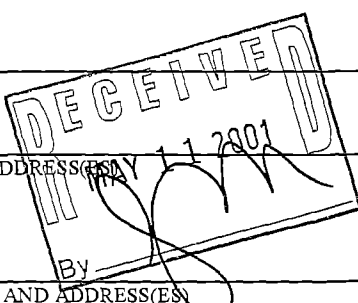


REPORT DOCUMENTATION PAGE

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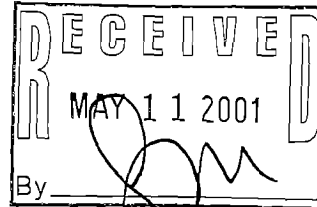
1. AGENCY USE ONLY (Leave Blank)		2. REPORT DATE 5-1-01	3. REPORT TYPE AND DATES COVERED Final: 5/1/99 - 8/31/00
4. TITLE AND SUBTITLE Tunable Optical Polymer Systems		5. FUNDING NUMBERS DADD19-99-1-0206	
6. AUTHOR(S) Samson Jenekhe			
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) University of Rochester Rochester, NY 14627			
9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES) U. S. Army Research Office P.O. Box 12211 Research Triangle Park, NC 27709-2211		8. PERFORMING ORGANIZATION REPORT NUMBER	
10. SPONSORING / MONITORING AGENCY REPORT NUMBER 39836-CH-MUR ✓ .15			
11. SUPPLEMENTARY NOTES The views, opinions and/or findings contained in this report are those of the author(s) and should not be construed as an official Department of the Army position, policy or decision, unless so designated by other documentation.			
12 a. DISTRIBUTION / AVAILABILITY STATEMENT Approved for public release; distribution unlimited.		12 b. DISTRIBUTION CODE	
13. ABSTRACT (Maximum 200 words) 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.			
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CONTRACT/GRANT NUMBER: DAAD19-99-1-0206

REPORT TITLE: Tunable Optical Polymer System,

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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TUNABLE OPTICAL POLYMER SYSTEMS (TOPS)

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**, **Jenekhe** 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/organometallic nanocomposites, 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 reactions (**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 nanostructures: 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**, **Jenekhe**) 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

			PAGE
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	1
09:40 - Break	(20 min.)		
10:00 - Tunable Reflection Systems			
10:00 - Liquid Crystalline Polymers with Tunable Optical Properties	(25 min.)	Shaw Chen	11
10:25 - Liquid Crystalline Conjugated Polymers as Multifunctional Optical Materials	(30 min.)	Dimitris Katsis	15
10:55 - Chromogenic Block Copolymer Assemblies	(25 min.)	Paula Hammond	42
11:20 - TOPS Test Beds	(25 min.)	Lewis Rothberg	65
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	83
15:25 - Tunable Electroluminescence in Conjugated Polymers	(25 min.)	Katie Meeker	102
15:50 - Aggregation Quenching in EL Polymers	(25 min.)	Pei Wang	122
16:15 - ECL and Light Emitting Devices	(25 min.)	Al Bard	133
16:40 - Additional Questions and Discussions			
17:00 - TOPS TAB/EAB Executive Session			

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.**

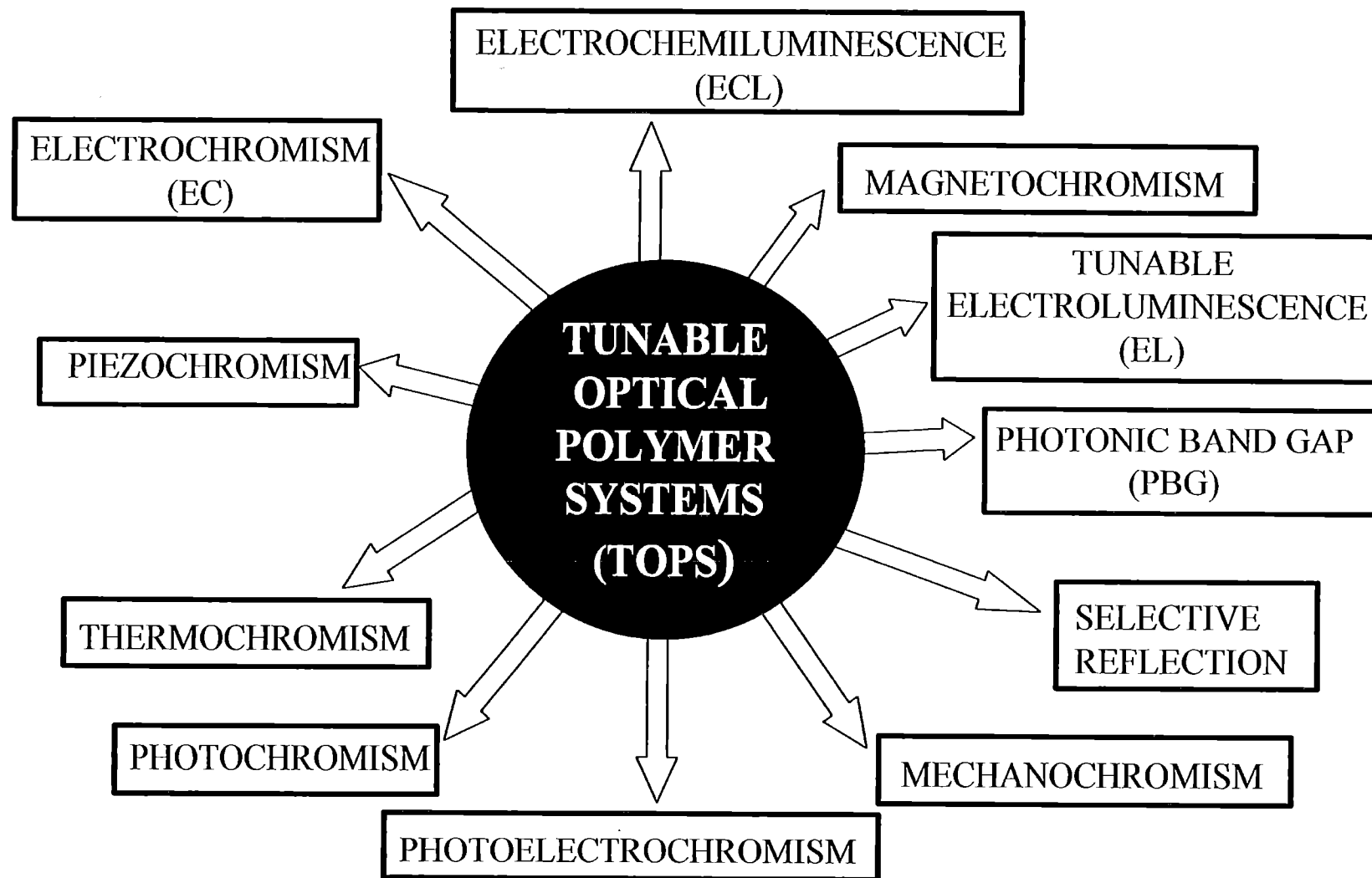
U. S. ARMY RESEARCH OFFICE
MURI GRANT #DAAD19-99-1-0206
TUNABLE OPTICAL POLYMER SYSTEMS (TOPS)

PUBLICATIONS

1. F. G. Gao and A. J. Bard "Solid-State Organic Light-Emitting Diodes Based on Tris(2,2'-bipyridine)ruthenium(II) Complexes" *J. Am. Chem. Soc.*, **122**, 7426-7427(2000).
2. X. Zhang and S. A. Jenekhe "Electroluminescence of Multicomponent Conjugated Polymers. 1. Roles of Polymer/Polymer Interfaces in Emission Enhancement and Voltage-Tunable Multicolor Emission in Semiconducting Polymer/Polymer Heterojunctions" *Macromolecules*, **33**, 2069-2082 (2000).
3. D. DeLongchamp and P. Hammond "Ion Conductive Polymer Multilayers for Electrochromic Applications" *ACS Polymer Preprints*, August (2000).
4. K. Meeker, L. Lu, S. A. Jenekhe, "Multicolor Emission and Tunable Electroluminescence from Blends of Conjugated Polymers" *ACS Polymer Preprints*, August (2000).
5. S. A. Jenekhe and S. Yi "Highly Photoconductive Nanocomposites of Metallophthalocyanines and Conjugated Polymers" *Adv. Mater.*, in press.
6. D. Katsis, H.-M. P. Chen, J. C. Mastrangelo, and S. H. Chen "Thermotropic Chiral-Nematic Poly(p-phenylene)s as Novel Multifunctional Optical Materials" *Adv. Mater.*, in press.
7. H. P. Chen, D. Katsis, J. C. Mastrangelo, K. L. Marshall, S. H. Chen, and T. H. Mourey, "Thermotropic Chiral-Nematic Poly(p-phenylene)s as a Paradigm of Helically Stacked π -Conjugated Systems" *Chem. Mater.*, in press.
8. H. P. Chen, D. Katsis, J. C. Mastrangelo, S. H. Chen, S. D. Jacobs, and P. J. Hood, "Glassy Liquid-Crystal Films with Opposite Chirality as High Performance Reflectors and Optical Notch Filters" *Adv. Mater.*, in press.
9. M. Quinto and A. J. Bard "Polymer Films on Electrodes. 29. Electropolymerized Poly(7,14-Diphenylacenaphtho[1,2-k]fluoranthene): Electrochemistry and Conductance of a Novel electrochromic Hydrocarbon Ladder Polymer Film" *J. Electroanalytical Chem.*, submitted.
10. D. Katsis, H. P. Chen, L. J. Rothberg, S. H. Chen, and T. Tsutsui, "Polarized Photoluminescence from Solid Films of Nematic and Chiral-Nematic Poly(p-phenylene)s" *Appl. Phys. Lett.*, submitted.
11. C. J. Collison, V. Tremanekarn, W. Oldham, and L. J. Rothberg "Aggregation Effect on the Structure and Optical Properties of a Model PV Oligomer" *Synthetic Metals*, submitted.
12. A. E. Pullen and T. M. Swager "Regiospecific Copolyanilines from Substituted Oligoanilines: Electrochemical Comparisons with Random Copolyanilines", *Macromolecules*, submitted.

13. T. Kar and S. Scheiner "Substituent Effect on the Protonation-Induced Red Shift of PPV-PyV Models", in preparation.
14. P. Wang, C. J. Collison, and L. J. Rothberg "Interchain Effects on Conjugated Polymer Photophysics", in preparation.
15. J. H. Hsu, W. S. Fann, L. J. Rothberg, K. R. Chuang, and S. A. Chen "Correlation Between Electronic Properties and Chain Length in a Phenylene Vinylene Conjugated Polymer", in preparation.
16. L. Marshall and L. J. Rothberg "Absolute Quantum Yield Determination in Thin Films Using Photoacoustic Calorimetry", in preparation.
17. J. D. Tovar and T. M. Swager "Naphthodithiophenes as a new class of functional electroactive materials: chemical and electrochemical investigations", in preparation for *J. Am. Chem. Soc.*
18. D. T. McQuade, A. H. Hegedus, and T. M. Swager "Signal Amplification of a Turn-On Sensor: Harvesting the Light Captured by a Conjugated Polymer," in preparation.
19. K. Meeker and S.A.Jenekhe " Effects of Inter- and Intrachain Emission Mechanisms and Selective Hole Injections on Tunable Luminescence of Polymer Blends," in preparation.
20. K. Meeker, S.A. Jenekhe, and A.J. Bard "Voltage-Tunable Multicolor Light-Emitting Diodes From Bilayers of Poly(p-phenylene vinylene)/Tris (2,2'-Bipyridine) Ruthenium Complexes" in preparation.
21. M. Quinto, S.A. Jenekhe, and A.J. Bard "Polymer Films on Electrodes. 30. Electrochemistry and SECM Characterization of Benzimidazole-Benzophenanthroline-Type Ladder (BBL) and Semiladder (BBB) Polymer Films" in preparation.
22. Alam, M.A. and S.A. Jenekhe, "Nanolayered Heterojunctions of Donor and Acceptor Conjugated Polymers of Interest in Light Emitting and Photovoltaic Devices: Photoinduced Electron Transfer at Polythiophene/Polyquinoline Interfaces" in preparation.

