text{A factor of 150 reduction in PL lifetime.}$
Photoinduced Charge Transfer at PPV/BBL Heterojunctions

\[ \lambda_{\text{ex}} = 429 \text{ nm} \]

Energy Level

- PPV
  - 2.7 eV
  - 4.4 eV
  - 5.1 eV
  - 6.3 eV

- BBL

**Relative PL Intensity**

- PPV(7 nm)
- PPV(7 nm)/BBL

**% PL Quenching**

- PPV/BBL(7/36 nm)
- PPV/BBL(7/21 nm)

Film Thickness of PPV (nm)

Glass
PPV
BBL

ARO TOPS MURI

S. A. JENEKHE
PHOTOVOLTAIC PROPERTIES OF SEMICONDUCTING POLYMER HETEROJUNCTIONS

- Role of Polymer/Polymer Interface
  -(ΔIP, ΔEA)
  -Charge Depletion (Space Charge) Region?
  -Built-In Potential (Field)

- Finite Size Effects
- Ohmic Contacts
PPV/BBL SOLAR CELLS

![Chemical structures of PPV and BBL](image)

**Light intensity vs. Voltage and Current**

- **$I_{sc}$**: 0.4 - 1.2 mA/cm²
- **$V_{oc}$**: 0.7 - 1.2 V
- Fill Factor (FF) = \( \frac{(IV)_{max}}{V_{oc}I_{sc}} = 0.41 - 0.43 \)
- Power Conversion Efficiency $\eta_p = 1.4 - 2.0\%$
CHARGE COLLECTION FROM PPV/BBL SOLAR CELLS

\[ L = 0.4-0.5 \text{ mW/cm}^2 \]

- Maximum Photon-to-Current Conversion Efficiency = 49 %
- Maximum External Quantum Efficiency = 66 %
- Maximum Power Conversion Efficiency \((\eta_p)\) = 2.0 %
- Finite Size Effects (Exciton Diffusion Limitations)
SUMMARY

Efficient Solar Cells from PPV/BBL Junctions

- Photoinduced Charge Separation at Interface (PL Quenching, Complete EL Quenching)
- Role of Electron Affinity of n-Type Polymer Critical
- Ohmic Contacts at Polymer/Metal Interfaces
- Charge Depletion (Space Charge) Region Around Interface
- Finite Size Effects (Exciton Diffusion Limitations)

Further Improvement of Polymer Solar Cells

- High Electron Affinity n-Type Conjugated Polymers
- Small Band Gap Polymers
- High Purity Materials (Trap-Free?)
Tunable Electroluminescence in Conjugated Polymers: Bilayer and Blend Structures

Kathleen Meeker
August, 2000
MURI Annual Review

Outline
• Goals and Background
• Bilayer Tunable Photoluminescence
  • PPV/PCZPQ
  • PPV/Ru(bpy)$_3^{2+}$
• Bilayer Tunable Electroluminescence
• Coupling Bilayers and Blends
• Environmentally Responsive EL Polymers
• Conclusions
Project Goals

Explore tunable optical properties of a variety of polymer-based systems

Extend the spectral range of tunable electroluminescence and photoluminescence in polymer thin films and other structures to encompass red, green, blue and other colors throughout the CIE color space
Background: Tunable EL in Polymer Heterojunctions

Zhang and Jenekhe, Macromolecules 2000, 2069-2082.
Approaches to Tunable Electroluminescence

Emissive layers comprised of polymer blends can potentially provide tunable EL; each polymer contributes its emission spectrum.

Two polymer layers can improve charge injection/transport and provide for selective excitation.
Materials Explored

Poly- and oligoquinolines

Polyanthenazolines

p-type materials

Metal Complexes

BPQ-VPV

PCZPQ

PBPQ

PPQ

PPV

TAPC

Ru(bpy)₃(ClO₄)₂

Eu(bpy)₃(NO₃)₃

PSPQ

PVK

PDMDA

From the Bard group

ARO TOPS MURI

KATHLEEN MEEKER
Tunable Bilayer Photoluminescence

BPQ-VPV

PPV

ARO TOPS MURI

KATHLEEN MEEKER
Voltage-Tunable EL from PPV/PCZPQ Bilayers

ITO/PPV/PCZPQ/Al

Red (6V) ↔ Green (12V)
Effects of Film Thickness on Bilayer EL Color

ITO/PPV (70 nm)/ Ru(bpy)$_3$(ClO$_4$)$_2$ (30 nm)/Al

80 Cd/m$^2$
turn on at 6 V

ITO/PPV (30 nm)/ Ru(bpy)$_3$(ClO$_4$)$_2$ (50 nm)/Al

200 Cd/m$^2$
turn on at 6 V
Tunable EL: ITO/PPV/Ru(bpy)$_3$(ClO$_4$)$_2$/Al

ITO/PPV (40 nm) / Ru(bpy)$_3$(ClO$_4$)$_2$ (50 nm)/Al

Spectrum acquired at intermediate voltage. Microcavity effects?
Bilayer LED Performance

ITO/PPV (40 nm)/Ru(bpy)$_3$(ClO$_4$)$_2$ (50 nm)/Al
EL of Polymer Blends

Anode (ITO) | Blend | Cathode (Al)

Possible Problems
A. Photophysical Processes
   • Energy Transfer
   • Exciplex Formation
   • Photoinduced Electron Transfer
B. Control of Phase Separation
Origin of New Blue Peak in Blends

- Intrachain Excitons
- Excimers in Pure Films

640 nm peak
- 4.4 ns 46%
- 0.91 ns 36%
- 0.14 ns 18%

540 nm peak
- 3.9 ns 32%
- 0.78 ns 38%
- 0.15 ns 30%

470 nm peak
- 48.5 ps 85%
- 0.57 ns 12%
- 7.9 ns 3%
Electroluminescence of Ternary Blends: BuN-PPQ, PDMPQ, PCZPQ (2:2:1)

ITO/blend/Al

Wavelength

BuN-PPQ

PDMPQ

PCZPQ
Tunable EL: Ternary Blends

BuN-PPQ:PDMPQ:PCZPQ

2:2:1

ITO/PPV/Blend/Al

Tunability of ITO/PPV/Blend/Al identical to that of ITO/PPV/PCZPQ/Al

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KATHLEEN MEEKER
Selective Emission from Ternary Blends

BuN-PPQ
\[ \lambda_{EL} = 424 \text{ nm} \]
\[ \text{IP} = 5.71 \text{ eV} \]

PDMPQ
\[ \lambda_{EL} = 540 \text{ nm} \]
\[ \text{IP} = 5.44 \text{ eV} \]

PCZPQ
\[ \lambda_{EL} = 640 \text{ nm} \]
\[ \text{IP} = 5.27 \text{ eV} \]

Ionization potential?
- PVK: 5.8 eV
- TAPC:PS: 5.3 eV
- PPV: 5.11 eV

Emission from blend?
- blue
- red
- red

Selective emission?
- yes
- yes
- yes

Tunability?
- no
- no
- yes

Vacuum Level

\[ \Phi_a \]
\[ \Delta E_h \]
\[ \Delta E_a \]
\[ \Delta IP \]
\[ \text{Blend} \]
\[ \Phi_c \]

ITO
HTL
Emissive layer
Al

ARO TOPS MURI
KATHLEEN MEEKER
Environmentally Responsive Light Emitting Polymers

$PBPQ$

*yellow-orange EL*

70-80 nm red shift

*red EL*
• Tunable multicolor electroluminescence obtained from bilayers of PPV/tris(bipyridine) ruthenium (II) complex

• Blending polyquinolines altered emission mechanisms; blend composition dramatically affected EL and PL spectra

• White light LEDs obtained from single-layer polyquinoline blends

• Selective emission from blend components upon incorporation of a hole-transport layer, suggests selective charge injection from hole-transport layer to individual polymers in blends

• Tunable electroluminescence from environmentally responsive light emitting polymers demonstrated; sulfonic acid molecular structure has a significant effect on PL and EL.
Acknowledgments

Army Research Office MURI
DAAD19-99-1-0206

Jenekhe Research Group

Bard Research Group

Bernard Panzarella (undergraduate student)

Dr. Chris Collison
Solvent-induced Morphological Effects on the Picosecond Photophysics of a Conjugated Polymer

Pei Wang, Chris Collison, Lewis Rothberg
Department of Chemistry, University of Rochester, New York 14627

Support: TOPS ARO MURI
Motivation: Aggregation quenching limits luminescence efficiency in solid state polymer samples. Understand the origin of aggregation quenching in order to control it and make better device.

Method: Study the photophysics while controlling aggregation by addition of poor solvents. Use femtosecond transient absorption and stimulated emission to identify excited states and investigate their dynamics.

Electroluminescent polymer: MEH-PPV (Poly(2-methoxy, 5-(2-ethylhexoxy)-paraphenylenevinylene))

L.Rothberg, Rochester

ARO MURI
Energy Diagram illustrating the principle of pump-probe experiments

PL = Photoluminescence, PA = Photo-induced Absorption, SE = Stimulated Emission, PB = Photo Bleaching, only singlet excited states are shown.
**Experimental Set-up**

- **800nm, 100fs, 1mJ, 1KHz**
- **BS**
- **<1%**
- **BBO Crystal**
- **SHG**
- **400nm**
- **Sapphire Plate**
- **white light**
- **Chopper, 500Hz**
- **Sample (MEH-PPV solution)**
- **Monochromator**
- **488nm**
- **Argon ion laser**
- **Photo-detector**
- **PC**

_L. Rothberg, Rochester_
Solvatochromism in MEH-PPV

L. Rothberg, Rochester

ARO MURI
Transient Absorption (MEH-PPV/toluene)

ΔT / T (Arb. Unit)

400 500 600 700 800

Wavelength (nm)

L.Rothberg, Rochester

ARO MURI
MEH-PPV Dynamics at 650 nm

- Toluene
- 1:1 Toluene/Hexane

ΔT / T (Arb. Unit)

Time (ps)

L. Rothberg, Rochester

ARO MURI
MEH-PPV Photoinduced Absorption (750 nm)

\[ \Delta T / T \text{ (Arb. Unit)} \]

- Toluene
- 1:1 Toluene/Hexane

Time (ps)

L. Rothberg, Rochester

ARO MURI
MEH-PPV Dynamics at 550 nm

1:1 Toluene/Hexane

Toluene

Single Exponential Fit

0.0 0.2 0.4 0.6 0.8 1.0 1.2

0.0 0.2 0.4 0.6 0.8 1.0 1.2

Time (ps)

Time (ps)
Comparison of Good and Bad Solvent Dynamics

\[ \Delta T/T \text{ (Arb. Unit)} \]

- Subtraction at 500 nm
- Subtraction at 550 nm
- Subtraction at 750 nm

Time (ps)

L. Rothberg, Rochester

ARO MURI
Conclusions

1. About 50% of the excitations in the more aggregated polymer solution become some species which decays non-radiatively within 50 ps at room temperature.