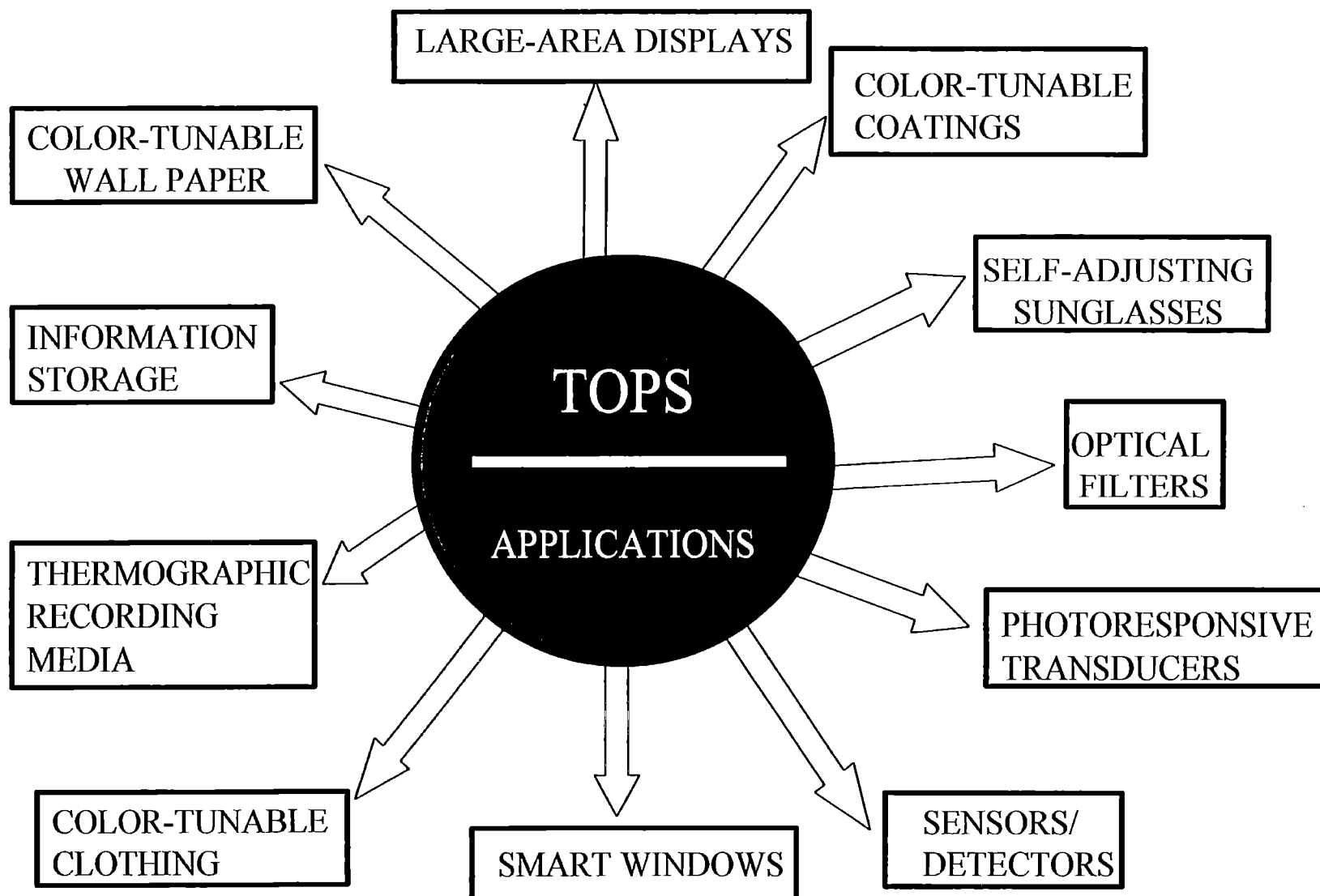
CHROMOGENIC PHENOMENA IN POLYMERS



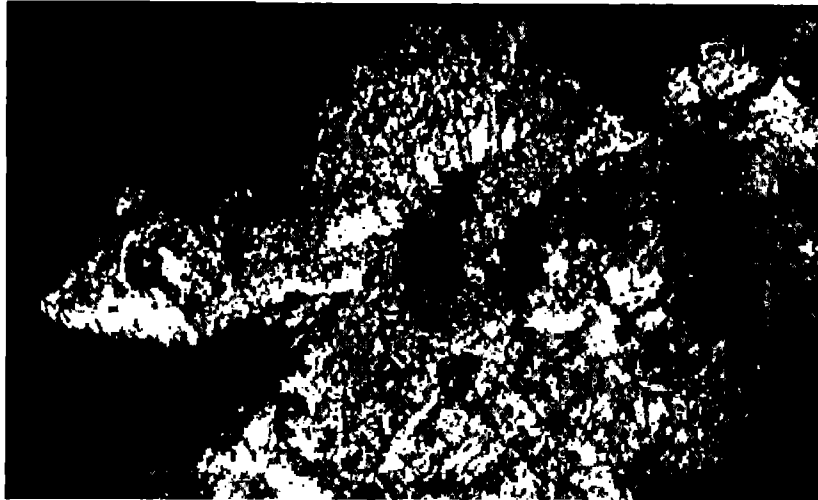
S. A. JENEKHE

ARO TOPS MURI

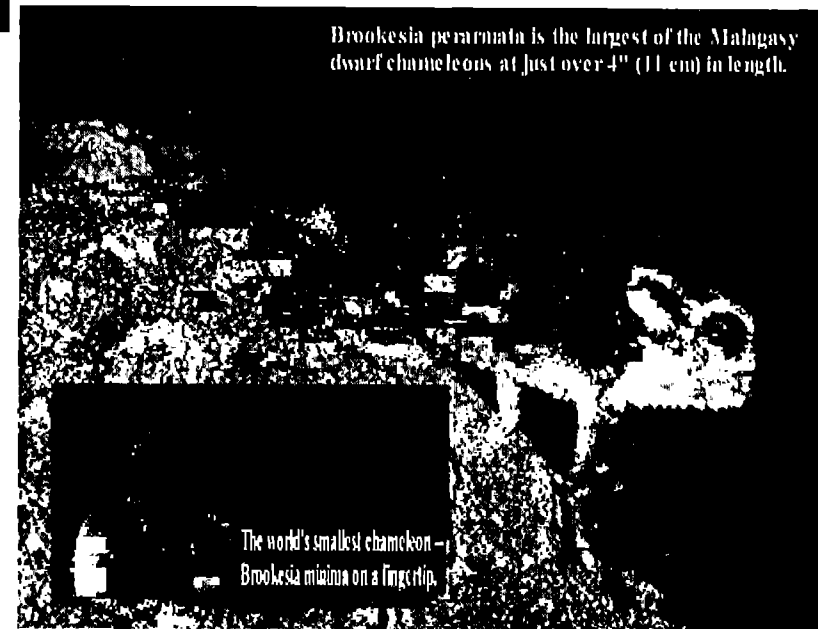
TUNABLE OPTICAL POLYMER SYSTEMS



CHAMELEONS AND THE FUTURE OF TOPS



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



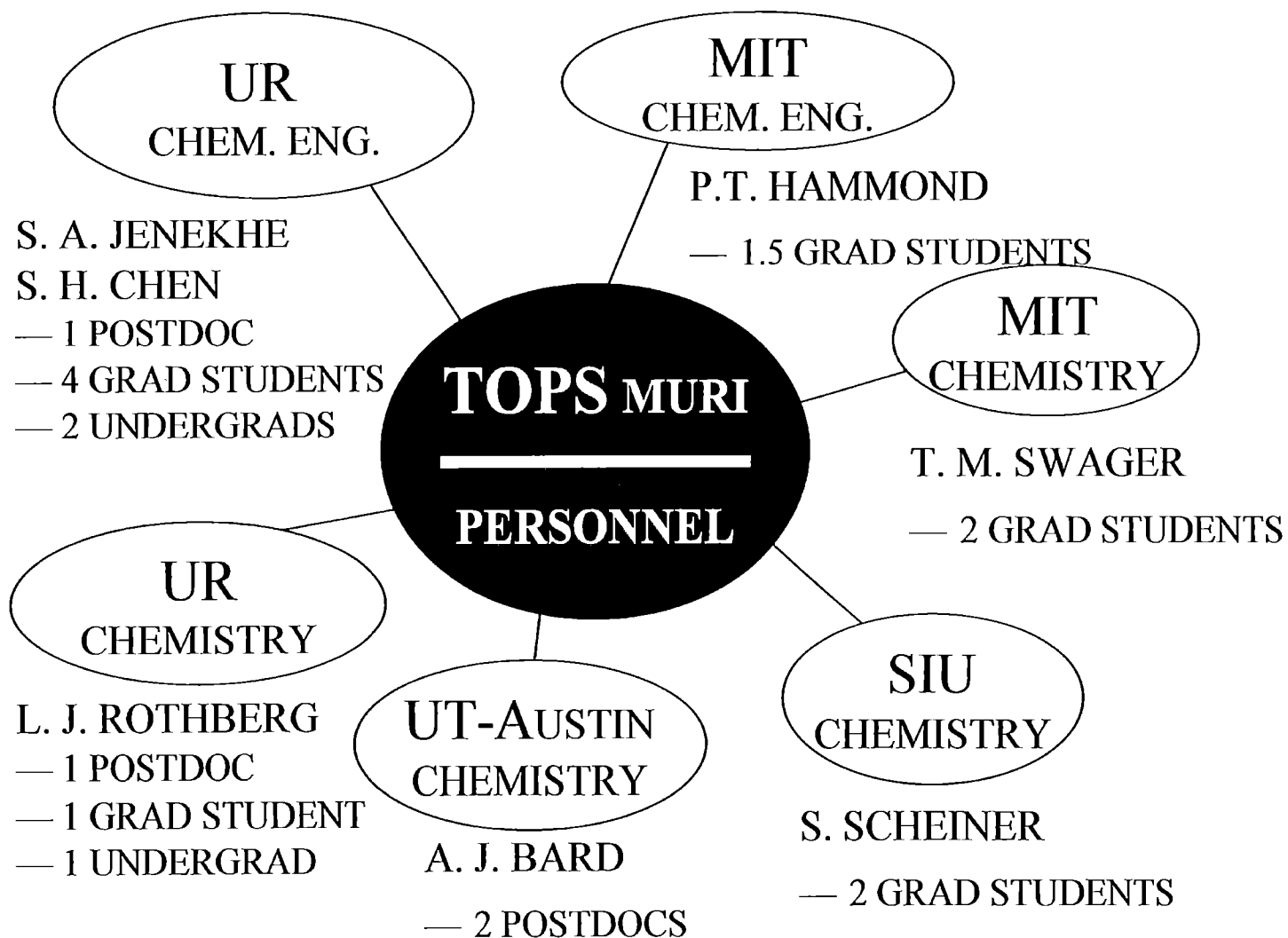
Brookesia perarmata is the largest of the Malagasy dwarf chameleons at just over 4" (11 cm) in length.

The world's smallest chameleon –
Brookesia minima on a fingertip.

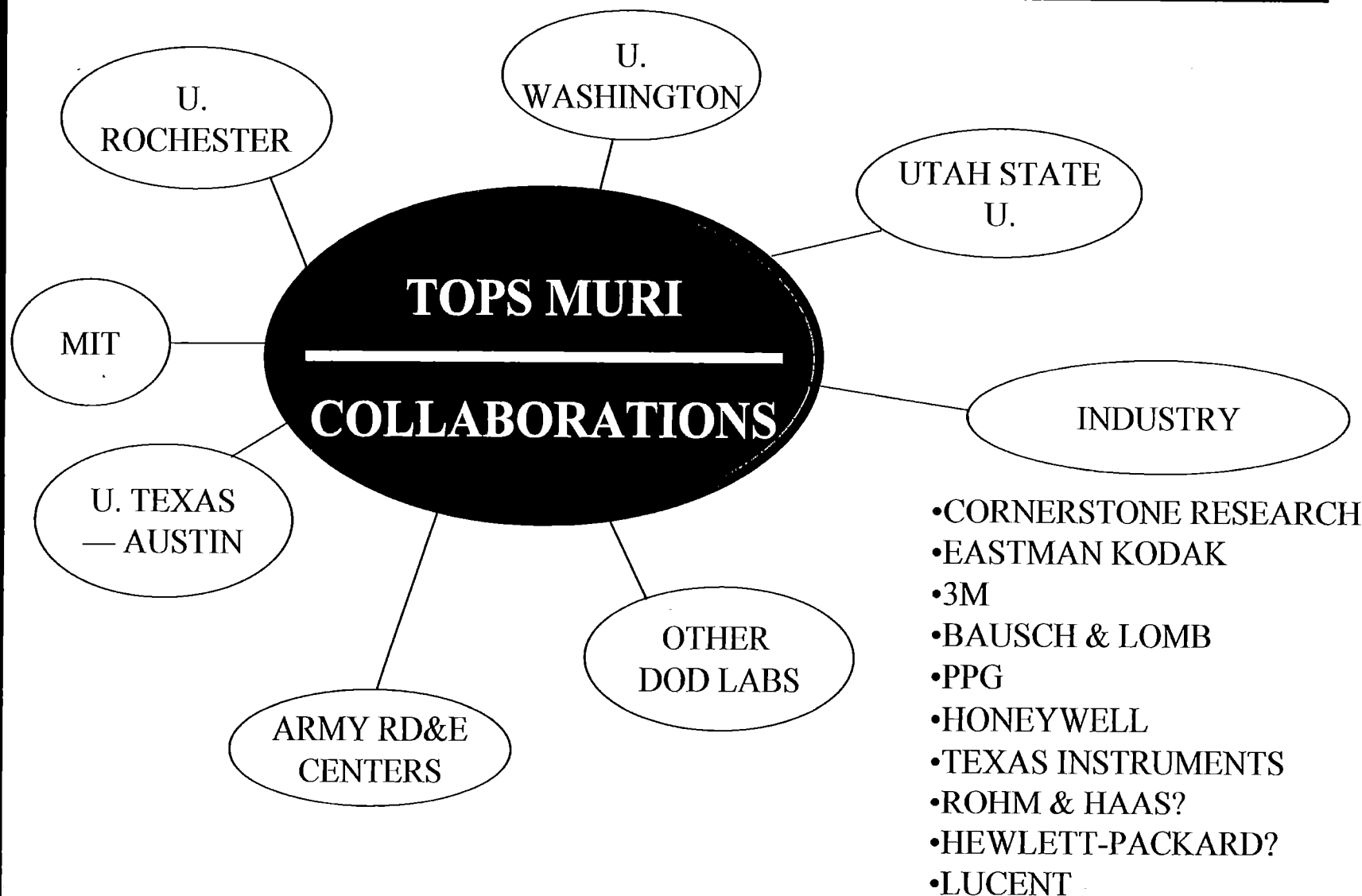
ARO TOPS MURI

S. A. JENEKHE

ACADEMIC RESEARCH PERSONNEL



INSTITUTIONAL COLLABORATIONS



S. A. JENEKHE

ARO TOPS MURI

SCIENTIFIC GOALS OF TOPS MURI

I. Design, synthesis, characterization and processing of new generation of chromogenic polymers for optoelectronic and photonic applications

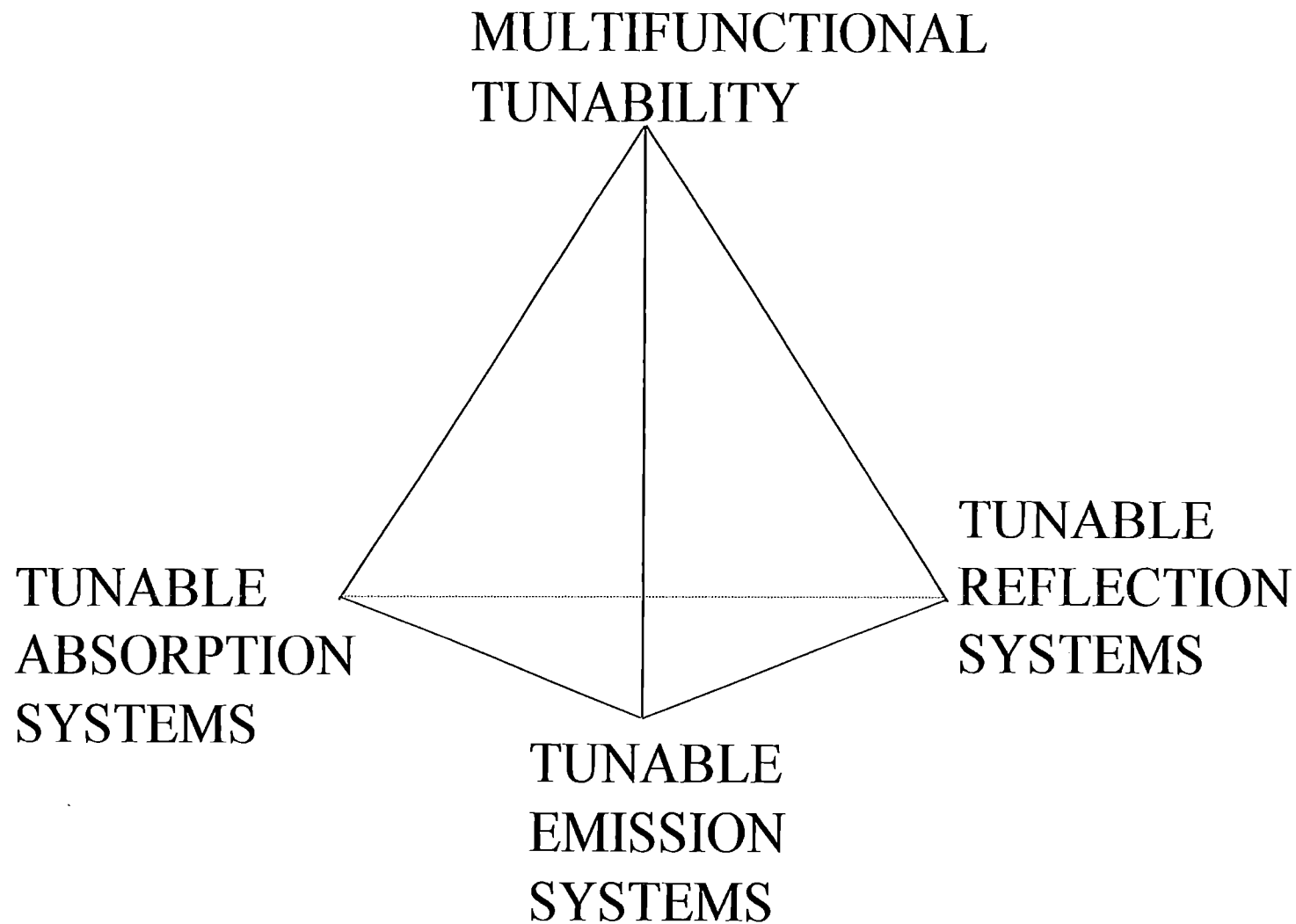
- Structural design at the electronic, molecular, supramolecular, nanostructure and macroscopic levels
- New synthetic methodologies
- New paradigms for self-assembly of nanostructures and for polymer processing
- Enhanced chromogenic effects
- Lower switching energies
- Improved durability and switching 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

TOPS MURI RESEARCH GROUPS



S.A. JENEKHE

ARO TOPS MURI

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-Assembly 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

yi5099s3rep

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

yi5099s3rep

S.A. JENEKHE

ARO TOPS MURI

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

yi5099s3rep

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)₃²⁺ 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**
 - pigmentary 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 $\Rightarrow$ “smart skins”
 - nervous control of color change $\Rightarrow$ “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**
 - H. P. Chen, D. Katsis, J. C. Mastrangelo, K. L. Marshall, S. H. Chen, and T. H. Mourey, "Thermotropic Chiral-Nematic Poly(*p*-phenylene)s as a Paradigm of Helically Stacked π -Conjugated Systems," *Chem. Mater.* (in press).
 - H. P. Chen, D. Katsis, J. C. Mastrangelo, S. H. Chen, S. D. Jacobs, and P. J. Hood, "Glassy Liquid-Crystal Films with Opposite Chirality as High Performance Reflectors and Optical Notch Filters," *Adv. Mater.* (in press).
 - D. Katsis, H. P. Chen, L. J. Rothberg, S. H. Chen, and T. Tsutsui, "Polarized Photoluminescence from Solid Films of Nematic and Chiral-Nematic Poly(*p*-phenylene)s," *Appl. Phys. Lett.* (submitted).