2. The long-lived photo-induced absorption at 750 nm is due to triplet states.

Future Work

Carry out measurements on film, compare the spectra of unknown species in solution and film.
Electrochemiluminescent Systems

Allen Bard, Sam Jenekhe
Guoqiang Gao, Mihai Buda
Rebecca Lai, Eve Fabrizio
Types of Electroluminescent (EL) Devices

- Inorganic EL
- Electrogernated Chemiluminescence (ECL)
- Organic EL (Polymer, Alq)
- Hybrid Systems

Applications
- Displays
- Lasers
- Analytical Devices
Key Issues - Devices

- Efficiency
- Stability (Life)
- Cost
- Manufacturability
Key Issues - Science

• Degradation mechanisms
  • Materials, substrates, contacts

• Mechanism of light generation
  • Radiative vs. nonradiative processes
  • Singlet:triplet ratios

• Electroluminescent vs. Electrochemical Mechanisms
  • Injection contacts

• Carrier Mobility
Solid State Organic Light-Emitting Diode (OLED)

Calcium, aluminum, In/Ga
Organic molecules, polymers
ITO (Indium/Tin Oxide)
Glass or plastic

Light
Solid State $\text{Ru(bpy)}_3(\text{ClO}_4)_2$ Cell

Positive contact

Negative contact

M = Ga:In, Ga:Sn, Bi:In: Pb:Sn, or Al

100 nm

ITO

Light
Thin Film of 3 Layers Spin-Coated On ITO

G091820

Film

Bare ITO
Luminescence Spectrum of An OLED

Inset: UV-vis Absorption Spectrum Of The Film

Light Intensity (a.u.)

Wavelength (nm)

456 nm

715 nm
Light-Voltage (red) And Current-Voltage (blue) Plots For An OLED
Light Emission Intensity Of 200 cd/m² At 5 V Was Realized For An OLED
Light And Current As A Function Of Time Upon 0 - 3 V Voltage Steps

![Graph showing light and current as a function of time with voltage steps.](image-url)
Light Output As A Function Of Time
(2.8 V hold)
Cartoon Of The Bimolecular Hopping Transport Of Electrons Between Ru(II) And Ru(III) Sites And Ru(I) And Ru(II) Sites
Current-voltage and luminance-voltage characteristics (50 mV/s)
ITO/Ru(bpy)$_3$(ClO$_4$)$_2$ (~150 nm)/Ga:Sn;
Current-voltage and luminance-voltage characteristics (50 mV/s)

ITO/Ru(bpy)$_3$(ClO$_4$)$_2$($\sim$100 nm)/Au;
Quantum efficiencies (50 mV/s)  
ITO/Ru(bpy)$_3$(ClO$_4$)$_2$/Ga:Sn
Current-time and luminance transients
2.75 V hold
ITO/Ru(bpy)$_3$(ClO$_4$)$_2$ ($\sim$150 nm)/Ga:Sn
Current-time and luminance transients
2.25 V hold
ITO/Ru(bpy)$_3$(BF$_4$)$_2$ (≈150 nm)/Ga:Sn
Current-time and luminance transients

2.5 V hold

ITO/Ru(bpy)$_3$($\text{PF}_6$)$_2$ (~200 nm)/Ga:Sn
Transient luminance at short times:
ITO/Ru(bpy)$_3$ClO$_4$)$_2$(~100 nm)/Ga:Sn

\[ y = y_0 + a \times \text{erfc}\left(\frac{b}{\sqrt{t}}\right) \]

<table>
<thead>
<tr>
<th>Anion</th>
<th>$D_{\text{app}}$ (cm$^2$/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BF$_4^-$</td>
<td>$\sim 10^{-9}$</td>
</tr>
<tr>
<td>ClO$_4^-$</td>
<td>$\sim 10^{-10}$</td>
</tr>
<tr>
<td>PF$_6^-$</td>
<td>$\sim 10^{-13}$</td>
</tr>
<tr>
<td>AsF$_6^-$</td>
<td>$\sim 10^{-14}$</td>
</tr>
</tbody>
</table>
Electrochemistry and ECL of Bis(4-phenylquinoline)-10-Methylphenothiazine (BPQ-PTZ)
Absorption and Photoemission of BPQ-PTZ in Benzene/MeCN
Cyclic Voltammogram of BPQ-PTZ (0.67 mM) in 0.1 M TBAP in Benzene/MeCN at Pt Electrode at 250 mV/s
ECL of BPQ-PTZ in Benzene/MeCN
Thin Film
Electrochromic Devices

ARO TOPS MURI

Dean M. DeLongchamp
Professor Paula T. Hammond
Electrochromism

- Color by Reduction - *Cathodic electrochrome*
  
  $+ \rightarrow o$  \hspace{1cm} \text{or} \hspace{1cm}  \hspace{1cm} o \rightarrow -$ 

- Color by Oxidation - *Anodic electrochrome*

  $- \rightarrow o$ \hspace{1cm} \text{or} \hspace{1cm} o \rightarrow +$

Transition: \hspace{1cm} IR $\rightarrow$ Vis \hspace{1cm} or \hspace{1cm} UV $\rightarrow$ Vis
Current Shortcomings of ECDs

- Switching speed of electrochromic devices (ECDs) is too slow for advanced applications.
  - Smart Windows: seconds to minutes ✓
  - Displays: milliseconds ✗
  - Optical Switches: even faster ✗

- Cycle lifetime is too short for many products.
  - Smart Windows: $10^4$-$10^5$ deep cycles ✓
  - Displays: $10^9$-$10^{10}$ deep cycles ✗
  - Optical Switches: $10^{17}$-$10^{18}$ deep cycles ✗

- Contrast and spectral range is often poor.
Objective

Create electrochromic devices with enhanced performance using multilayering techniques.

Optimize response time, cycle life, and spectral range by choice of materials and appropriate architecture.
Multilayering Advantages

- **Switching speed**
  - Sequester polymer electrochrome at electrode
  - Combine electrochrome and transport material
  - Finely control element thicknesses

- **Cycle lifetime**
  - Attain high material homogeneity
  - Achieve freedom from structural defects
  - Protect from elements with cladding layers

- **Contrast and spectral range**
  - Influence color/contrast with counterpolyion
  - Pattern multiple electrochromes
Dual Focus

● Electrolyte
  - Evaluate the performance of ion-conducting multilayered systems
  - Determine the optimum system for ECDs

● Electrochromism
  - Characterize the electrochemistry of electrochromic multilayered systems
  - Study effects of material system and deposition conditions
Focus: Electrolyte

- High ionic conductivity
- Low electronic conductivity
- Chemically robust
- Mechanically robust

Diagram showing anode, electrolyte, and cathode.
Ion-Conducting Polyelectrolytes

PEI
Poly(ethylene imine)

PAMPS
Poly(2-acrylamido-2-methyl-1-propanesulfonic acid)

NAFION
Impedance Analysis

Experimental Setup

Equivalent Circuit

ITO

multilayered polymer film

Al

electrolyte resistance

interface capacitance

electrode/contact resistance

electrolyte capacitance
Typical Impedance Response

BPEI/PAMPS at pH 3.0

Ionic conductivity
\[ \sigma = 3.8 \cdot 10^{-10} \text{ S/cm} \]
BPEI/NAFION Conductivity Trend

\[
\begin{align*}
\sigma & (S/cm) \\
\text{pH} & 1 \quad 2 \quad 3 \quad 4
\end{align*}
\]
BPEI/PAMPS Conductivity Trend

\[
\sigma (S/cm)
\]

\[
1.0 \times 10^{-5} \quad 1.0 \times 10^{-6} \quad 1.0 \times 10^{-7} \quad 1.0 \times 10^{-8} \quad 1.0 \times 10^{-9} \quad 1.0 \times 10^{-10}
\]

\[
\begin{array}{c}
\text{pH} \\
1.8 \\
2.0 \\
2.3 \\
3.0 \\
5.0
\end{array}
\]

Error bars at 95% confidence
Electrolyte Summary

**NAFION/BPEI System:**
- Thickness is greatest near acid pKa
- Less charge density → more polymer per charge
- No trend in conductivity observed

**PAMPS/BPEI System:**
- Thickness is greatest near acid pKa
- Conductivity is also greatest near acid pKa
- Less charge density → More preserved charge carriers (protons)
- Conductivity 3-4 orders of magnitude higher than NAFION/BPEI system
Focus: Electrochemistry

- Ionic and electronic conductivity
- Profound chromic shift
- Well-characterized electrochemistry
Polyelectrochromes

PXV
Polyhexyliologen

PEDOT
Poly(3,4-ethylenedioxythiophene)

PANi
Polyaniline
Thickness Dependence on Salt

![Bar chart showing thickness dependence on NaBr concentration. The x-axis represents NaBr concentration in M, ranging from 0.25 to 1.50. The y-axis represents thickness in Å. The chart contains bars for 5 Bilayers PXV/SPS and 10 Bilayers PXV/SPS at different NaBr concentrations.](Image)
Cyclic Voltammetry Results

- PXV/SPS System

- second reduction
- first reduction

* Thanks to Bard Lab
Electrochromism Summary

**PXV/BPEI System:**
Thickness control achievable with salt or pH
Characterizable, reversible electrochromism

**PEDOT/BPEI and PANi/BPEI Systems:**
Typical film growth via multilayering
CV results pending
One working prototype constructed as above. Displayed blue/green color, ~5s turn-on time and required ~10V to drive the device. Failure after ~10 cycles at atmospheric conditions.
Proposed Patterned Device

Requires deposition selectivity of electrically conducting polymer. Speed, lifetime, color contrast.
Acknowledgments

- Army Research Office (ARO TOPS MURI)
- Bard Lab
- Rubner Lab
- Hammond Lab
- Department of Defense NDSEG Fellowship
Naphthodithiophenes: A new class of electroactive materials

John D. Tovar and Timothy M. Swager*

Department of Chemistry
Massachusetts Institute of Technology
77 Massachusetts Avenue
Cambridge, MA (USA) 02139
Current interest in planar fused thiophenes

Challenging synthetic approach ... could thiophenes allow for easier functionalization?
- Halogenation to provide monomers
- Fine-tuning of molecular properties
- Incorporation into LC or sensory polymers

High mobility organic FET materials
- polycyclic aromatics
- well-defined oligomers

Structural similarity to triphenylene: New discotic core mesogens?


Synthesis of α-thienyl systems

This strategy also applies to extended aromatic systems:
Cyclization-redox activity: \( \alpha \)-blocked models

Both display a loss of irreversible oxidation after chemical cyclization.
Sodium binding with a 15-crown-5 monomer

The shift to higher potential suggests communication between the benzene bridge and the fused bithiophene moiety.

Could this be exploited in a polymer?
Moving on to β-thiophenones

Here, quinoid resonances must disrupt pendant ring aromaticity ...

... while here, conjugation mainly through the planar poly(bithiophene) backbone
Planar thiophene polymerizations: Chemical and electrochemical methods

Thiophene polymerizations:

\[
\begin{align*}
\text{FeCl}_3 & \quad \text{(in theory)} \\
\text{(reality)} & \\
\end{align*}
\]

Lack of regioregularity leads to lower conductivities

Quinoidal monomers


Planarized monomers


Disruption of planarity

Synthesis of β-thienyl monomers

Preliminary CV studies

Lack of reduction activity implies discrete chemical reactions ...

No polymer growth is observed until scanning to the second oxidation potential.
Deconvoluting the electrochemistry:

Synthesis of model compounds ...

\[ \text{FeCl}_3 \] (71%)

1) Br$_2$/CH$_2$Cl$_2$ (87%)
2) Phl(OCOCF$_3$)$_2$/I$_2$ (75%)
3) ArB(OH)$_2$/Suzuki (17%)
4) a. n-BuLi; b. AcOH (77%)

"Intra-blocked"

... and verification of the connectivity through independent syntheses

\[ \text{FeCl}_3 \] (>75%)

1) Br$_2$ (87%)
2) ArB(OH)$_2$/Suzuki (90%)

No evidence for β-coupling
Selective α-bromination
CV studies: Tandem cyclization-polymerization

Two distinct monomer oxidations

[Chemical structures and graph showing electrochemical behavior]

Only one monomer oxidation!
Assessing the regioregularity: bulk electrolysis

Ethylhexyl for solubility:
- GPC shows oligomers

**Constant potential electrolyses:**

<table>
<thead>
<tr>
<th>Potential/V</th>
<th>e-/mol</th>
<th>A</th>
<th>B</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.75</td>
<td></td>
<td>0.96</td>
<td>0.04</td>
</tr>
<tr>
<td>0.85</td>
<td>1.09</td>
<td>0.49</td>
<td>0.51</td>
</tr>
<tr>
<td>0.85</td>
<td>2.02</td>
<td>0.03</td>
<td>0.97</td>
</tr>
</tbody>
</table>

(74% isolated)

(Isolate the cyclized dimer alongside oligomers)
Attempts toward more diverse systems

For redox-active NO sensors?

Spectroelectrochemical studies:
assessing the electrochromicity

Substitution on the pendant phenyl moieties should allow for tuning of optical absorption/conductivity
Demonstrations of facile functionalization

future directions

Liquid crystals?

Tuneable electroactivity?

Incorporation into conducting polymers?
Acknowledgements

Prof. Timothy M. Swager

The Swager Group
Dr. Anthony E. Pullen
Mr. Hsiao-hua Yu

Prof. Hsiu-Fu Hsu
Dr. Hindy E. Bronstein
Dr. Zhengguo Zhu

ARO (MURI)
DARPA
MODEL SYSTEMS

PPV-PyV  poly(phenylene vinylene pyridyl vinylene)

absorption shifted to red by protonation

replace hydrocarbon chain by H

may not need terminal vinyl group

Steve Scheiner, SIU  Tunable Absorption Systems  ARO MURI
electrons shift from phenyl to pyridine in excited state

substituent enhances pyridine's ability to hold electrons. ought to lower band gap
PROCEDURE
• Optimize geometry

INDIVIDUAL MOs
• Calculate MOs
• Display HOMO and LUMO
  a) Does LUMO in fact have more density on right than HOMO?
• LUMO - HOMO energy difference as measure of absorption wavelength

TOTAL ELECTRON DENSITY $\rho$
• Display $\rho$ for ground state
• Display $\rho$ for first excited state ($1\pi\pi^*$)
• Display $\rho_{\text{excited}} - \rho_{\text{ground}}$
  Does excited state in fact have more density on right than ground state?

• $E_{\text{excited}} - E_{\text{ground}}$ as measure of absorption wavelength

• Repeat entire process for protonated and methylated molecule
• Use the analysis to identify important parts of molecule for modification

Steve Scheiner, SIU Tunable Absorption Systems ARO MURI
Steve Scheiner, SIU Tunable Absorption Systems ARO MURI
Energy Levels

unprotonated

LUMO

protonated

HOMO
identification of "hot spots"

unprotonated

protonated

HOMO

LUMO

areas of potential substitution

Steve Scheiner, SIU  Tunable Absorption Systems  ARO MURI
UNPROTONATED HOMO/LUMO

Steve Scheiner  Tunable Absorption Systems  ARO MURI
PROTONATED HOMO/LUMO
total electron density shifts caused by excitation

unprotonated (blue=gain; red=loss)

protonated

Steve Scheiner       Tunable Absorption Systems       ARO MURI
difference in density shifts:

shift in protonated – shift in unprotonated

(blue=gain; red=loss)
Using frontier MOs and total density as a guide, there would appear to be a great deal of excitation-induced density shift from first to second aromatic ring in protonated case, little if any when unprotonated.

check to see if this is correct:

Natural population atomic charges

<table>
<thead>
<tr>
<th></th>
<th>unprotonated</th>
<th>protonated</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>ring 1</td>
<td>ring 2</td>
</tr>
<tr>
<td>S° charge</td>
<td>-0.028</td>
<td>0.053</td>
</tr>
<tr>
<td>ππ* charge</td>
<td>-0.014</td>
<td>0.297</td>
</tr>
<tr>
<td>change</td>
<td>+0.014</td>
<td>+0.245</td>
</tr>
</tbody>
</table>

protonation does in fact cause electron density to shift from ring 1 to ring 2 upon excitation

very similar results are obtained when N is methylated or when Mulliken charges are used

atomic charges in ground and excited states confirm and quantify ideas arising from HOMO/LUMO shapes
EXCITATION ENERGIES

Differences in energy between ground and excited states (eV)

<table>
<thead>
<tr>
<th></th>
<th>unprotonated</th>
<th>protonated</th>
<th>difference</th>
</tr>
</thead>
<tbody>
<tr>
<td>6-31G*</td>
<td>4.72</td>
<td>4.33</td>
<td>-0.39</td>
</tr>
<tr>
<td>3-21G</td>
<td>4.90</td>
<td>4.48</td>
<td>-0.42</td>
</tr>
</tbody>
</table>

Protonation lowers excitation energy by 0.39 – 0.42 eV
good consistency from one basis set to the next

PROBLEM: What modifications of the molecule might produce a large effect upon the magnitude of this protonation-induced change in excitation energy?

Attack problem by replacing various H atoms by F
big change in electronegativity

Where to make these replacements?
use MOs as a preliminary guide.
changes in individual atomic charges caused by excitation:

<table>
<thead>
<tr>
<th>atom</th>
<th>Mulliken</th>
<th>natural</th>
<th>Mulliken</th>
<th>natural</th>
</tr>
</thead>
<tbody>
<tr>
<td>C1</td>
<td>0.011</td>
<td>0.021</td>
<td>0.021</td>
<td>0.041</td>
</tr>
<tr>
<td>C2</td>
<td>-0.006</td>
<td>-0.002</td>
<td>0.022</td>
<td>0.047</td>
</tr>
<tr>
<td>C3</td>
<td>-0.005</td>
<td>-0.021</td>
<td>-0.008</td>
<td>-0.029</td>
</tr>
<tr>
<td>C4</td>
<td>0.016</td>
<td>0.037</td>
<td>0.036</td>
<td>0.068</td>
</tr>
<tr>
<td>C5</td>
<td>-0.005</td>
<td>-0.005</td>
<td>0.027</td>
<td>0.064</td>
</tr>
<tr>
<td>C6</td>
<td>-0.015</td>
<td>-0.037</td>
<td>-0.013</td>
<td>-0.043</td>
</tr>
<tr>
<td>C7</td>
<td>0.002</td>
<td>0.010</td>
<td>-0.021</td>
<td>-0.055</td>
</tr>
<tr>
<td>C8</td>
<td>-0.007</td>
<td>-0.009</td>
<td>0.058</td>
<td>0.127</td>
</tr>
<tr>
<td>C9</td>
<td>0.003</td>
<td>0.016</td>
<td>-0.038</td>
<td>-0.068</td>
</tr>
<tr>
<td>C10</td>
<td>-0.017</td>
<td>-0.034</td>
<td>-0.080</td>
<td>-0.136</td>
</tr>
<tr>
<td>C11</td>
<td>0.020</td>
<td>0.027</td>
<td>0.041</td>
<td>0.062</td>
</tr>
<tr>
<td>C12</td>
<td>-0.024</td>
<td>-0.028</td>
<td>-0.088</td>
<td>-0.125</td>
</tr>
<tr>
<td>N13</td>
<td>0.008</td>
<td>0.004</td>
<td>-0.013</td>
<td>-0.027</td>
</tr>
<tr>
<td>C14</td>
<td>-0.003</td>
<td>0.007</td>
<td>0.039</td>
<td>0.069</td>
</tr>
<tr>
<td>C15</td>
<td>0.008</td>
<td>0.004</td>
<td>0.031</td>
<td>0.041</td>
</tr>
<tr>
<td>C16</td>
<td>-0.007</td>
<td>-0.005</td>
<td>-0.042</td>
<td>-0.070</td>
</tr>
<tr>
<td>O17</td>
<td>0.003</td>
<td>0.002</td>
<td>0.015</td>
<td>0.014</td>
</tr>
<tr>
<td>O18</td>
<td>0.012</td>
<td>0.011</td>
<td>0.030</td>
<td>0.028</td>
</tr>
</tbody>
</table>

in unprotonated case, atomic charges are largely unaffected by excitation, generally less than 0.03.

for protonated molecule, charge changes are much larger. note especially C8, C10, and C12, also C16.
PROTONATED HOMO/LUMO
EXCITATION ENERGIES

Differences in energy between ground and excited states (eV) all calculated with 6-31G* basis set

<table>
<thead>
<tr>
<th>F-substitution</th>
<th>unprotonated</th>
<th>protonated</th>
<th>difference</th>
</tr>
</thead>
<tbody>
<tr>
<td>none</td>
<td>4.72</td>
<td>4.33</td>
<td>-0.39</td>
</tr>
<tr>
<td>C2</td>
<td>4.76</td>
<td>4.35</td>
<td>-0.40</td>
</tr>
<tr>
<td>C6</td>
<td>4.75</td>
<td>4.45</td>
<td>-0.31</td>
</tr>
<tr>
<td>C8*</td>
<td>4.78</td>
<td>4.30</td>
<td>-0.48</td>
</tr>
<tr>
<td>C10*</td>
<td>4.75</td>
<td>4.36</td>
<td>-0.38</td>
</tr>
<tr>
<td>C14</td>
<td>4.73</td>
<td>4.19</td>
<td>-0.54</td>
</tr>
</tbody>
</table>

*predicted to change excitation energy drop based on atomic charge changes

C8 is predicted correctly to change and C2 to be static however, C10 shows little change in excitation energy drop despite charge sensitivity C6 shows a substantial decrease in excitation energy drop even though not much change in charge C14 opposite of C6, large increase in excitation energy drop (perhaps due to proximity to N?)