Liquid Crystalline Conjugated Polymers as Multifunctional Optical Materials

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

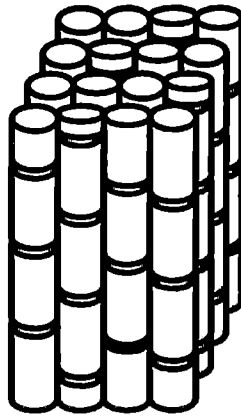
**Department of Chemical Engineering, Materials Science Program
Laboratory for Laser Energetics, Room 1210, COI, University of Rochester**

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

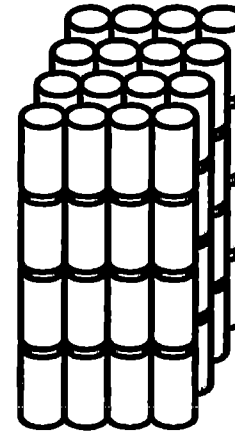
TOPS MURI Review Meeting, 15-16 August 2000, Natick, MA

Four Types of Liquid Crystalline Order

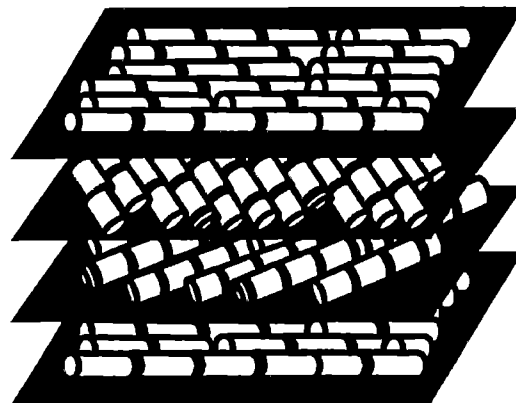
Nematic



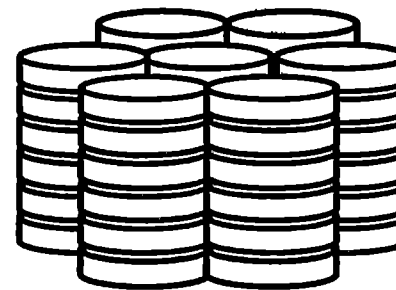
Smectic



Cholesteric



Columnar



Characteristic Textures of Liquid Crystals Observed with Polarizing Optical Microscopy

Nematic



Smectic



Cholesteric

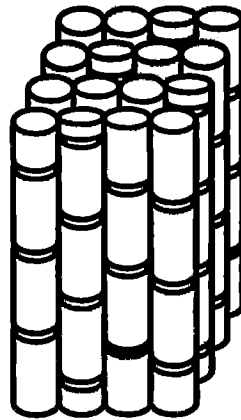


Columnar

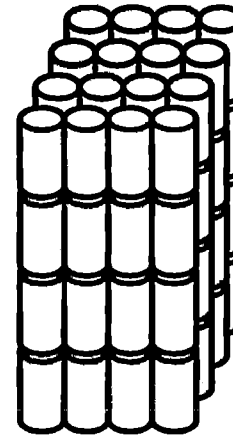


Four Types of Liquid Crystalline Order

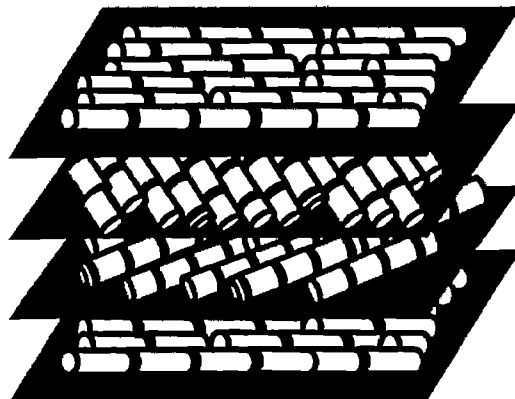
Nematic



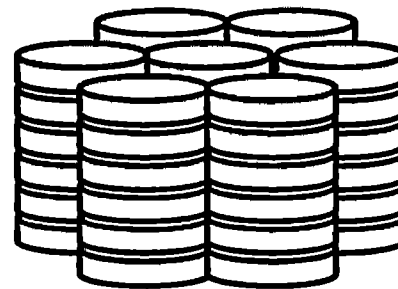
Smectic



Cholesteric

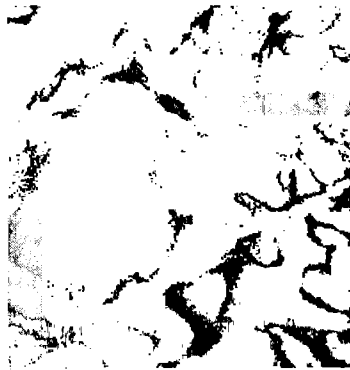


Columnar



Characteristic Textures of Liquid Crystals Observed with Polarizing Optical Microscopy

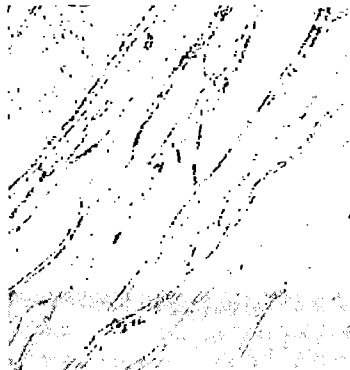
Nematic



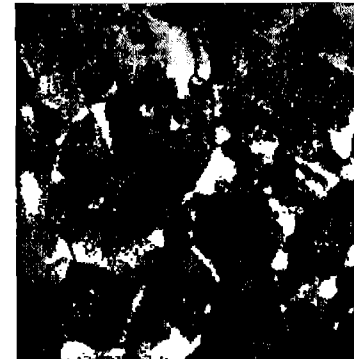
Smectic



Cholesteric

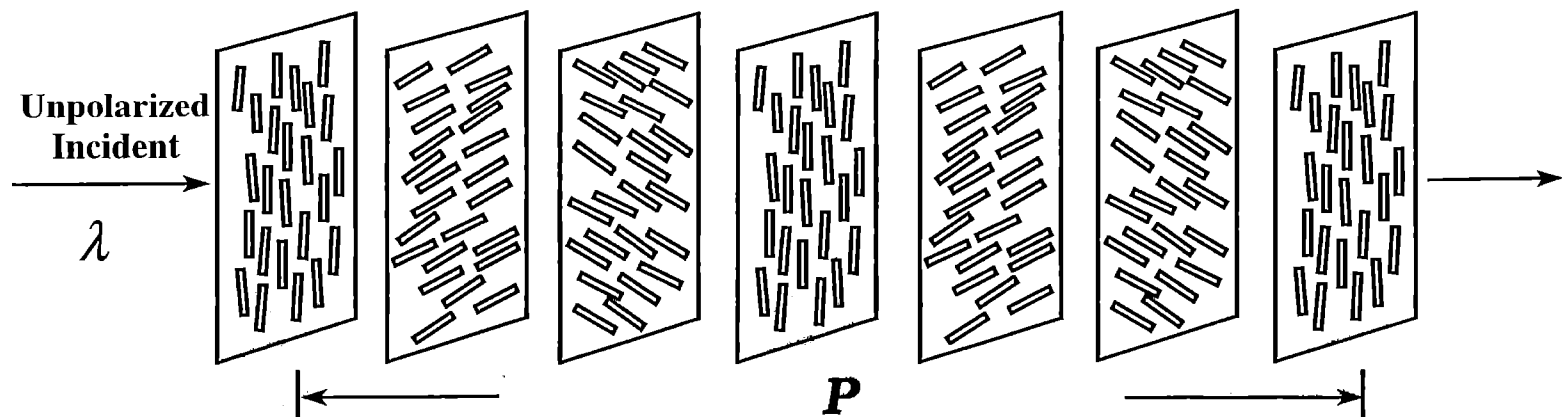


Columnar



Coloration via Selective Reflection

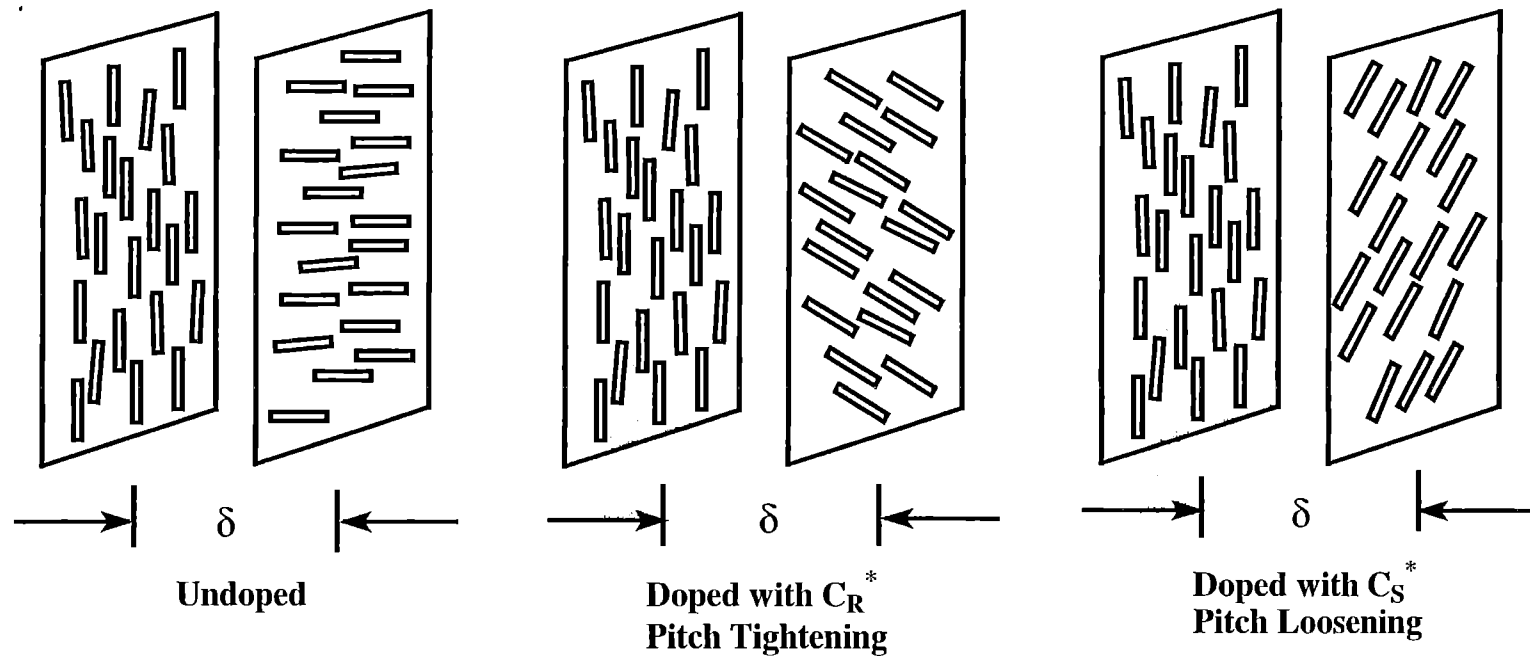
- Chiral-nematic liquid crystalline film as a helical stack of quasinematic layers, illustrated below with a LH structure:



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



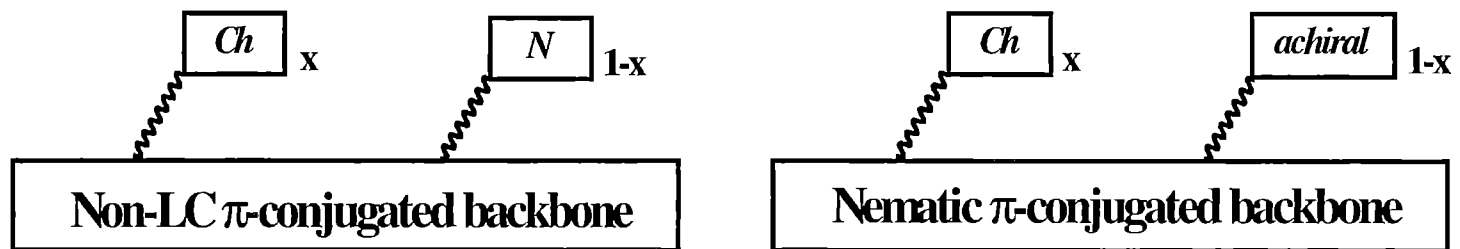
Existing Chiral-Nematic Materials

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

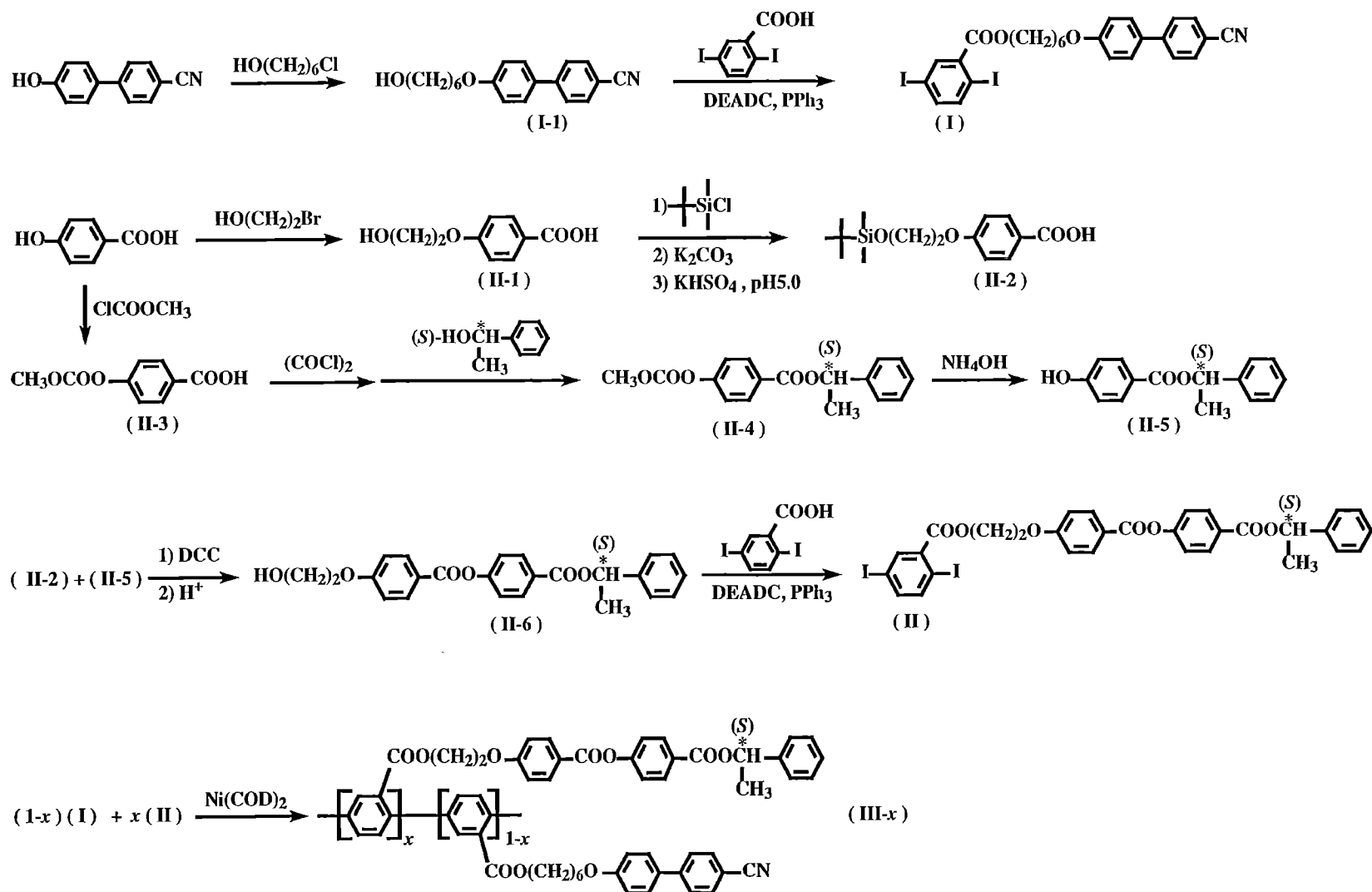
All these are nonconjugated systems with tunable reflection color by various means