Steve Scheiner  Tunable Absorption Systems  ARO MURI
calculations with smaller 3-21G basis set

<table>
<thead>
<tr>
<th>F-substitution</th>
<th>unprotonated</th>
<th>protonated</th>
<th>difference</th>
</tr>
</thead>
<tbody>
<tr>
<td>none</td>
<td>4.90</td>
<td>4.48</td>
<td>-0.42</td>
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<tr>
<td>C2</td>
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</tr>
<tr>
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<td>-0.32</td>
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<tr>
<td>C14</td>
<td>4.89</td>
<td>4.28</td>
<td>-0.61</td>
</tr>
<tr>
<td>C8*</td>
<td>4.95</td>
<td>4.44</td>
<td>-0.51</td>
</tr>
<tr>
<td>C10*</td>
<td>4.91</td>
<td>4.46</td>
<td>-0.45</td>
</tr>
<tr>
<td>C16*</td>
<td>4.91</td>
<td>4.44</td>
<td>-0.47</td>
</tr>
</tbody>
</table>

*predicted to change excitation energy based on atomic charge changes

consistent with larger basis set:
• increase in excitation energy drop at C8, decrease at C6
• large increase at C14
• some small increases at C10 and C16

other substitution – nitro group

<table>
<thead>
<tr>
<th></th>
<th>unprotonated</th>
<th>protonated</th>
<th>difference</th>
</tr>
</thead>
<tbody>
<tr>
<td>none</td>
<td>4.90</td>
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<td>-0.42</td>
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<tr>
<td>C8-F</td>
<td>4.95</td>
<td>4.44</td>
<td>-0.51</td>
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<td>C8-NO₂</td>
<td>4.50</td>
<td>4.51</td>
<td>0.01*</td>
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<tr>
<td>C10-F</td>
<td>4.91</td>
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<td>C10-NO₂</td>
<td>4.49</td>
<td>4.14</td>
<td>-0.35</td>
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</tbody>
</table>

*strong repulsions make this planar structure not a minimum

nitro group has effect opposite to F, reducing excitation energy drop in C10

Steve Scheiner        Tunable Absorption Systems        ARO MURI
removal of planarity constraint

3-21G basis set

<table>
<thead>
<tr>
<th>F-substitution</th>
<th>unprotonated</th>
<th>protonated</th>
<th>difference</th>
</tr>
</thead>
<tbody>
<tr>
<td>none pl</td>
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<td>4.33</td>
<td>-0.39</td>
</tr>
<tr>
<td>none npl</td>
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<td>-0.32</td>
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<tr>
<td>C10-F pl</td>
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<td>-0.38</td>
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<tr>
<td>C10-F npl</td>
<td>4.91</td>
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<td>+0.12</td>
</tr>
<tr>
<td>C8-F pl</td>
<td>4.78</td>
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<td>-0.48</td>
</tr>
<tr>
<td>C8-F npl</td>
<td>5.27</td>
<td>4.72</td>
<td>-0.54</td>
</tr>
<tr>
<td>C8-F npl (HB)</td>
<td>5.13</td>
<td>4.70</td>
<td>-0.43</td>
</tr>
</tbody>
</table>

relaxing planarity constraint
lowers the amount of the excitation energy drop for unsubstituted molecule and for C10-F
raises it for C8 (if no H-bond), lowers in case of H-bond

Steve Scheiner
Tunable Absorption Systems
ARO MURI
other substitutions - (all nonplanar)

<p>| | | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>none</td>
<td>5.00</td>
<td>4.68</td>
<td>-0.32</td>
</tr>
<tr>
<td>C10-F</td>
<td>4.91</td>
<td>4.65</td>
<td>-0.26</td>
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<tr>
<td>C10-CH₃</td>
<td>5.15</td>
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<td>-0.37</td>
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<tr>
<td>C10-NO₂</td>
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<tr>
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<td>4.68</td>
<td>-0.32</td>
</tr>
<tr>
<td>C8-F</td>
<td>5.13</td>
<td>4.70</td>
<td>-0.43</td>
</tr>
<tr>
<td>C8-NO₂</td>
<td>4.42</td>
<td>4.26</td>
<td>-0.16</td>
</tr>
</tbody>
</table>

for C10, NH₂ has little effect, F lowers drop, CH₃ and NO₂ increase drop
for C8, F raises drop, NO₂ decreases drop

in both cases, F and NO₂ are opposite to one another
CONCLUSIONS

• Calculations support the notion that protonation acts to promote a red shift via a mechanism involving charge transfer from one ring to another as a result of electronic excitation.

• Atomic charges are of some help in identifying “hot spots”, but this help is limited.

• For F substitution, C14 and C8 enhance the magnitude of the red shift, C6 does the reverse.

• C2 does very little, C10 and C16 mild increases.

• So this is not just a matter of substitution on one ring or another.

---

Steve Scheiner, Tunable Absorption Systems, ARO MURI
• changing from F to other substituents produces results that are not easily understood yet

• nitro group produces large perturbations, but not the same as F

• removing planarity constraint tends to lower the magnitude of red shift

• other substituents (methyl, nitro, amino) produce results which are not yet easily interpreted

When M=Cu, Ni, reversible electrochromism Zn, Co, Fe irreversible.

The authors had little understanding of this difference. Their hypothesis: M changes electron state of the pc ring.

If M highly electronegative
- sucks density out of pc ring, making latter more difficult to oxidize, i.e. higher oxidation potential.
- after ionization to cation, positive charge will tend to localize on pc ring.

when M less electronegative, get the reverse.
also hypothesize that positive charge of cation is localized at certain positions of the pc ring. these can be thought of as electrically isolated domains, subject to attack by anions present in the solution.
can such small changes in electronegativity (~0.1) account for these differences?

Address problem by ab initio calculations.
Large size of system, coupled with close-lying electronic states, makes routine application of high-level ab initio theory problematic.

HF  Hartree-Fock  standard workhorse, questionable for transition metals

MP2  perturbation theory  means of including electron correlation, but also questionable for transition metals

B3LYP  density functional  “standard” variant of DFT; includes electron correlation

LANL2DZ  basis set  effective core potential on M
6-31G*  no effective cores used

ADF  less standard DFT, does not use “basis sets” as such
### Binding Energies of Metals to Pc\(^a\), eV

<table>
<thead>
<tr>
<th></th>
<th>FePc</th>
<th>CoPc</th>
<th>NiPc</th>
<th>CuPc</th>
<th>ZnPc</th>
<th>MgPc</th>
</tr>
</thead>
<tbody>
<tr>
<td>B3LYP (A)(^b)</td>
<td>-4.39</td>
<td>-9.38</td>
<td>-7.81</td>
<td>-6.03</td>
<td>-5.12</td>
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<tr>
<td>HF (A)</td>
<td>1.67</td>
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<tr>
<td>MP2 (A)</td>
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<td>-8.35</td>
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<td></td>
<td></td>
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<tr>
<td>B3LYP (B)(^c)</td>
<td>-7.87</td>
<td>-8.44</td>
<td>-10.21</td>
<td>-10.06</td>
<td>-7.56</td>
<td>-8.07</td>
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<tr>
<td>HF (B)</td>
<td>-6.74</td>
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<td>-9.04</td>
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<td>-5.66</td>
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<tr>
<td>MP2 (B)</td>
<td>-11.25</td>
<td>-10.95</td>
<td>-13.43</td>
<td>-8.87</td>
<td>-9.57</td>
<td></td>
</tr>
<tr>
<td>ADF</td>
<td>-9.81</td>
<td>-10.49</td>
<td>-9.90</td>
<td>-6.96</td>
<td>-5.66</td>
<td>-8.14</td>
</tr>
</tbody>
</table>

\(^a\)Negative quantity indicates favorable binding

\(^b\)LanL2DZ

\(^c\)6-31G*

HF probably useless; correlation very important

**MP2:** Ni > Fe > Co > Zn > Cu

**B3LYP:** Ni ~ Cu > Co > Fe ~ Zn

B3LYP makes Cu a better binder

**ADF:** Co > Ni ~ Fe > Cu > Zn

Co,Ni,Fe  >  Cu,Zn

Binding energies are in the 5 – 10 eV range
### IONIZATION POTENTIALS, eV

<table>
<thead>
<tr>
<th></th>
<th>Pc</th>
<th>FePc</th>
<th>CoPc</th>
<th>NiPc</th>
<th>CuPc</th>
<th>ZnPc</th>
<th>MgPc</th>
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</thead>
<tbody>
<tr>
<td>B3LYP (A)</td>
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<tr>
<td>HF (A)</td>
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<td>4.54</td>
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<td></td>
</tr>
<tr>
<td>MP2 (A)</td>
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<tr>
<td>B3LYP (B)</td>
<td>6.93</td>
<td>6.02</td>
<td>6.24</td>
<td>6.08</td>
<td>7.30</td>
<td>6.06</td>
<td>5.97</td>
</tr>
<tr>
<td>HF (B)</td>
<td>4.50</td>
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<td>4.54</td>
<td>4.66</td>
<td>4.54</td>
<td></td>
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<tr>
<td>MP2 (B)</td>
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<tr>
<td>ADF</td>
<td>7.02</td>
<td>6.46</td>
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<td>6.56</td>
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<td>ADF (T)</td>
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<td>6.51</td>
<td>6.52</td>
<td>6.48</td>
<td></td>
</tr>
</tbody>
</table>

B3LYP (B): Cu hardest to ionize, harder than uncomplexed pc
all other metals have lower IP, roughly the same.

ADF: all metals lower IP, little to distinguish one metal from another

### (ADF) HOMO - LUMO SEPARATIONS, eV

<table>
<thead>
<tr>
<th></th>
<th>Fe</th>
<th>Co</th>
<th>Ni</th>
<th>Cu</th>
<th>Zn</th>
<th>Mg</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1.38</td>
<td>1.96</td>
<td>1.47</td>
<td>1.42</td>
<td>1.91</td>
<td>1.38</td>
</tr>
<tr>
<td>1e_g→2e_g</td>
<td>1e_g→2e_g</td>
<td>a_1u→b_1g</td>
<td>b_1g→2e_g</td>
<td>a_1u→2e_g</td>
<td>a_1u→2e_g</td>
<td></td>
</tr>
</tbody>
</table>

Fe, Ni, Cu have lowest separation, followed by Zn and Co.
except for Fe, this conforms to expt.

note also: HOMO-LUMO separation pattern different than IP.  

---

Steve Scheiner  
Tunable Absorption Systems  
ARO MURI
Charge assigned to metal atom

<table>
<thead>
<tr>
<th></th>
<th>FePc</th>
<th>CoPc</th>
<th>NiPc</th>
<th>CuPc</th>
<th>ZnPc</th>
<th>MgPc</th>
</tr>
</thead>
<tbody>
<tr>
<td>B3LYP (A)</td>
<td>0.27</td>
<td>0.60</td>
<td>0.55</td>
<td>0.73</td>
<td>1.15</td>
<td></td>
</tr>
<tr>
<td>HF (A)</td>
<td>0.45</td>
<td>0.57</td>
<td>1.02</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>MP2 (A)</td>
<td></td>
<td>0.63</td>
<td></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>B3LYP (B)</td>
<td>1.20</td>
<td>0.71</td>
<td>0.80</td>
<td>0.88</td>
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<td>1.07</td>
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<td>HF (B)</td>
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<td>1.34</td>
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<td>MP2 (B)</td>
<td>1.23</td>
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<td>0.90</td>
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<tr>
<td>ADF</td>
<td>0.71</td>
<td>0.59</td>
<td>0.50</td>
<td>0.65</td>
<td>0.64</td>
<td>0.77</td>
</tr>
</tbody>
</table>

B3LYP: Zn > Cu > Co ~ Ni
but Fe very sensitive to basis set

MP2: Zn high, but now followed by Ni > Cu > Co

ADF: Zn ~ Cu > Co > Ni

no obvious patterns here, except high charge of Zn

whereas low electronegativity of Zn is manifest by high + charge, high electronegativities of Ni and Cu don’t seem to be apparent in charges

Steve Scheiner Tunable Absorption Systems ARO MURI
ELECTRON AFFINITIES, EV

<table>
<thead>
<tr>
<th></th>
<th>Fe</th>
<th>Co</th>
<th>Ni</th>
<th>Cu</th>
<th>Zn</th>
<th>Mg</th>
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</thead>
<tbody>
<tr>
<td>MPC</td>
<td>-2.92</td>
<td>-3.19</td>
<td>-2.14</td>
<td>-1.74</td>
<td>-2.23</td>
<td>-2.16</td>
</tr>
</tbody>
</table>

electrons are drawn to each species (negative values)
Cu and Ni the weakest, with Cu < Ni
among others, Zn < Fe < Co

this pattern generally consistent with electronegativities:
Zn < Fe ~ Co < Cu ~ Ni
in that Ni and Cu have weakest pull for an electron,
but Zn out of place here.
MORE DETAIL OF METAL CHARGE

<table>
<thead>
<tr>
<th>orbital</th>
<th>Fe</th>
<th>Co</th>
<th>Ni</th>
<th>Cu</th>
<th>Zn</th>
<th>Mg</th>
</tr>
</thead>
<tbody>
<tr>
<td>3d</td>
<td>6.59</td>
<td>7.63</td>
<td>8.61</td>
<td>9.50</td>
<td>10.0</td>
<td>0.42 (3d)</td>
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<tr>
<td>4s</td>
<td>0.42</td>
<td>0.41</td>
<td>0.42</td>
<td>0.39</td>
<td>0.55</td>
<td>0.36 (3s)</td>
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<tr>
<td>4p</td>
<td>0.29</td>
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<td>0.48</td>
<td>0.46</td>
<td>0.81</td>
<td>0.45 (3p)</td>
</tr>
<tr>
<td>Q&lt;sub&gt;M&lt;/sub&gt;</td>
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<td>0.59</td>
<td>0.50</td>
<td>0.65</td>
<td>0.64</td>
<td>0.77</td>
</tr>
</tbody>
</table>

- total (positive) charge: Ni < Co < Zn ~ Cu < Fe
- orbital populations (invert charge)
  - 3d shell: Zn < Cu < Ni < Co < Fe
  - 4s shell: Zn < Fe ~ Co ~ Ni < Cu
  - 4p shell: Zn < Ni ~ Cu < Co < Fe

None of these show expt behavior.
### ATOMIC CHARGES AROUND THE PC SYSTEM

<table>
<thead>
<tr>
<th></th>
<th>M = Fe</th>
<th>M = Co</th>
<th>M = Ni</th>
<th>M = Cu</th>
<th>M = Zn</th>
<th>M = Mg</th>
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</thead>
<tbody>
<tr>
<td>$Q_M$</td>
<td>0.71</td>
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<td>0.50</td>
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<td>0.64</td>
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<tr>
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<td>-0.49</td>
<td>-0.57</td>
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<tr>
<td>$Q_{N2}$</td>
<td>-0.33</td>
<td>-0.33</td>
<td>-0.33</td>
<td>-0.33</td>
<td>-0.33</td>
<td>-0.33</td>
</tr>
<tr>
<td>$Q_{C1}$</td>
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<td>0.32</td>
<td>0.32</td>
<td>0.32</td>
<td>0.32</td>
<td>0.33</td>
</tr>
<tr>
<td>$Q_{C2}$</td>
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<td>0.09</td>
<td>0.09</td>
<td>0.09</td>
<td>0.08</td>
<td>0.08</td>
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<tr>
<td>$Q_{C3}$</td>
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<td>0.14</td>
<td>0.14</td>
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<td>0.13</td>
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<tr>
<td>$Q_{C4}$</td>
<td>0.17</td>
<td>0.17</td>
<td>0.17</td>
<td>0.17</td>
<td>0.17</td>
<td>0.17</td>
</tr>
<tr>
<td>$Q_{H1}$</td>
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<td>-0.18</td>
<td>-0.19</td>
<td>-0.18</td>
<td>-0.18</td>
<td>-0.18</td>
</tr>
<tr>
<td>$Q_{H2}$</td>
<td>-0.18</td>
<td>-0.18</td>
<td>-0.18</td>
<td>-0.18</td>
<td>-0.18</td>
<td>-0.18</td>
</tr>
</tbody>
</table>

Nature of metal has very little effect upon the charges of the atoms around the pc ring. This belies the idea that the different behavior is moderated by the electron density on the periphery of the pc system, induced by change in metal electronegativity.
same properties of cation:

<table>
<thead>
<tr>
<th>orbital</th>
<th>Fe</th>
<th>Co</th>
<th>Ni</th>
<th>Cu</th>
<th>Zn</th>
<th>Mg</th>
</tr>
</thead>
<tbody>
<tr>
<td>3d</td>
<td>6.59</td>
<td>7.64</td>
<td>8.61</td>
<td>9.50</td>
<td>10.0</td>
<td>0.40</td>
</tr>
<tr>
<td>4s</td>
<td>0.40</td>
<td>0.36</td>
<td>0.40</td>
<td>0.37</td>
<td>0.54</td>
<td>0.31</td>
</tr>
<tr>
<td>4p</td>
<td>0.27</td>
<td>0.39</td>
<td>0.47</td>
<td>0.45</td>
<td>0.80</td>
<td>0.40</td>
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<tr>
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<td>0.52</td>
<td>0.68</td>
<td>0.65</td>
<td>0.90</td>
</tr>
</tbody>
</table>

total (positive) charge: Ni < Co < Zn < Cu < Fe
orbital populations (invert charge)
3d shell: Zn < Cu < Ni < Co < Fe
4s shell: Zn < Fe ~ Ni < Co ~ Cu
4p shell: Zn < Ni ~ Cu < Co < Fe

patterns in cation very much the same as in neutral
CONCLUSIONS

• problem is a difficult one

• metal electronegativity oversimplified and not indicative enough

• electron correlation needed for accuracy
different methods can be at odds with one another

• ionization potentials of MPc are all quite similar

• HOMO-LUMO separation pattern different than IPs
  (HOMO not the same symmetry for all)
• $b_{1g}$ orbital most sensitive to nature of metal ($d_{x^2-y^2}$)

• atomic charges (metal or PC atoms) not helpful indicators
  same true for individual atomic orbitals (4s, 4p, 3d)

• electron affinities are smallest for CuPc and NiPc
Synthesis of Electroactive and Emissive Conjugated Polymers

MIT Team:  J.D. Tovar (100% MURI effort)
Dr. Anthony Pullen (now at E-ink)
Ashleigh H. Hegedus (UG-Yale)
Irina Gorodetskaya (UG)
Bruce Yu (50% MURI effort)
D. Tyler McQuade (NIH PD fellow)
Dr. Zhengguo Zhu (Funded by DARPA)
Cationic PPEs

\[
\begin{align*}
&\text{HO} - \text{I} - \text{I} - \text{OH} \\
&\xrightarrow{1,3 \text{ dibromopropane}, \text{K}_2\text{CO}_3, \text{acetone, } 70^\circ\text{C}} \\
&\xrightarrow{40\% \text{ Trimethylamine in water, ethanol, acetone}} \\
&\text{HO} - \text{I} - \text{I} - \text{OH}
\end{align*}
\]

\[
\begin{align*}
&\text{Br} - \text{O} - \text{O} - \text{Br} \\
&\xrightarrow{\text{Pd(PPh}_3)_4, \text{CuI, DMF}} \\
&\xrightarrow{\text{Et}_3\text{N, Water}} \\
&\text{Br} - \text{O} - \text{O} - \text{Br}
\end{align*}
\]

\[
\begin{align*}
&\xrightarrow{\text{Pd(PPh}_3)_4, \text{CuI, DMF}} \\
&\xrightarrow{\text{Et}_3\text{N, Water}} \\
&\text{HO} - \text{O} - \text{O} - \text{OH}
\end{align*}
\]
Water Soluble Ionic PPEs

\[ \text{Pd(PPh}_3\text{)}_4, \text{CuI, THF, EtOH, Et}_3\text{N, 50°C} \]

\[ M_\text{n}=33,823 \quad \text{PDI=1.8} \]