Multifunctional LC Polymers

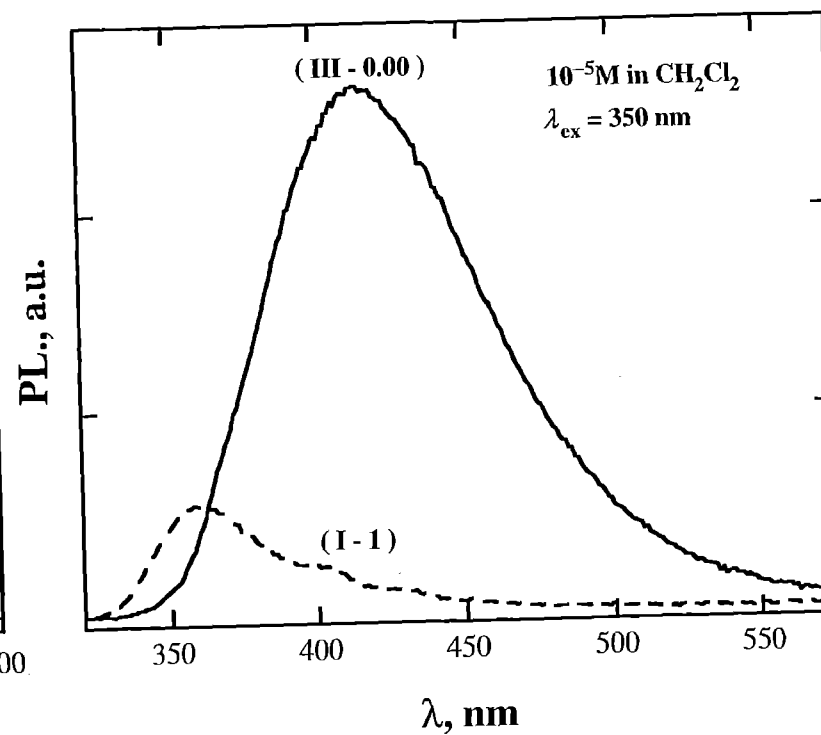
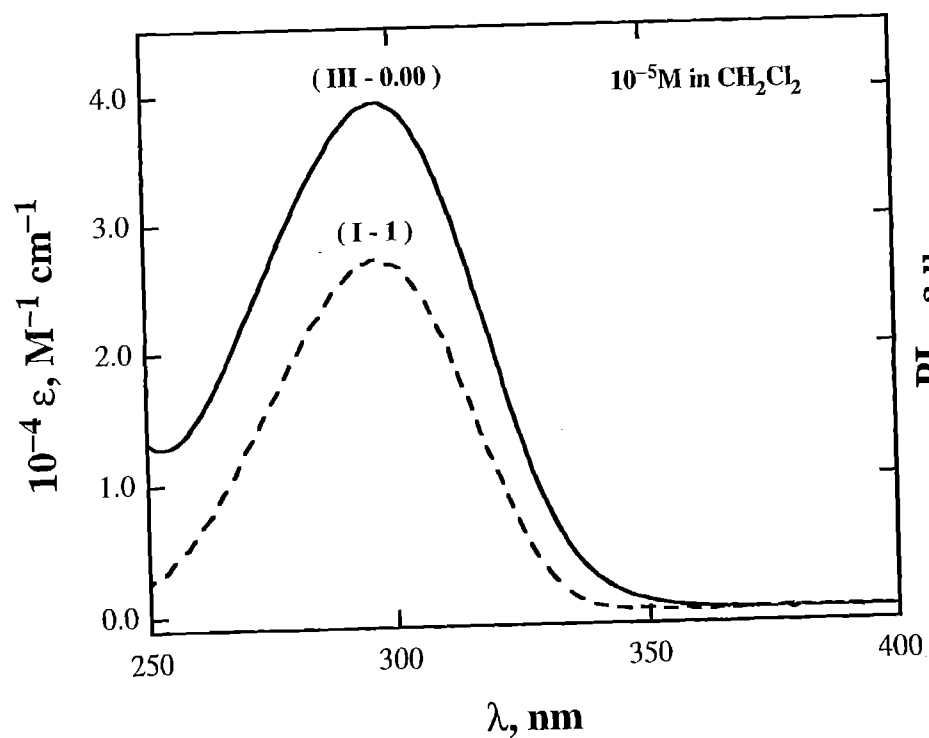
- Amorphous or crystalline conjugated polymers capable of tunable absorption and emission
- Chiral-nematic nonconjugated polymers capable of tunable reflection
- A new challenge: chiral-nematic conjugated polymers for multiple modes of tunability



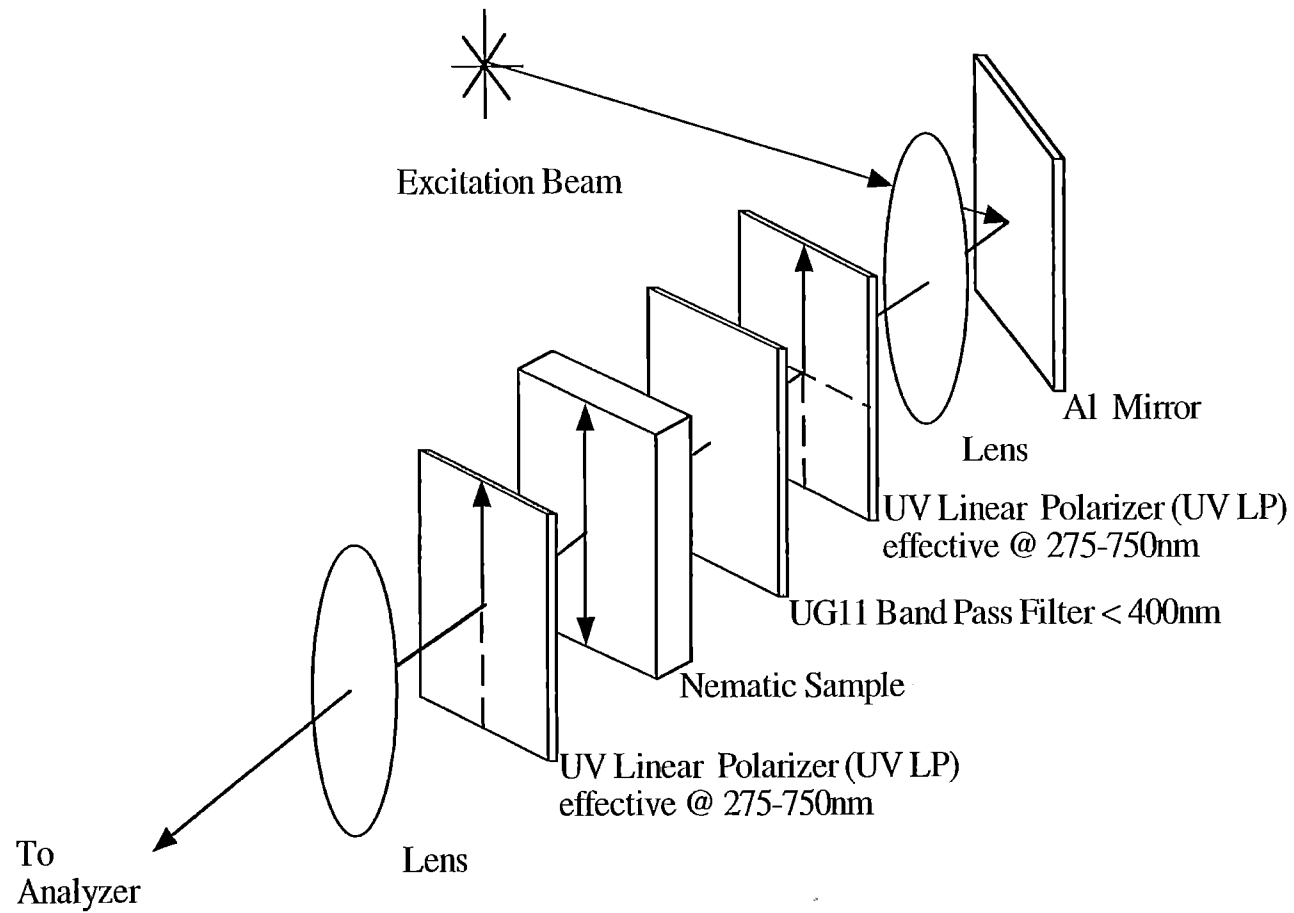
Synthetic Scheme for Chiral-Nematic Poly(*p*-phenylene)s



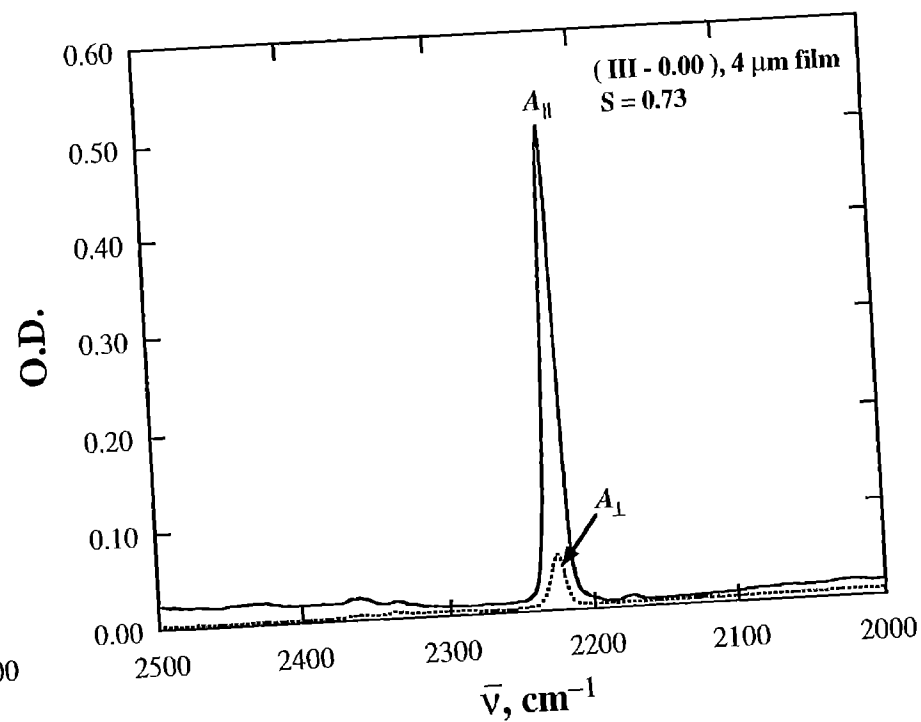
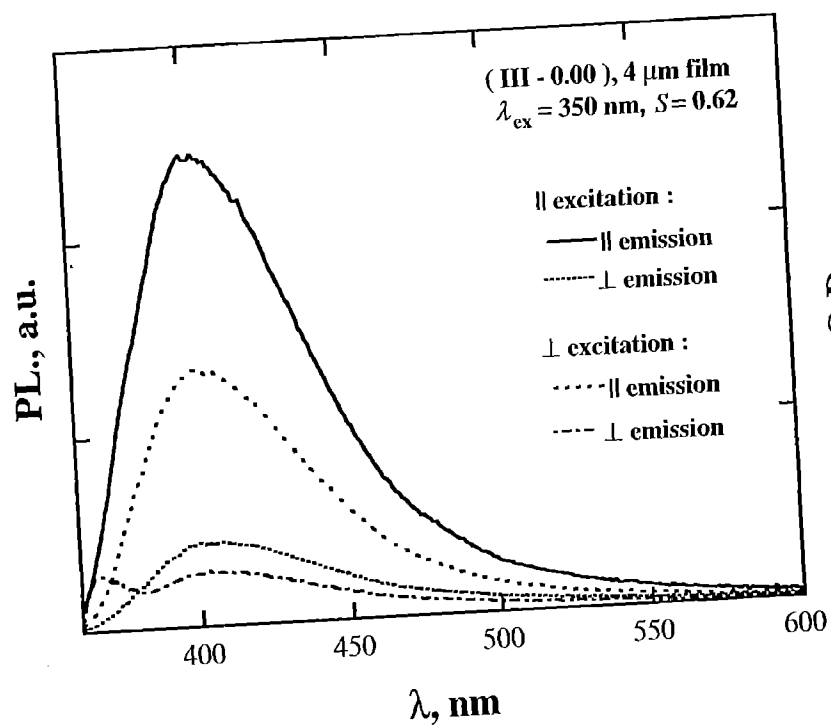
Absorption and Emission Spectra in Dilute Solution



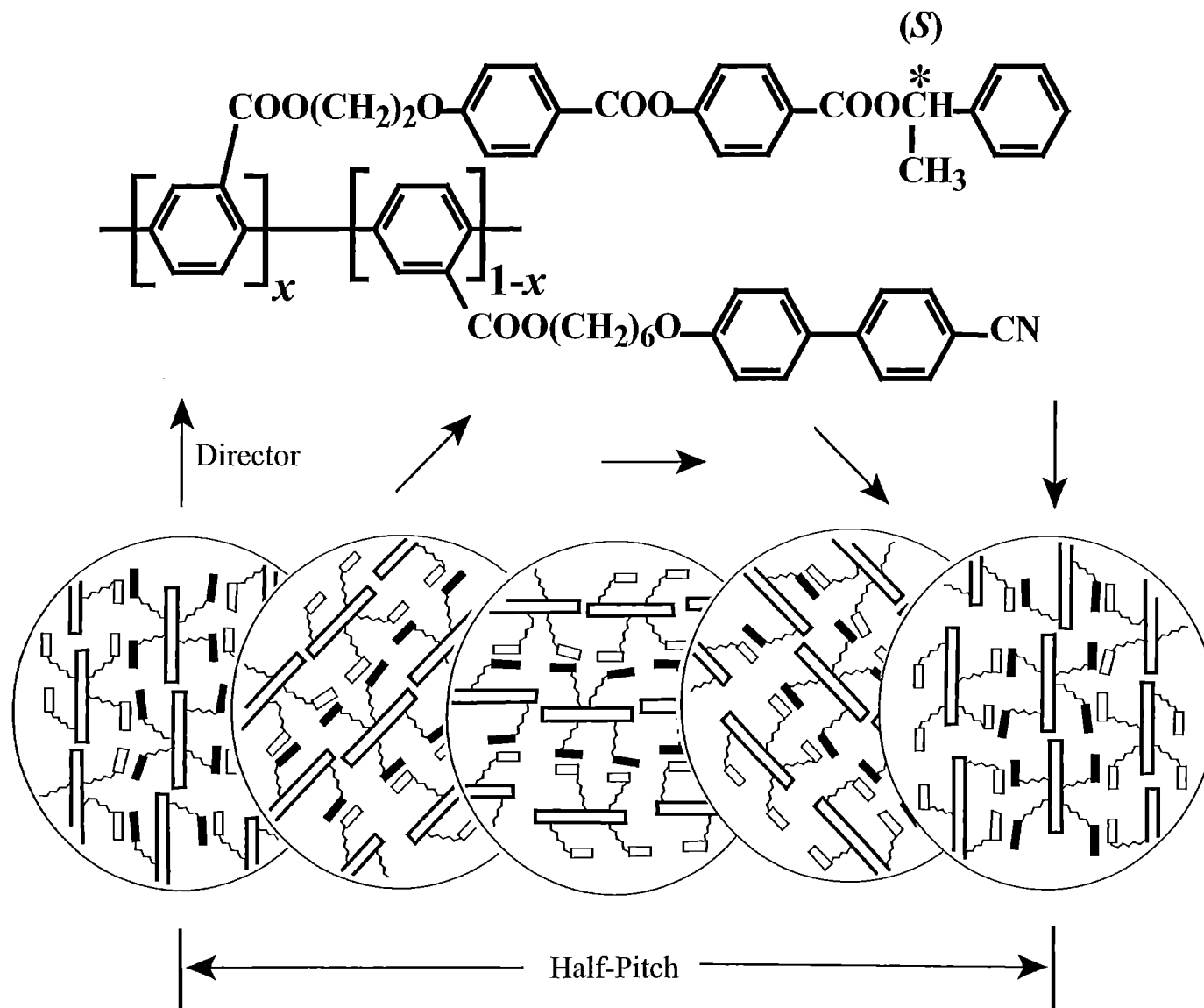
Optical Set-Up for Characterization of LPPL