Organic Soluble Precursor

Polymers for Layer By Layer Deposition

TOPS-MURI, T.M. Swager, MIT
Formation of a pH Sensitive Polymeric Dye

Fluoresceinamine
Emissive at High pH
Emission/Absorption of Donor and Acceptors

Wavelength (nm)

Absorbance Intensity (arb. units)

Fluorescence Intensity (arb. units)

TOPS-MURI, T.M. Swager, MIT
Two Layer Film
Produced in A Layer By Layer Method

The Difference Between the Ex. 420 and 500 Indicates Efficient Energy Transfer
pH Response of Three-Layer Films

Get a Lower QY of the Polymer

Ex. 420

pH 11

2:1 ratio

pH 8

Ex. 500

450 500 550 600 650

Wavelength (nm)

Fluorescence Intensity (arb. units)

TOPS-MURI, T.M. Swager, MIT
Regiospecific Synthesis of Aniline Copolymers

By Using Step-Wise Coupling
Precise More Structures can be Created

\[ \text{PhOCH}_3 + \text{BrPhNPh}_2 \xrightarrow{a} \text{PhOCH}_3\text{PhNPh}_2 \xrightarrow{b} \text{PhOCH}_3\text{PhNHPh}_2 \]

\[ \text{PhOCH}_3 + \text{BrPhNBOCPh}_2 \xrightarrow{c} \text{PhOCH}_3\text{PhNBOCPh}_2 \xrightarrow{d, b} \text{PhOCH}_3\text{PhNHPh}_2 \]

\( ^{a}(\text{Pd}_2\text{dba}_3, \text{rac-BINAP}, \text{NaOtBu}, \text{THF}, \text{reflux}) \)
\( ^{b}10\% \text{Pd/C, NH}_4\text{HCO}_2, \text{THF, EtOH, 60}^\circ \text{C} \)
\( ^{c}(\text{Pd}_2\text{dba}_3, \text{rac-BINAP}, \text{NaOtBu}, \text{THF, reflux}) \)
\( ^{d}160^\circ \text{C} \)
Electro-deposition of Dimer and Trimers

Dotted Line Indicates Initial Scan

TOPS-MURI, T.M. Swager, MIT
CV and Conductivity Profiles of Dimer and Trimer

Sharp CVs
Random Copolymers of Methoxy Aniline and Aniline

(a) Equal Amounts
(b) 2:1 (Aniline Excess)

Broader Electrochemistry
Slightly Lower Conductivity
Resonance Structures and The Charged States of Co-Polyanilines

An Organic Chemist’s View
Examples of Highly Luminescent PPVs

\[ \Phi = 28\% \]


\[ \Phi = 65\% \]


\[ \Phi = 82\% \]


TOPS-MURI, T.M. Swager, MIT
PPVs with Alternate Triptycene Units

Pincolborane, Tol., 90 °C, 50%

C₄F₉SO₂F, NEt₃, 90%

1. TMSA, Pddba₂, PPh₃, CuI, i-Pr₂NH, 86%
2. KOH, MeOH, 90%

H₂C₁₂⁻, O⁻C₁₂H₂₅

Mn = 10-13 kDa
Emission Spectra

Electronic Structure is Very Dependent Upon Ortho vs. Para Substitution Pattern

TOPS-MURI, T.M. Swager, MIT
PPVs with Greater Larger Interchain Distances
Synthesis of Triptycene PPV

1. AlCl₃
   2. H₂SO₄
   50%

O

1. 1,4-benzoquinone, xylenes
   2. HBr, HOAc, reflux
   78%

Br

NBS, benzene,
benzoyl peroxide, reflux
60%

NaH, DMF,
2-ethylhexylbromide
70%

TBuOK, THF

Highly Emissive
Very Stable

TOPS-MURI, T.M. Swager, MIT
Random Triptycene/MEH PPV Copolymers

50/50

Br
KOtBu, THF

Bright Orange Polymer
Highly Emissive
Emission of Triptycene PPV and Copolymer

TOPS-MURI, T.M. Swager, MIT
New Water Soluble PPVs

Carboxylates: Electron Withdrawing
Excellent for Functionalization
TO: (1) Chemistry Division Division
   (Kiserow, Douglas)
Report is ATTACHED for review.
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Shaw H. Chen

Professor Shaw H. Chen
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Room 1210 COL, University of Rochester
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Thermotropic Chiral–Nematic Poly(p-phenylene)s as a Paradigm of Helically Stacked \( \pi \)-Conjugated Systems


Department of Chemical Engineering, Materials Science Program, NSF Center for Photoinduced Charge Transfer, and Laboratory for Laser Energetics, Center for Optoelectronics and Imaging, University of Rochester, 240 East River Road, Rochester, New York 14623-1212

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As an emerging class of multifunctional optical materials, chiral–nematic poly(p-phenylene)s with cyanobiphenyl and (S)-1-phenylethyl pendants were synthesized and characterized. Nematic homopolymer was also synthesized for preparation into a uniaxially aligned film. Linearly polarized photoluminescence (LPPL) and FTIR dichroism revealed that both the conjugated backbone and the nematic pendant are oriented along the director with an orientational order parameter, \( S = 0.62 \) and 0.73, respectively. Films prepared with chiral–nematic copolymers were found to selectively reflect left-handed circularly polarized light in the ultraviolet, viable, and infrared region at a decreasing chiral content. The helically stacked poly(p-phenylene)s were further characterized in terms of circularly polarized photoluminescence (CPPL). On the basis of a recent theory, \( S = 0.67 \) was found for the orientational order of conjugated backbones within quasinematic layers comprising the chiral–nematic film. Within experimental uncertainty, the \( S \) values determined with the LPPL and CPPL techniques are in good agreement, thereby validating the proposed supramolecular structure on the basis of which theories governing light absorption, emission, and propagation in structured media were constructed.

I. Introduction

Conjugated polymers represent one of the most extensively investigated classes of advanced materials in the past two decades. Reasons for the extraordinary intensity of interest include the diverse structures and properties afforded by molecular design and synthesis, the ease of processing and low costs compared to inorganic materials, and the technological potential for advanced technologies, such as electronics, optics, photonics, and optoelectronics. In particular, feasibility has been demonstrated with amorphous or crystalline conjugated polymers for light-emitting diodes, organic lasers, thin film transistors, photoconductors, and nonlinear optical devices. Liquid crystalline conjugated polymers characterized by various modes of macroscopic order have added a new dimension in recent years. Mediated by nematic or smectic mesomorphism, axial alignment of \( \pi \)-conjugated segments has been shown to enhance electrical conductivity by orders of magnitude and to induce linearly polarized light emission. Conjugated polymers of the chiral–nematic (i.e., cholesteric) type, in which conjugated segments self-assemble into helically stacked, quasinematic layers, have remained literally unexplored. As a matter of fact, there exists only one paper at present reporting loosely pitched conjugated systems. This is an emerging class of multifunctional optical materials potentially capable of selective reflection accompanied by circular polarization of incident unpolarized light, circularly polarized luminescence, and electrochromism inherent to \( \pi \)-conjugated systems.

to which diethyl azodicarboxylate (DEADC; 4.43 g, 25.4 mmol) was collected for recrystallization from methanol to produce phenylphosphine (5.33 g, 29.3 mmol). The resultant salt was removed by hot filtration. The filtrate was slowly added to potassium iodide of DMF. The reaction mixture was stirred at room temperature overnight. Upon evaporation of the solvent under reduced pressure, the solid residue was dissolved in a small amount of methylene chloride for purification by flash column chromatography on silica gel, with a 98/2 mixture of methylene chloride and acetone as the eluent, followed by recrystallization from methanol to obtain 10.26 g in 93% yield. 1H NMR: δ 6.80–7.00 (m, aromatic, 11H), 4.38 (t, ArOCH2, 2H), 4.04 (t, ArOCH2CH2CH2CH2CH2OAr, 4H), 1.58 (m, COOC(CH2)6OAr, 2H), 0.70 (m, COOC(CH2)6OAr, 4H). Anal. Calcd: C, 47.95; H, 3.34; N, 2.15; I, 38.97. Found: C, 47.98; H, 3.34; N, 2.21; I, 39.40.

II. Experimental Section

Reagents and Chemicals. All chemicals, reagents, and solvents were used as received from the Aldrich Chemical Co. or VWR Scientific with the following exceptions. Bis(1,5-cyclooctadiene)nickel(0) (98%+, Strem Chemicals) was used without further purification. Tetrahydrofuran (99%) was dried by being refluxed over sodium in the presence of benzophenone and then distilled.

Material Synthesis. Syntheses of monomers and polymers were performed following Scheme 1 with the experimental procedures as described in what follows.

Scheme 1. Synthesis of Nematic and Chiral Monomers and of Nematic and Chiral-Nematic Poly(p-phenylene)

was slowly added. Under argon the reaction mixture was stirred at room temperature overnight. Upon evaporation of the solvent under reduced pressure, the solid residue was dissolved in a small amount of methylene chloride for purification by flash column chromatography on silica gel, with a 98/2 mixture of methylene chloride and acetone as the eluent, followed by recrystallization from methanol to obtain 10.26 g in 93% yield. 1H NMR: δ 6.80–7.00 (m, aromatic, 11H), 4.38 (t, ArOCH2, 2H), 4.04 (t, ArOCH2CH2CH2CH2CH2OAr, 4H), 1.58 (m, COOC(CH2)6OAr, 2H), 0.70 (m, COOC(CH2)6OAr, 4H). Anal. Calcd: C, 47.95; H, 3.34; N, 2.15; I, 38.97. Found: C, 47.98; H, 3.34; N, 2.21; I, 39.40.

4-(2-Hydroxyethyl)benzoic Acid, (II-1), 4-[2-(tert-Butylmethylsilyloxy)ethoxy]benzoic acid (II-2), 4-Methoxybenzoyloxybenzoic Acid (II-3), 4-Methoxybenzoyloxybenzoic Acid (S)-(-)-1-Phenylethyl Ester (II-4), and 4-Hydroxybenzoic Acid (S)-(-)-1-Phenylethyl Ester (II-5). The synthesis of all the intermediates leading to the chiral monomer II except II-6 has been reported previously.13,14

4-((S)-(−)-1-Phenylethyl)-4-(2-hydroxyethoxy)benzoyloxybenzoate (II-6). Intermediate II-2 (9.62 g, 32.5 mmol) II-5 (7.50 g, 30.8 mmol), N,N′-dicyclohexylcarbodiimide (DCC; 7.38 g, 35.2 mmol), and 4-pyrididinopyridinopropylidene (0.46 g, 3.3 mmol) were dissolved in 60 mL of anhydrous tetrahydrofuran. The reaction mixture was stirred at room temperature overnight under nitrogen. Upon evaporation of the solvent under reduced pressure, the crude product was purified by column chromatography on silica gel with a 75/25 mixture of methylene and n-hexane as the eluent. The resultant silyl ether was hydrolyzed by being stirred in a 60/20/20 mixture of acetic acid, tetrahydrofuran, and water. Upon neutralization with a NaHCO3 solution, column chromatography was carried out on silica gel with methylene chloride containing 0.5% acetone as the eluent.

the eluent. Recrystallization from hexane containing 2% ethanol produced 7.50 g in 60%.

2.5-Diiodobenzoic Acid, 4′-4′-[(S,S)−(−)−1-Phenylethyl(benzoxyloxy)benzoyloxy]-2-ethoxy Ether (II). Chiral monomer II was prepared using the same procedure as for the nematic monomer I, except recrystallization was done after the 20% mixture of acetone and ethanol to obtain a 86% yield. 1H NMR: δ 8.20−7.00 (m, aromatic, 16 H), 6.16 (q, −COOCF3(CH2)1), 4.75 (t, COOCH3(CH2)2H, 4.43 (t, ArOCH2(CH2)2H, 1.70 (d, CH2CH3, 3H). Anal. Calcd: C, 48.34; H, 3.17; N, 0.01. I, 33.29. Found: C, 49.63; H, 2.90; N, 1.35.

Nematic and Chiral–Nematic Polymers III-β. The procedure for N(0)-mediated polymerization is illustrated with copolymer III-0.23 as follows: Bis(1,5-cyclooctadiene)nickel(0) (Ni(COD)2; 0.84 g, 3.03 mmol), 2,2′-dipyridyl (0.47 g, 3.03 mmol), and 1,5-cyclooctadiene (0.33 g, 3.03 mmol) were dissolved in 8 mL of anhydrous DMP. To this solution were added I (0.50 g, 1.58 mmol) and II (0.45 g, 0.59 mmol). Precipitations against oxygen and moisture were taken by preparing the reaction mixture in a glovebox. Polymerization was carried under argon at 55 °C overnight. The crude product was precipitated into 100 mL of methanol containing 2 mL of concentrated hydrochloric acid. The precipitate was filtered and washed sequentially with methanol containing 2 mL of concentrated hydrochloric acid. The solution was reduced to 6 mL in volume for precipitation into 30 mL of heptane. A 0.6 g (21%) yield of copolymer III-g-0.33 was collected.

III-0.00: 1H NMR: δ 8.60−6.80 (m, aromatic, 11H), 4.50−3.70 (m, COOCH2(CH2)2CH2OAr, 4H), 2.00−1.00 (m, COOCH2(CH2)3CH2OAr, 8H). Anal. Calcd: C, 76.58; H, 5.84; N, 3.53. Found: C, 78.42; H, 6.03; N, 3.41. (III-0.07) 1H NMR: δ 8.50−6.50 (m, aromatic, x(26H)) + (1−x)(8H)), 6.14 (br, −COOCF3(CH2)3H), 4.70−3.70 (m, COOCH2(CH2)2CH2OAr and COOCH2(CH2)3CH2OAr, x(4H) + (1−x)(4H)), 1.90−1.10 (m, −CH2 and COOCH2(CH2)3CH2OAr, x(3H) + (1−x)(3H)). Anal. Calcd: C, 78.67; H, 5.74; N, 3.20. Found: C, 77.60; H, 5.83; N, 3.12. (III-0.12) 1H NMR: δ 8.50−6.50 (m, aromatic, x(26H) + (1−x)(8H)), 6.13 (br, −COOCF3(CH2)3H), 4.70−3.70 (m, COOCH2(CH2)2CH2OAr and COOCH2(CH2)3CH2OAr, x(4H) + (1−x)(4H)), 1.90−1.10 (m, −CH2 and COOCH2(CH2)3CH2OAr, x(3H) + (1−x)(3H)). Anal. Calcd: C, 77.46; H, 5.75; N, 3.01. Found: C, 77.46; H, 5.75; N, 3.01. (III-0.17) 1H NMR: δ 8.50−6.50 (m, aromatic, x(26H) + (1−x)(11H)), 6.14 (br, −COOCF3(CH2)3H), 4.70−3.70 (m, COOCH2(CH2)2CH2OAr and COO(CH2)2OAr, x(4H) + (1−x)(4H)), 1.90−1.10 (m, x(4H) + (1−x)(4H)), 1.90−1.10 (m, −CH2 and COOCH2(CH2)3CH2OAr, x(3H) + (1−x)(3H)). Anal. Calcd: C, 77.55; H, 5.63; N, 2.86. Found: C, 77.67; H, 5.77; N, 2.67. (III-0.23) 1H NMR: δ 8.50−6.50 (m, aromatic, x(26H) + (1−x)(11H)), 6.14 (br, −COOCF3(CH2)3H), 4.70−3.70 (m, COOCH2(CH2)2CH2OAr and COO(CH2)2OAr, x(4H) + (1−x)(4H)), 1.90−1.10 (m, −CH2 and COOCH2(CH2)3CH2OAr, x(3H) + (1−x)(3H)). Anal. Calcd: C, 77.06; H, 5.54; N, 2.54. Found: C, 76.53; H, 5.58; N, 2.49.

General Characterization Techniques. Chemical structures were elucidated with elemental analysis (performed by Oneida Research Services, Waltham, MA), and FTIR (Niclot 20 SXC) and 1H and 13C NMR (Avance-400, Bruker) spectroscopic techniques. Thermal transition temperatures were determined by differential scanning calorimetry (Perkin-Elmer DSC-7) with a continuous N2 purge at 20 m/ln. Liquid crystal mesomorphism was characterized with a polarizing optical microscope (Nikon). Films were prepared with a hot stage (FP82, Mettler) and a central processor (FP90, Mettler). The order parameter S was determined using a commercial DMLM. Linear polarization was performed with a high throughput light scattering detector, differential viscometer, and a polarizing optical microscope (Nikon). Optical properties were determined using a thermal analyzer (Perkin-Elmer Lambda 9) with a UV−vis−near-IR spectrophotometer. Chiral-nematic films were prepared with a differential scattering (DSC-7) of a nematic film, characterized using a FTIR spectrometer (FTIR, Polytec) with a UV−vis−near-IR spectrophotometer. Chiral-nematic films were prepared with a differential scattering (DSC-7) of a nematic film, characterized using a FTIR spectrometer (FTIR, Polytec).

Preparation of Films and Characterization of Optical Properties. Optical elements for the order parameter measurements were fabricated using optically flat, calcium fluoride substrates (1.00 in. diameter × 0.04 in. thickness, Optopac) that are transparent from the infrared region down to 200 nm. Optical elements for the reflection, transmission, and circular polarization measurements were fabricated using optically flat, fused silica substrates (1.00 in. diameter × 0.18 in. thickness, Esco Products) transparent down to 200 nm. In both cases, the substrates were cleaned, spin-coated with Nylon 66, and then buffed with a velvet roller. Sandwiched films were prepared by melting the powders between two substrates at a temperature 20 °C above Tc followed by annealing 20 °C below Tc for 1 h with subsequent cooling at −10 °C/h to room temperature. The film thickness was controlled by glass fiber spacers (EM Industries) to within 4.1 ± 0.2 µm, as determined by the interference fringes from the air gap between the substrates using a UV−vis−near-IR spectrophotometer. Single-substrate films were prepared by spin-coating from a solution of 2% by weight of sample in chloroform at 2500 rpm. Subsequent air-drying in a laminar flow hood for a few hours and vacuum-drying overnight at room temperature removed the last traces of solvent. The single-substrate film thickness was determined on a white light interferometer (Zygo New View 100).

Orientational order of the cyanobiphenyl pendant was characterized by linear dichroism using a FTIR spectrometer (Niclot 20 SXC). Two measurements were performed with the transmission axis parallel and perpendicular to the nematic director (i.e., the buffing direction) of the sample. A UV−vis−near-IR spectrophotometer (Perkin-Elmer Lambda 9) was employed to measure light absorption and transmission (both at normal incidence) and reflection (at 15° incidence from the surface) at normal room temperature. An aluminum mirror served as a specular reflection standard, and the results were reported as percent reflectivity of incident unpolarized light. In all measurements, Fresnel reflections from the two-air−glass interfaces were accounted for using a reference cell comprising an index-matching fluid sandwiched between two surface-treated substrates. Photoluminescence spectra were collected with a spectrophotometer (Photon Technology International Quantam Master C-60SPE). A liquid light guide (2 mm diameter × 1 m long, Photon Technology International) was used to direct the UV excitation through the center of the film through a glass filter (UG11, Schott Glass Technologies). The light guide also served as a polarization randomizer for the excitation source. In the case of circularly polarized photoluminescence (CFPL), polarization analysis was performed via a circular analyzer with maximum polarization efficiency greater than 95% at 425 nm. At 580 nm the efficiency dropped to 90%. In the case of linearly polarized photoluminescence (LPL), two identical UV−via linear polarizers were used for the polarization of the incident light and the analysis of the emitted light. Their efficiency was better than 99%, across a wide wavelength range, from 275 to 725 nm. All the polarized photoluminescence spectra (both LPL and CFPL) were recorded for both the efficiency and the transmission dispersion of the analyzer. The order parameter governing the poly(p-phenylene) backbone was determined by the LPL and CFPL spectra of a nematic and chiral−nematic film, respectively. In all cases, the order parameter was measured with an uncertainty of ±0.05 of the mean.