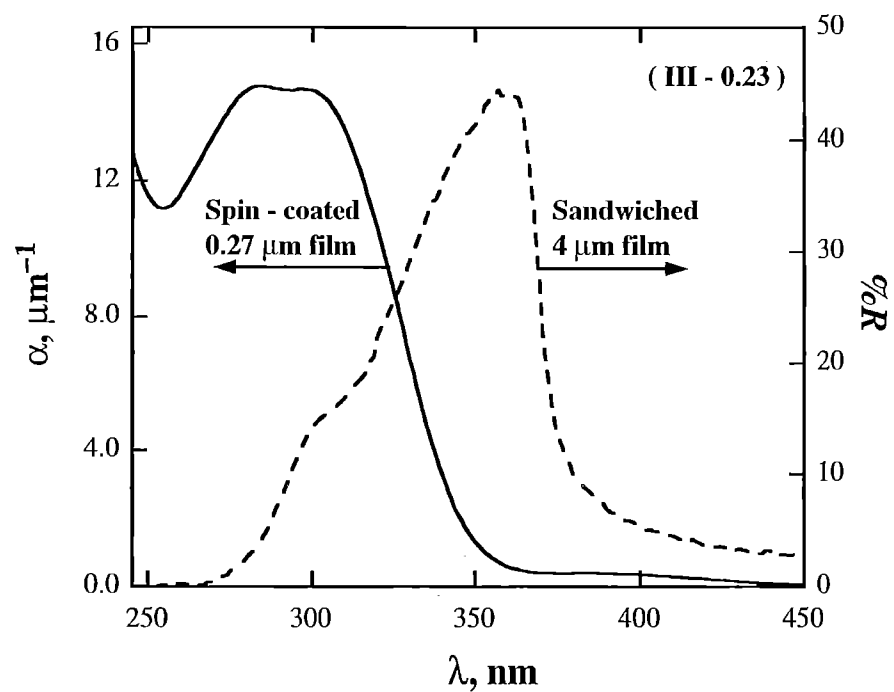
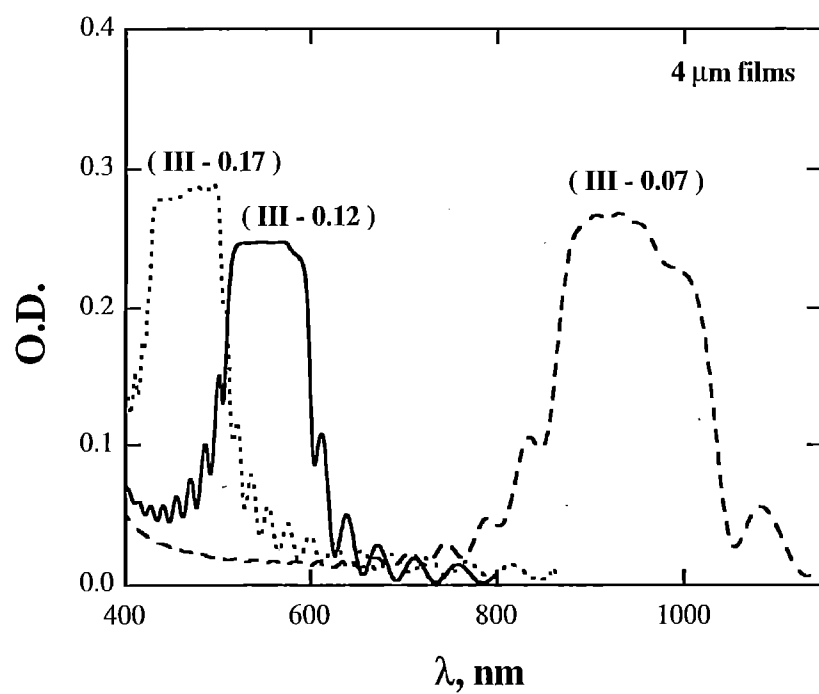
Characterization of the Alignment of Conjugated Backbones and Nematic Pendants



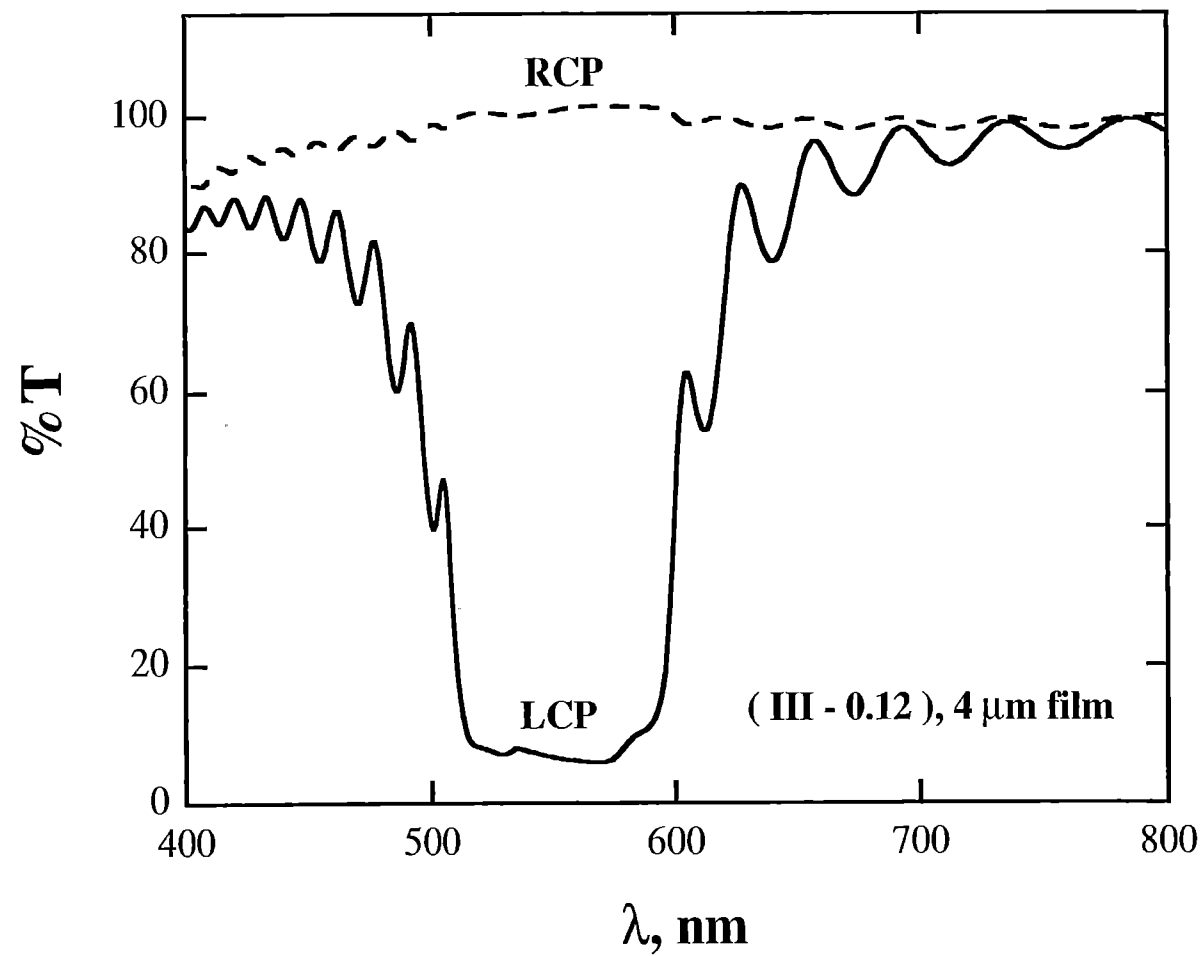
Supramolecular Structure of Chiral-Nematic Poly(*p*-phenylene)s



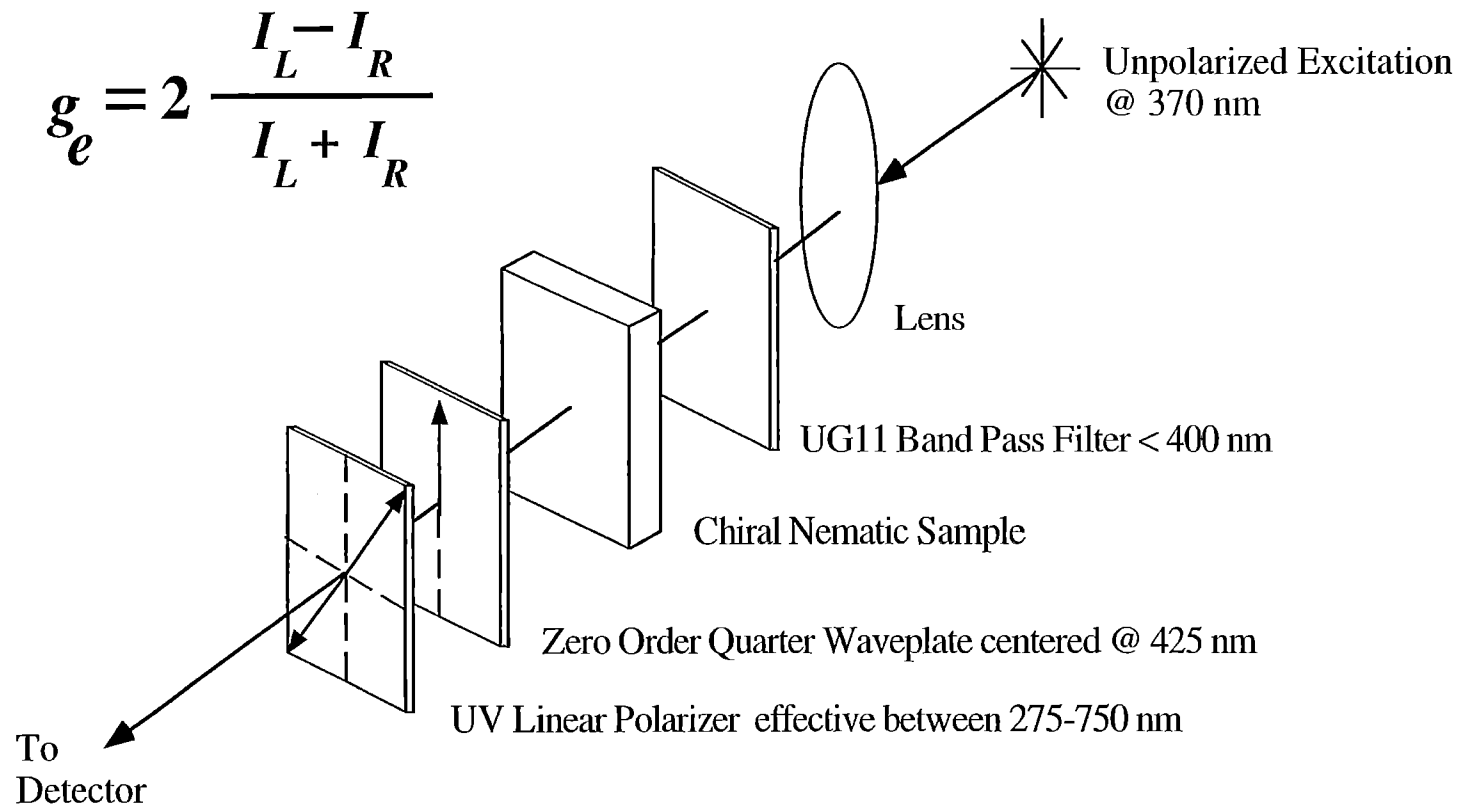
Absorption and Selective Reflection of Thin Films



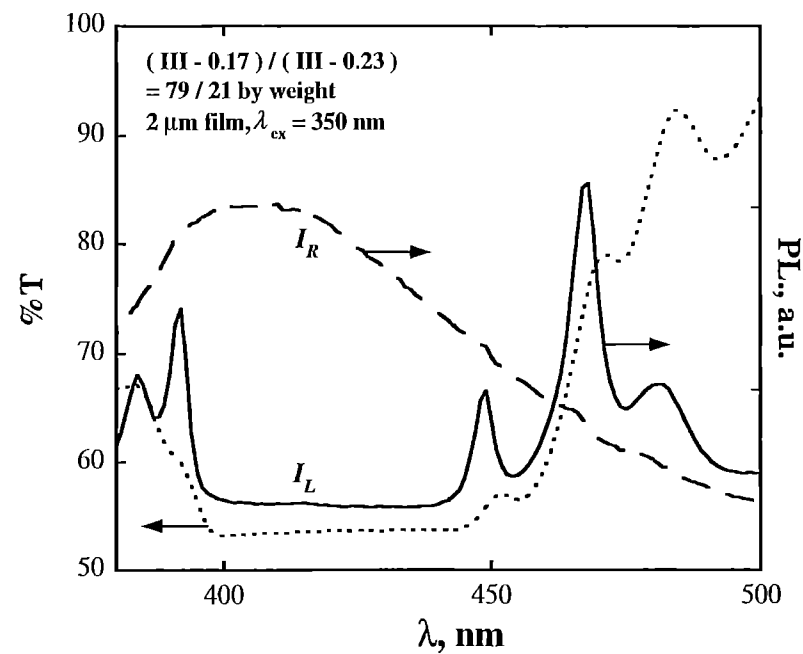
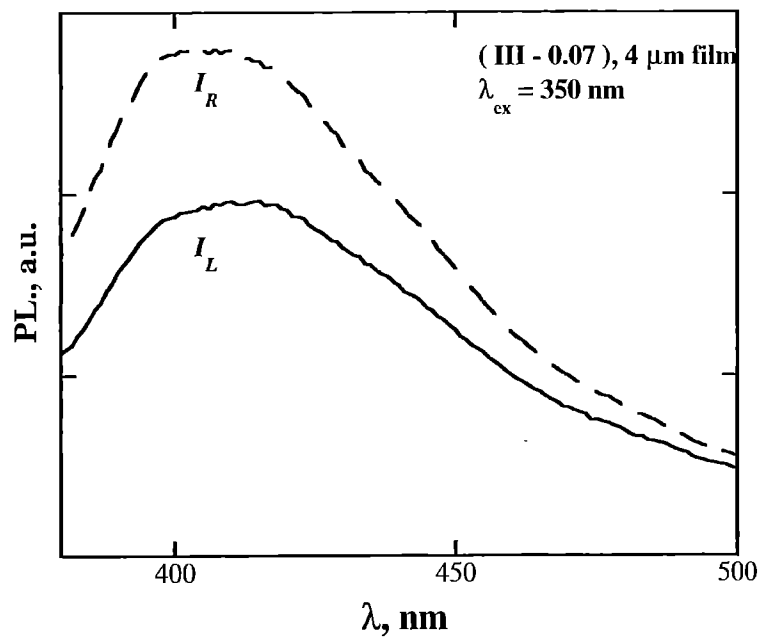
Transmission of Circularly Polarized Light



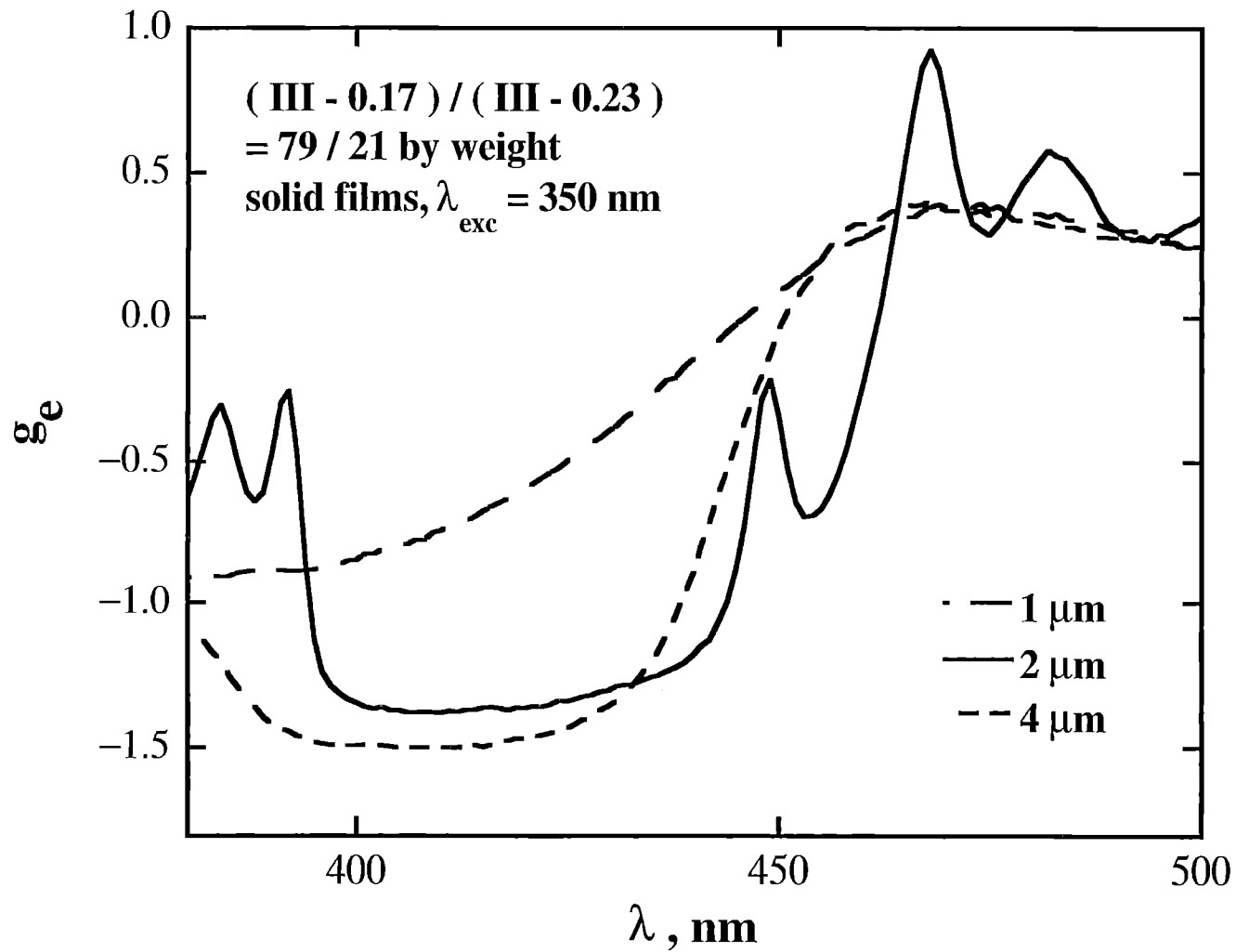
Optical Set-Up for Characterization of CPPL