III. Results and Discussion

The molecular structures of nematic and chiral monomers, I and II as well as nematic and chiral−nematic...
The absorption (a) and photoluminescence (b) spectra of poly(p-phenylene) were determined with aggregation in solution. The depicted polymer structures were consistent with analytical data for which the degree of polymerization determined with size-exclusion chromatography and on the basis of the observation that hydrogen atoms represent the end groups. Also reported in Table 1 are the glass transition temperatures, \(T_g\), and the nematic-to-isotropic transition (i.e., clearing) temperatures, \(T_c\), based on the clearance of the 20 °C/min heating scans of samples preheated to 200 °C with subsequent cooling to room temperature.

The resultant system III-x represents conjugated polymers functionalized with nematic and chiral-nematic mesogens, the latter being a mixture of the nematic and chiral pendants depicted as I-1 and II-6, respectively, in Scheme 1. Through such functionalization, the conjugated segments are induced to align in a manner dictated by the pendant groups. The orientation of the pendant with respect to the backbone remains to be probed with spectroscopic techniques. The fact that the nematic and chiral pendants do not crystallize independently of the poly(p-phenylene) backbone suggests some extent of coupling between the structural elements through the methylenic spacer. In fact, the hybrid system III-x was found to undergo glass transition, thereby permitting the liquid crystalline order to be frozen in the vitreous state upon cooling. The UV-vis absorption and photoluminescence spectra are compiled in Figure 1 for the nematic precursor depicted as I-1 in Scheme 1 and the nematic homopolymer III-0.00 in methylene chloride at 10⁻⁵ M repeat units.
Figure 2. (a) Linearly polarized photoluminescence and (b) FTIR dichroism of a film of nematic homopolymer III-0.00 for the evaluation of the orientational order parameter governing the conjugated backbone and the nematic pendant, respectively.

indicates that the nematic pendant is essentially non-absorbing above 340 nm in comparison to the backbone. Excited with $\lambda_{ex} = 350$ nm, the poly(p-phenylene) backbone showed an emission peak at 410 nm, whereas the cyanobiphenyl group produced a minor emission peak at 360 nm, as shown in Figure 1b.

Anisotropic light absorption and emission involving an axially aligned film were characterized to independently evaluate the orientational order of the conjugated backbone and that of the nematic pendant. A 4 µm thick film was prepared with III-0.00 between two surfacetreated calcium fluoride substrates for the characterization of LPPL. One characteristic of these substrates is the direction in which the nylon alignment coating is buffed with a velvet roller. The buffing direction defines the "nematic director". All the nematic and chiral-nematic films prepared for the present work are contained between two substrates with their directors parallel to each other. The results are shown in Figure 2a, in which the emission intensity is presented with reference to the director. As an example, $I_{\parallel}$ denotes the emission intensity linearly polarized parallel to the director with UV excitation linearly polarized perpendicular to the director. The observed LPPL spectra indicate that the emission intensities parallel to the director are consistently higher than those perpendicular regardless of the polarization state of the excitation source. On the basis of the available data on p-terphenyl and other linear luminophores, it is believed that the

absorption and emission transition moments of poly(p-phenylene) lie parallel to its long axis. It is thus concluded that the axis of poly(p-phenylene) lies parallel to the director. On the basis of the linearly polarized intensities observed at 410 nm, the orientational order parameter, $S$, was evaluated at 0.62 using eq 39 in ref 20 based on a theory of LPPL. Orientational order of the nematic pendant was probed by FTIR dichroism involving the stretching vibration of C≡N at (2224 cm$^{-1}$), as shown in Figure 2b. The absorbances parallel ($A_{\parallel}$) and perpendicular ($A_{\perp}$) to the nematic director were used to calculate the dichroic ratio, $R = A_{\parallel}/A_{\perp}$, from which the orientational order parameter emerged, $S = (R - 1)/(R + 2)$, with its transition moment lying parallel to the long molecular axis of the cyanobiphenyl group. It was found that $S = 0.73$, indicating that the pendant is also oriented along the director.

To appraise the ability of III-x to form vitrified chiral-nematic films, 4 µm thick films were prepared for the characterization of selective wavelength reflection. Comprising a helical stack of quasinematic layers, a chiral-nematic film is capable of selective reflection


with simultaneous circular polarization of incident unpolarized light.\textsuperscript{20} The result is that the incident intensity is equally divided between the reflected and the transmitted components with opposite handedness in circular polarization. Thus, an optical density of 0.30 is expected of unpolarized light at normal incidence on a perfectly ordered chiral–nematic film. Polymers III-x were found not to absorb light in the visible or infrared region, where the observed attenuation of incident light can be attributed to reflection. As shown in Figure 3a, chiral–nematic films prepared with III-x were found to have an increasing selective reflection wavelength, $\lambda_R$, at a decreasing $x$ value. At $x = 0.25$ a selective reflection band was observed in the ultraviolet region, part of which was diminished by light absorption between 300 and 350 nm, as shown in Figure 3b. Traditionally, handedness of the helical stack is defined by that of the reflected circularly polarized component.\textsuperscript{22} Whereas handedness of a chiral–nematic film is related to the absolute configuration of the chiral pendant, no correlation between the two has been established.\textsuperscript{22} To determine the handedness presented by films of III-x containing (S)-(−)-1-phenylethanol, the transmittances of both left- and right-handed circularly polarized light at normal incidence were measured, as illustrated with a film of III-0.12 in Figure 3c. Since left-handed circularly polarized light is selectively reflected, it is concluded that the film prepared with III-x presents a left-handed, helical stack of quasinematic layers. Within each layer, both the poly(p-phenylene) backbone and the cyano(biphenyl) pendant are oriented parallel to the director, as evidenced by LPPL of the nematic film prepared with III-0.00. Thus, the supramolecular structure of a chiral–nematic film is as depicted in Figure 4, with the chiral pendants (not shown) providing the rotation between adjacent quasinematic layers. The schematic diagram also reflects the lack of regioregularity and the antiparallel arrangement of cyanobiphenyl pendants from neighboring poly(p-phenylene) backbones.

To determine the orientational order parameter governing the helically stacked π-conjugated segments, a 4 µm thick film of III-0.07 was prepared for the characterization of CPPL. With unpolarized excitation at 350 nm targeting the poly(p-phenylene) backbone, an emission peak emerged between 350 and 550 nm, which is far removed from the selective reflection band centered at 945 nm of the III-0.07 film. At normal incidence of both excitation and emission, left- and right-handed circularly polarized emission intensities, $I_L$ and $I_R$, were measured for the calculation of the degree of circular polarization, $g_e = 2(I_L - I_R)/(I_L + I_R)$.

The experimental setup described previously\textsuperscript{24} was simplified with a liquid light guide directing the excitation source directly onto the film. On the basis of the CPPL spectra, $g_e = -0.35$ was evaluated at 410 nm. The fact that a significant extent of CPPL resulted from emission outside the selective reflection band can be attributed to the circular polarization of linearly polarized emission originating in all quasinematic layers.\textsuperscript{24}

For light emission outside the selective reflection band of a chiral–nematic film, a CPPL theory has been constructed and validated with experimental observations without resorting to adjustable parameters.\textsuperscript{20} The observed $g_e$ value was employed to evaluate $S$ governing the helically stacked poly(p-phenylene) backbones as the predominant light emitter with excitation at 350 nm, according to Figure 1b. To accomplish this, the average refractive index ($\overline{n}$) and the optical birefringence ($\Delta n$) of the quasinematic layer at both the excitation and emission wavelengths were determined a priori. The optical properties of a nematic homopolymer III-0.00, reported previously\textsuperscript{24} served as the basis for parameter estimation: $\overline{n} = 1.75$ and $\Delta n = 0.30$ at 350 nm and $\overline{n} =$

\begin{itemize}
  \item [(21)] Khoo, I. C.; Wu, S.-T. \textit{Optics and Nonlinear Optics of Liquid Crystals}; World Scientific: Singapore, 1993; p 64.
  \item [(23)] Krishnamurthy, S.; Chen, S. H. \textit{Macromolecules} 1991, 24, 3481.
\end{itemize}
1.63 and $\Delta n = 0.25$ at 410 nm. In addition, the average absorbance per unit thickness reported previously\textsuperscript{5} for the nematic homopolymer, 0.651 $\mu$m$^{-1}$ at 350 nm, was adopted here as another input parameter. With the absorption and emission transition moments lying along the conjugated backbone, the agreement between the predicted and the observed $g_e$ values was secured with $S = 0.67$. Thus, the orientational order characterizing quasinematic layers comprising a chiral–nematic film is consistent with that observed in a nematic film, $S = 0.62$, within an experimental uncertainty of $\pm 0.05$.

Summary

A series of poly(p-phenylene)s functionalized with nematic and chiral pendants were synthesized and characterized as a novel class of multifunctional optical materials. Elemental analysis and $^1$H and $^{13}$C NMR spectroscopic techniques were employed to determine the lack of regioregularity with hydrogen atoms as the terminal groups to poly(p-phenylene)s. The degree of polymerization was found to vary from 9 to 17 by size-exclusion chromatography with universal calibration. A uniaxially aligned film was prepared with homopolymer to assess the orientation of the conjugated backbone and the nematic pendant with reference to the nematic director as defined by the direction of buffing on the substrates. With an excitation source at 350 nm, LPPL revealed the alignment of the conjugated backbone with the nematic director and an orientational order parameter, $S = 0.62$. The cyanobiphenyl pendant was found to align with the nematic director as well, as shown by FTIR dichroism of the C=O stretching vibration observed at 2224 cm$^{-1}$, resulting in $S = 0.73$. At a decreasing chiral mole fraction, films prepared with chiral–nematic copolymers showed a selective reflection band in the ultraviolet to visible and infrared regions. Moreover, the chiral–nematic film was found to consist of a left-handed helical stack of quasinematic layers with \((S)\cdot(-)-1\)-phenylethanol as the chiral moiety. The supramolecular structure representing the chiral–nematic film was further characterized with CPPL. On the basis of a recent theory, the orientational order of the conjugated backbone was evaluated at $S = 0.67$. The agreement between the $S$ values determined with the LPPL and CPPL techniques, 0.62 versus 0.67 within experimental uncertainty, validates the proposed supramolecular structure on the basis of which theories governing light absorption, emission, and propagation in structured media were constructed.

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Supporting Information Available: $^{13}$C NMR spectra of I, II, III-0.00, and III-0.23. This material is available free of charge via the Internet at http://pubs.acs.org.

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