Spectra of Circularly Polarized Photoluminescence from Thin Films

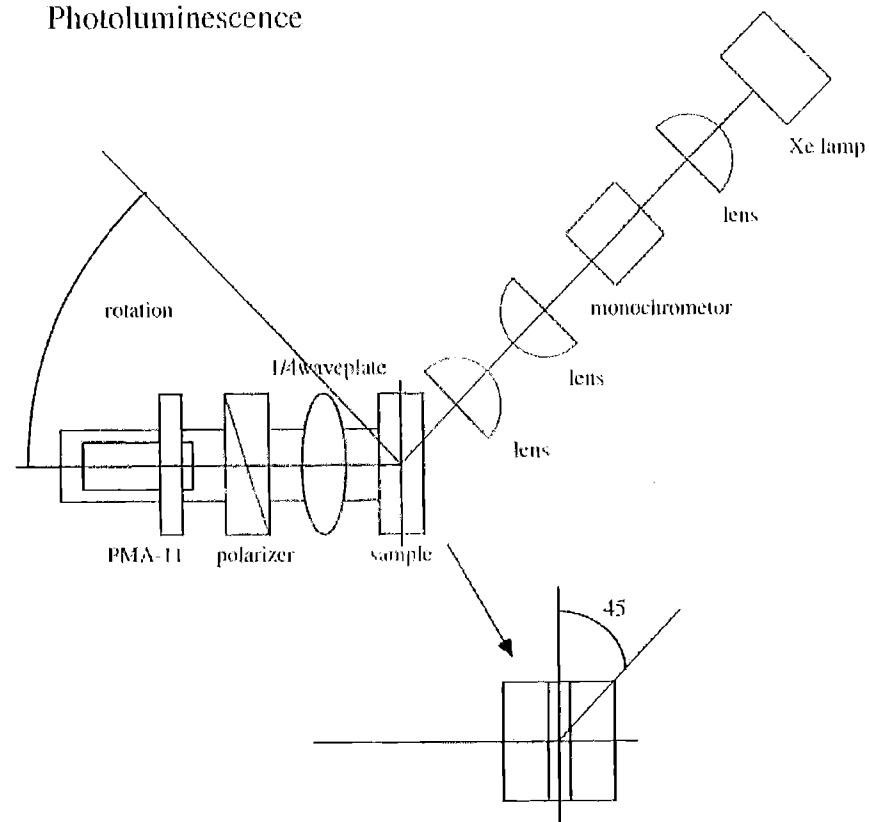


Effect of Film Thickness on Degree of Circular Polarization

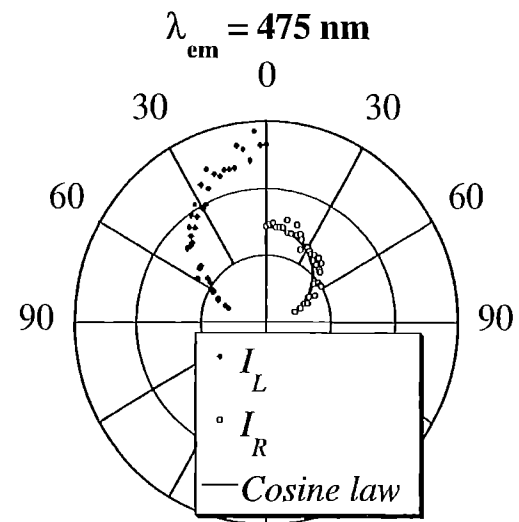
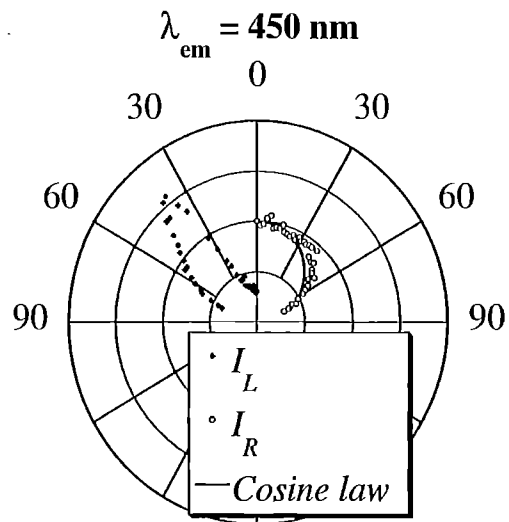
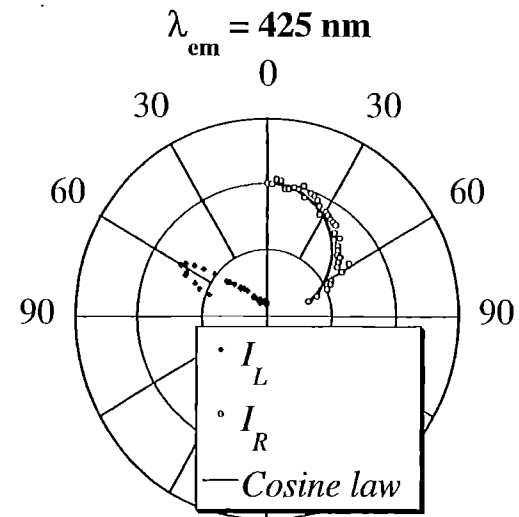
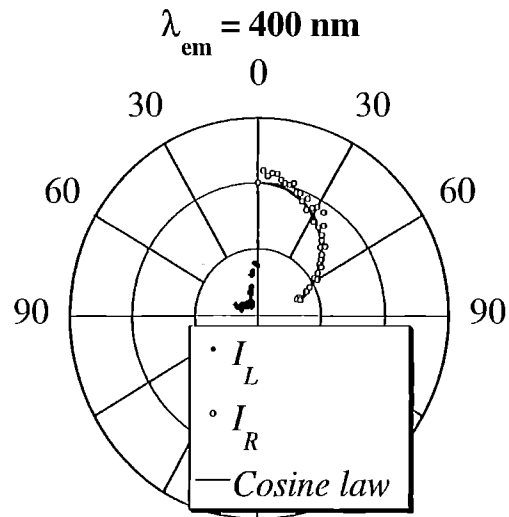


Optical Set-Up for Characterization of Viewing Angle Dependence

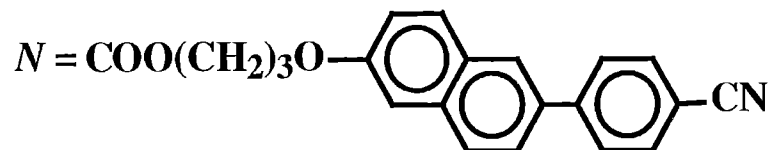
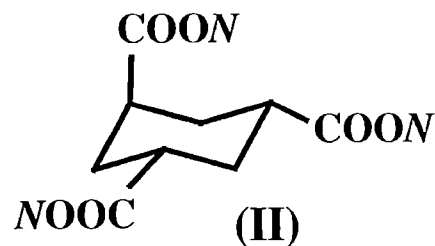
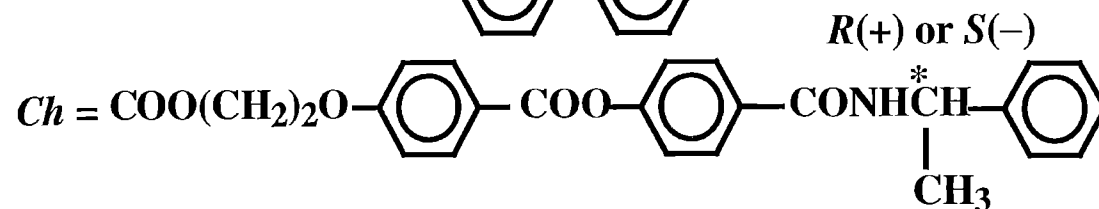
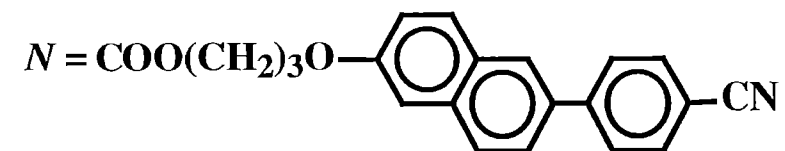
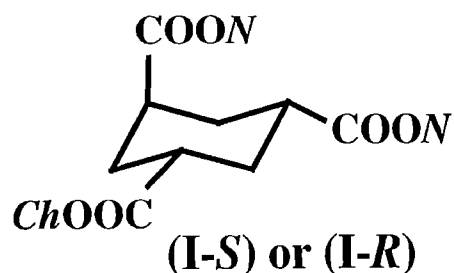
Photoluminescence



Viewing Angle Dependence Of CPPL

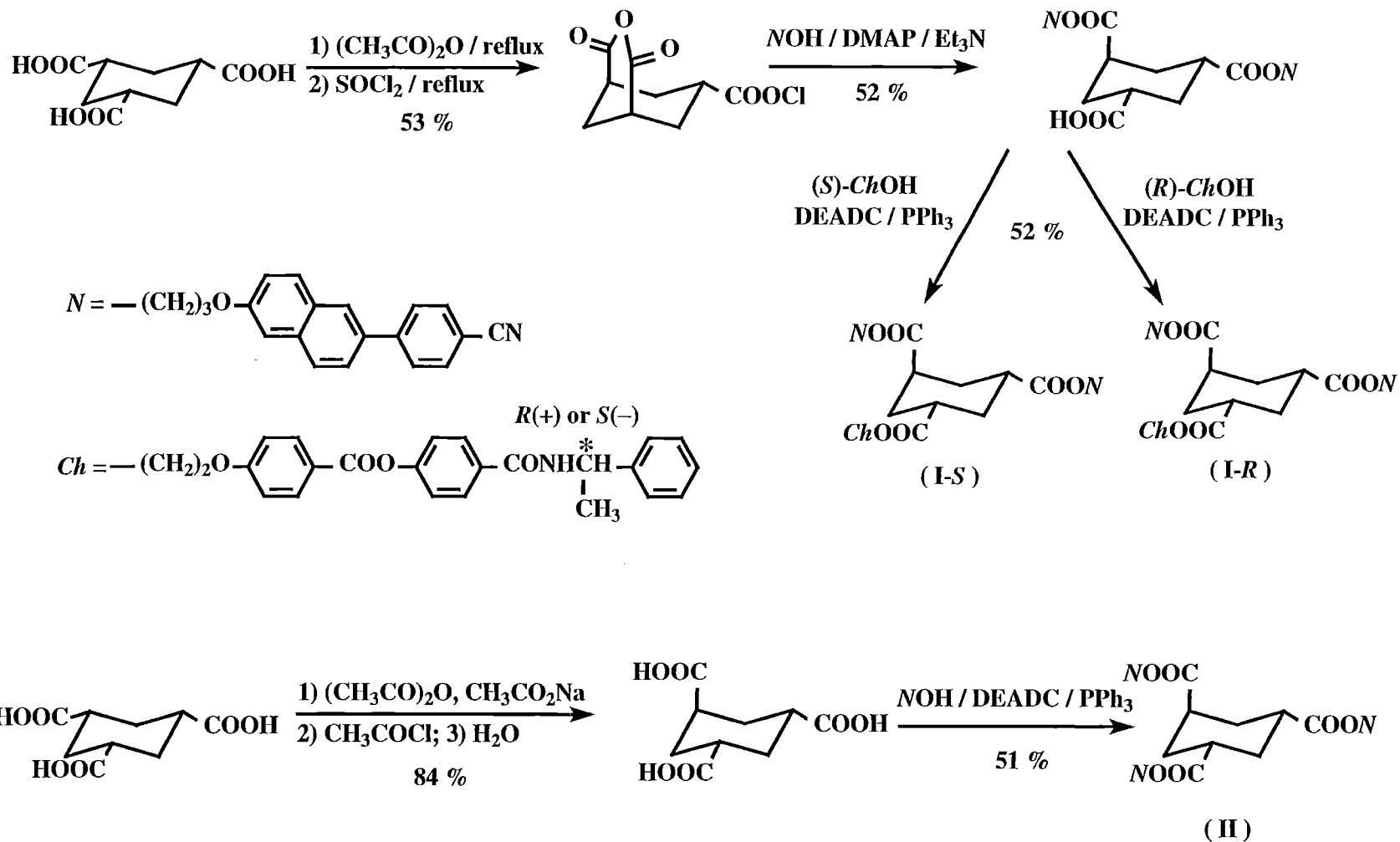


Glass-Forming Chiral-Nematic Liquid Crystals



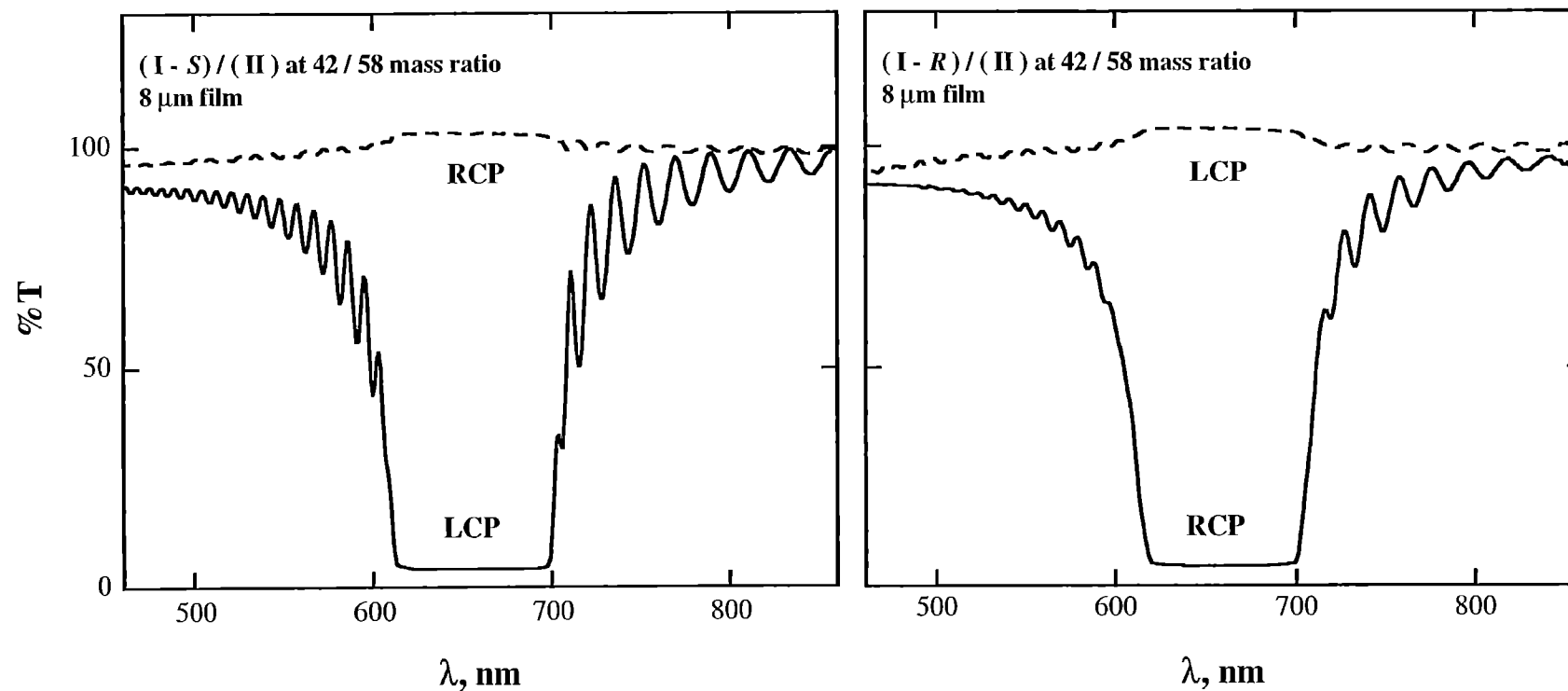
- Ease of processing into large area, monodomain, vitrified films
- Environmental durability
- Availability of both enantiomers
- Selective reflection tunable from UV to IR depending on ratio (I)/(II)

Material Synthesis

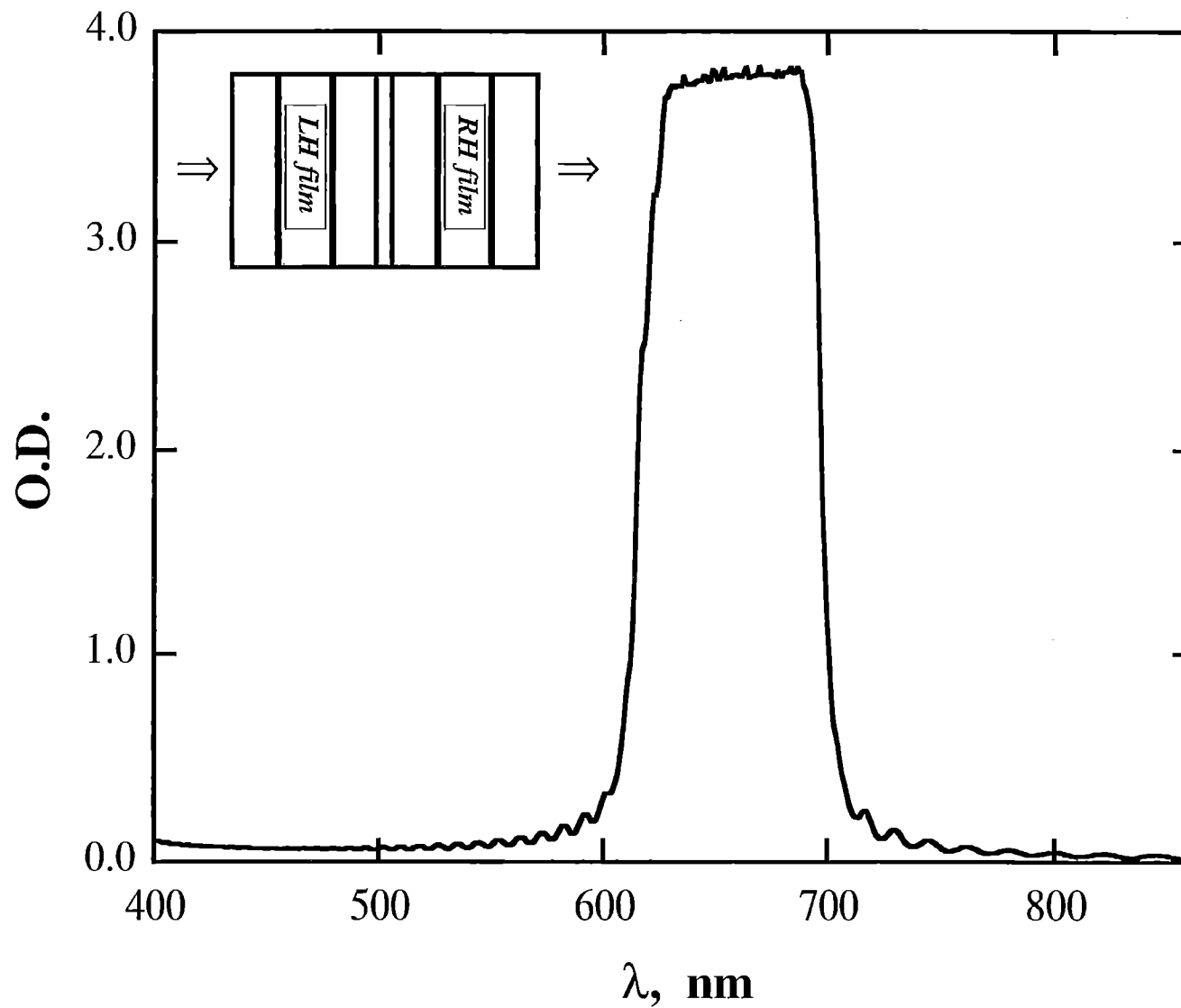


DMAP: 4-(dimethylamino)pyridine; DEADC: diethyl azodicarboxylate; PPh₃: triphenylphosphine

Transmission of Circularly Polarized Light through Glassy Chiral-Nematic Films



High-Performance Reflector and Notch Filter



Conclusions

- Chiral-nematic poly(*p*-phenylene)s were shown to self-assemble into helically stacked π -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

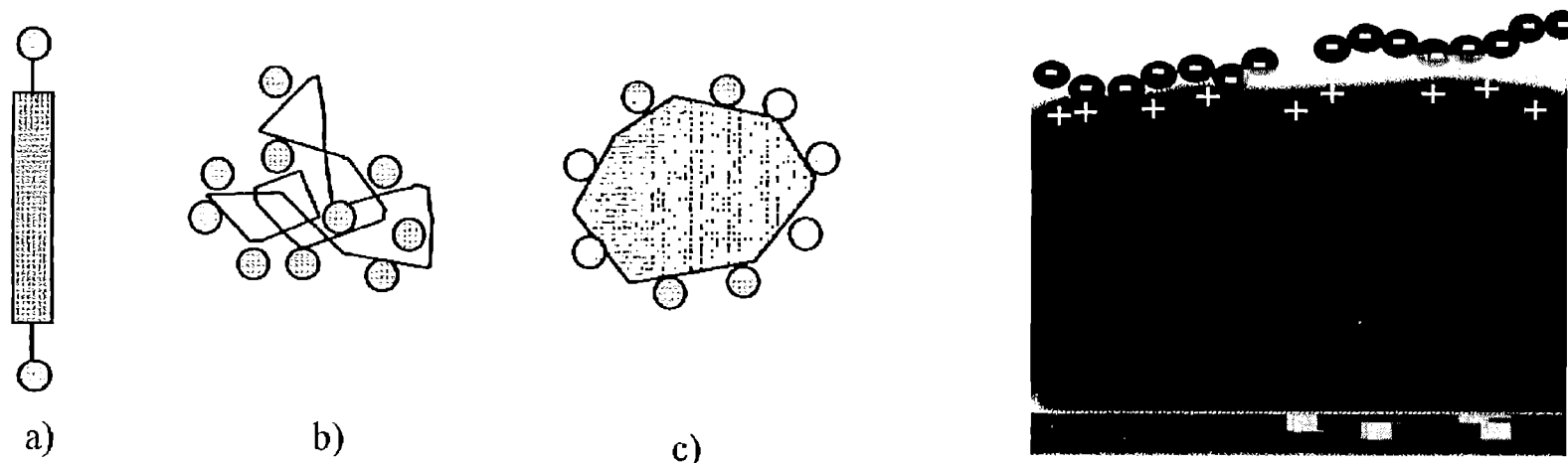
ARO MURI

TOPS Objectives - Mesostuctured 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

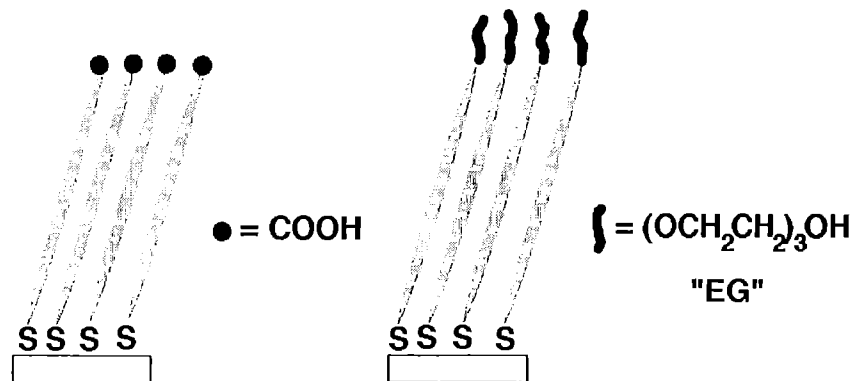
Photolithography

- expensive both in capital and operating cost
- not suitable for patterning non-planar surface
- ineffective in generating 3-D structures
- difficult for introducing specific chemical functionality

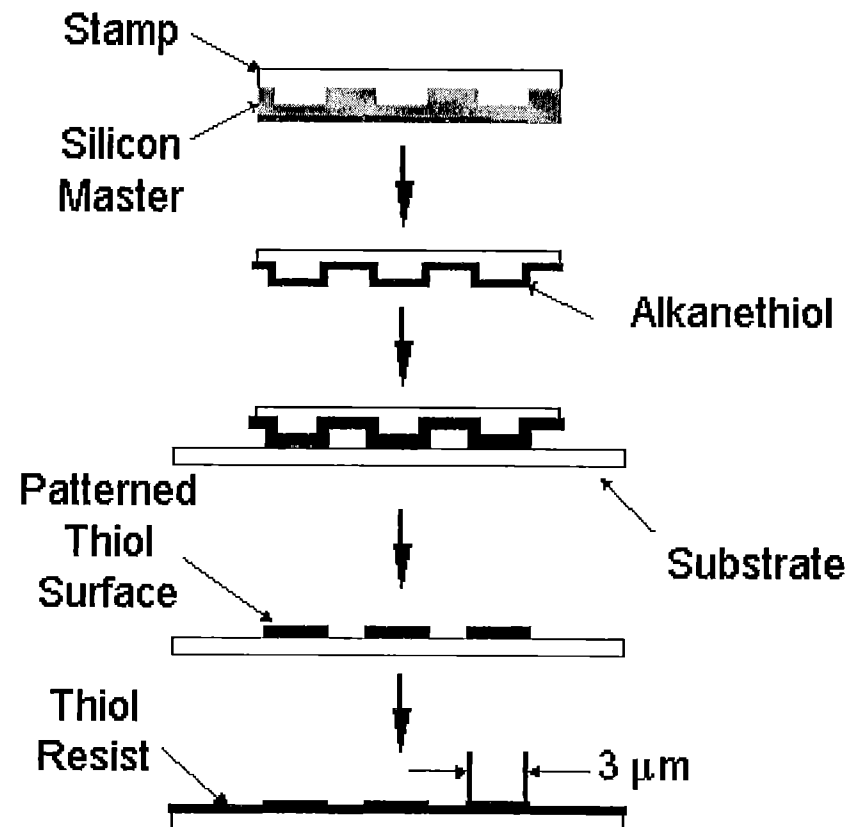
Chemistry-templated assembly

- little capital investment, procedurally simple
- access to new types of surfaces, optical structures, sensors and prototype devices etc.
- not subject to the limitations set by optical diffraction and optical transparency

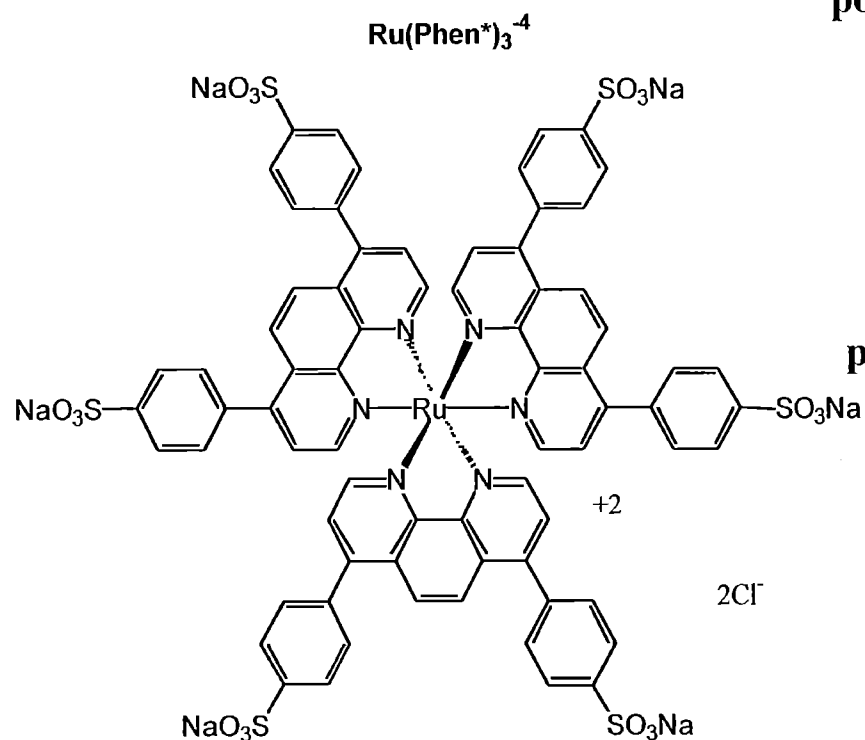
Self-Assembled Monolayers(SAMs) and Micro-contact Printing(μ CP)



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

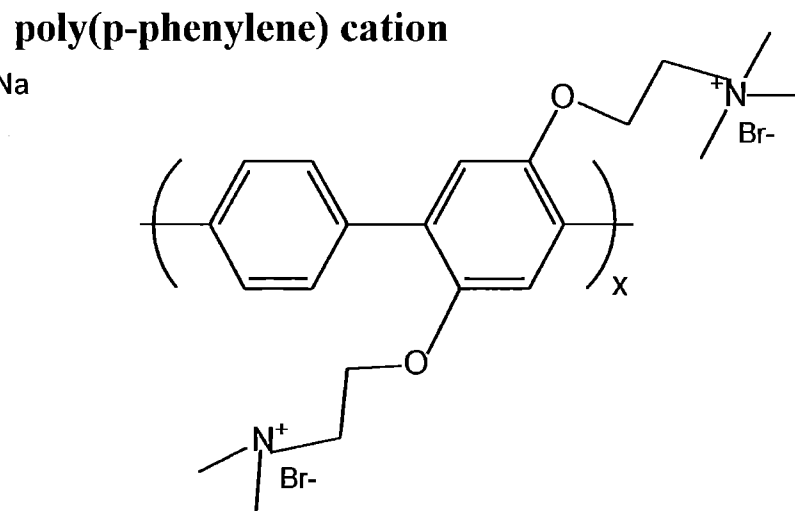
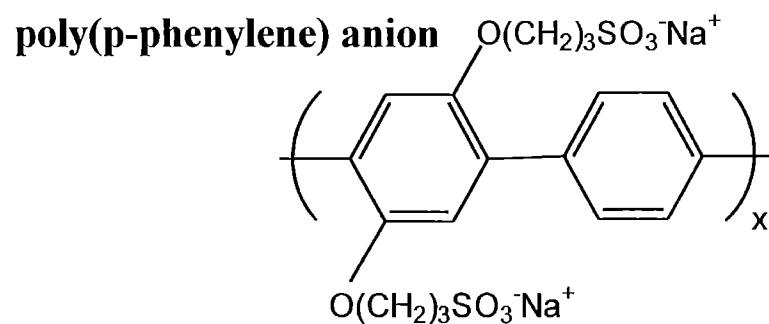


Luminescent dyes



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

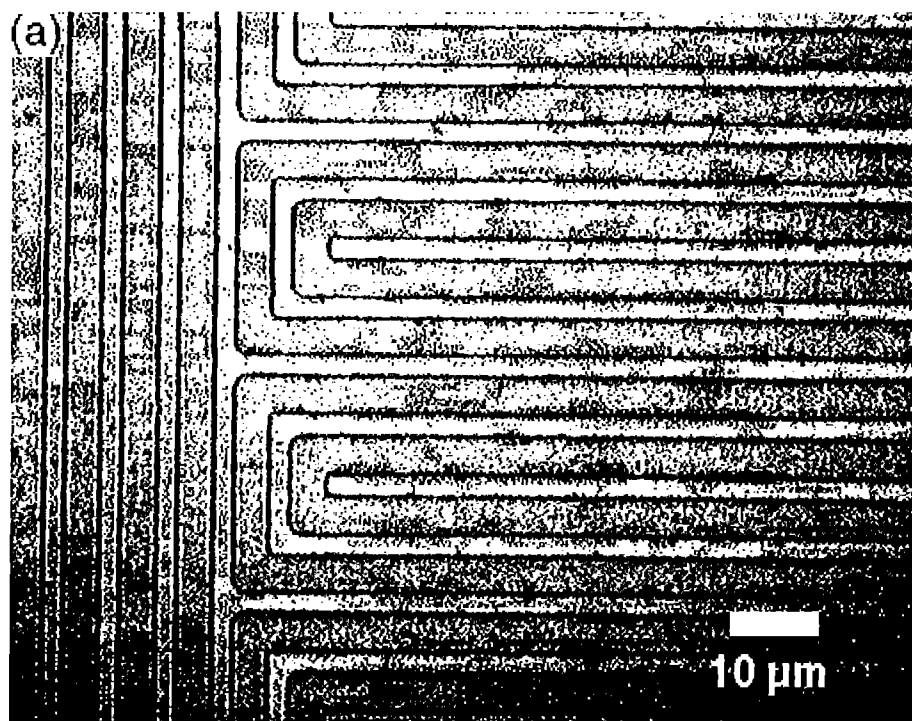
(supplied by Rubner group at MIT)



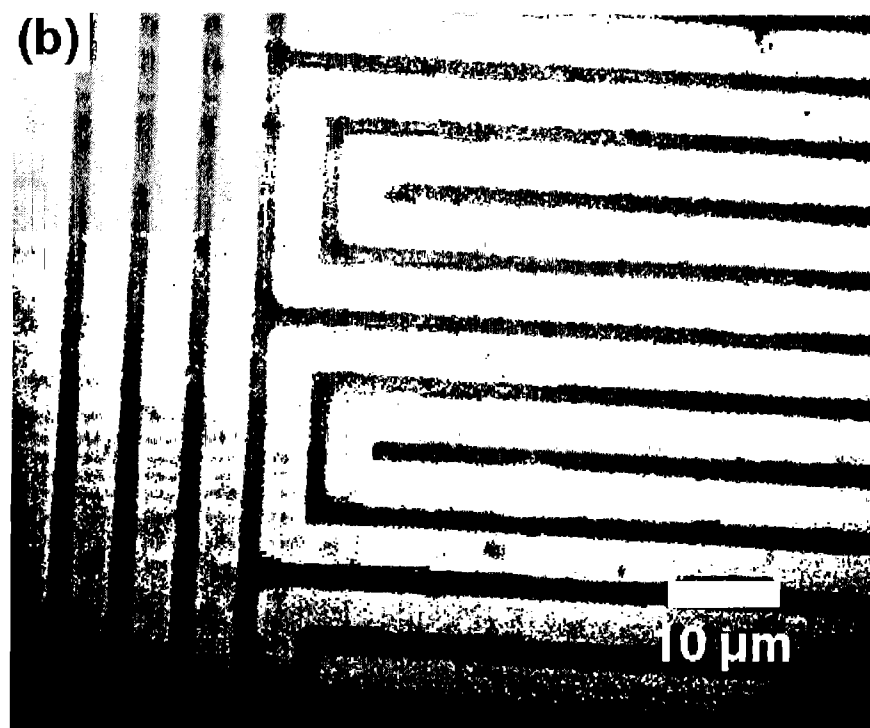
absorbance max. 350nm
emission max. 420nm (blue)

Microscopy of Patterned Ru Dye Multilayers

Optical Microscopy

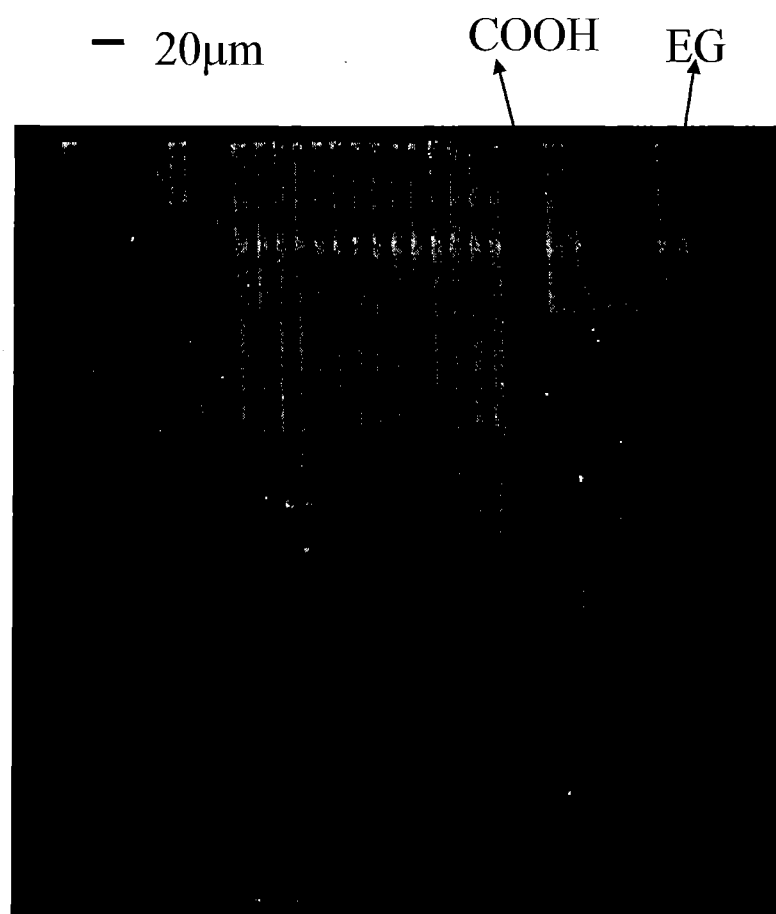


Fluorescence Microscopy

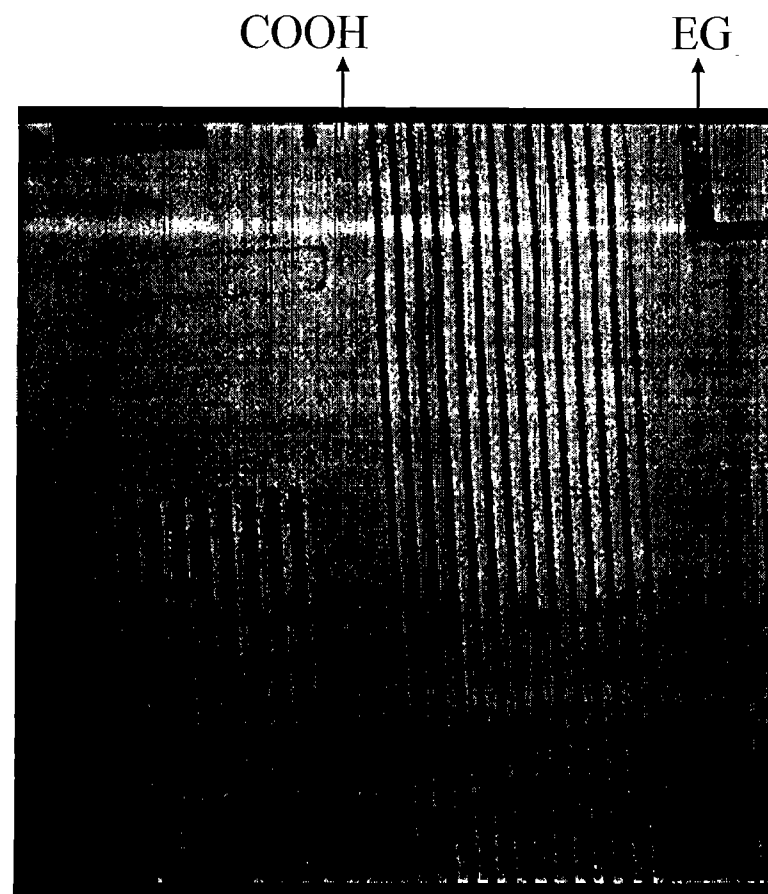


Ten bilayers of Ru/LPEI on five bilayers of PAA/LPEI
adsorbed at pH 4.8.

Patterning Ru dye with different polyamine ---- fluorescence micrographs



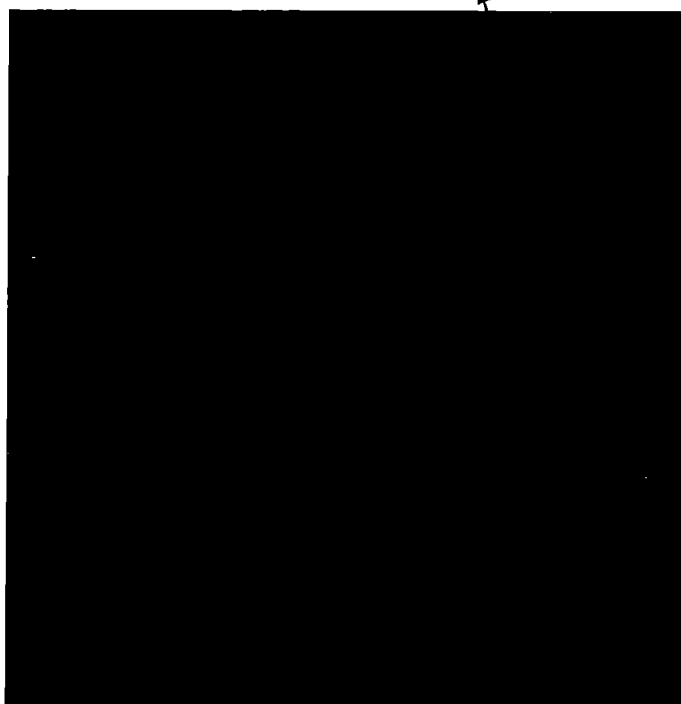
(PAH/PAA)5(PAH/Ru)10, pH4.8



(LPEI/PAA)5(LPEI/Ru)10, pH4.8

Combination of two dyes into patterned thin film

EG (PAH/Ru)₁₀



(PAH/Ru)₁₀ under Fluorescence
Microscope using red filter

COOH (PDAC/PPP(-))₁₀



(PDAC/PPP(-))₁₀ under Fluorescence
Microscope using DAPI filter

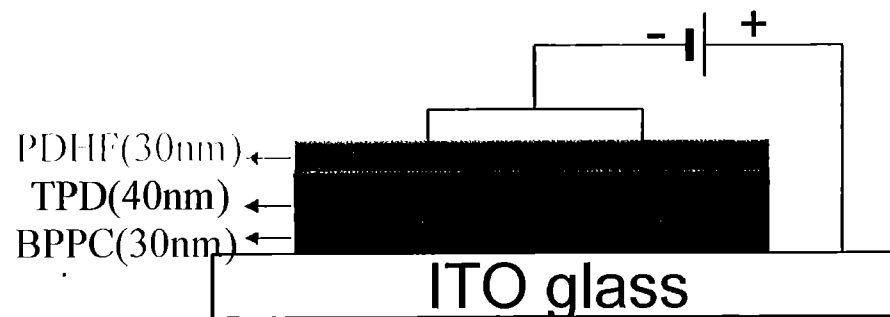
Hammond et al., 2000

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



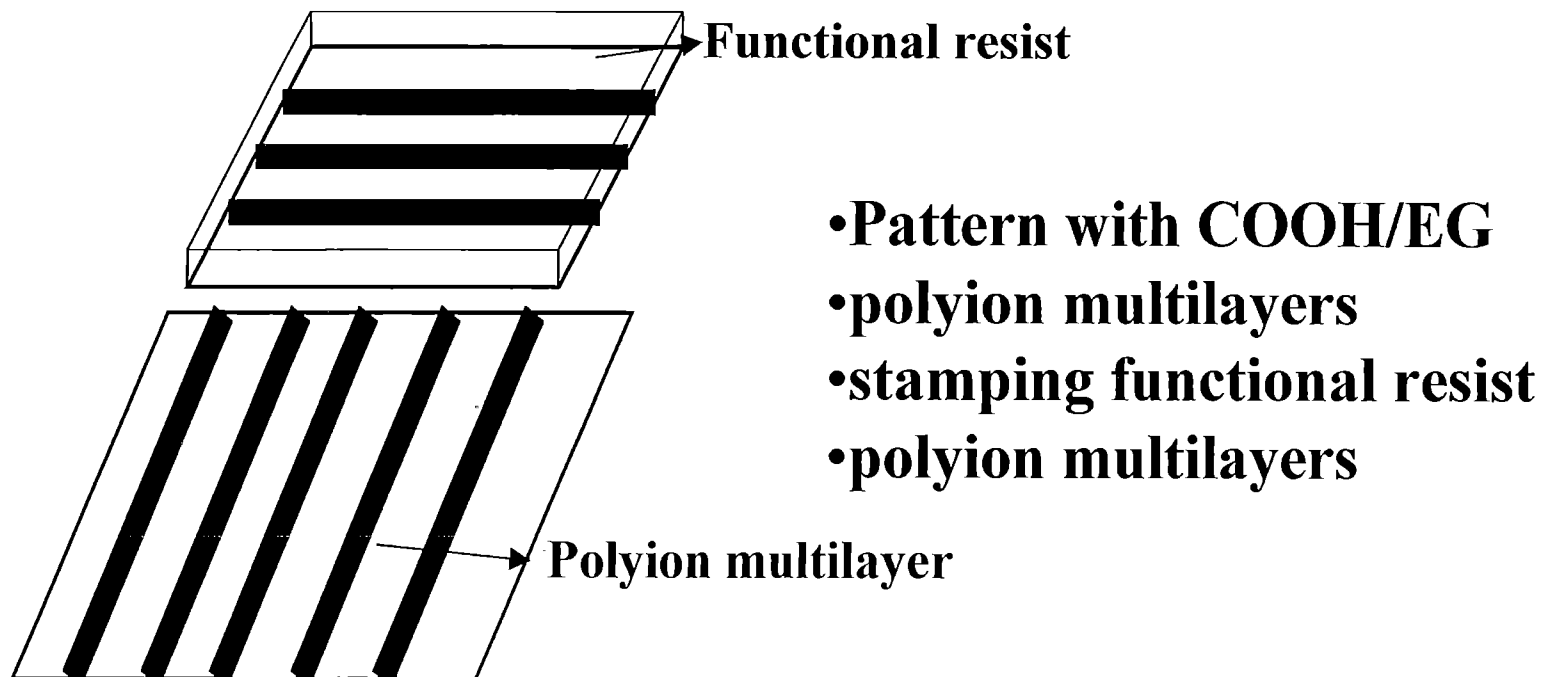
Old:

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

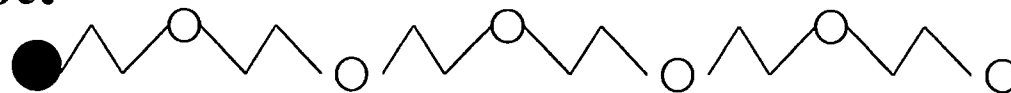
New:

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

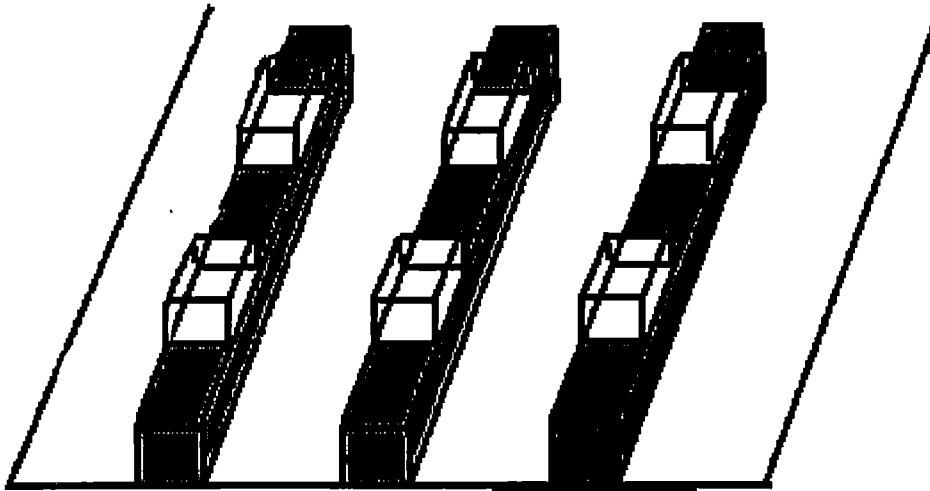
Multilevel Patterning



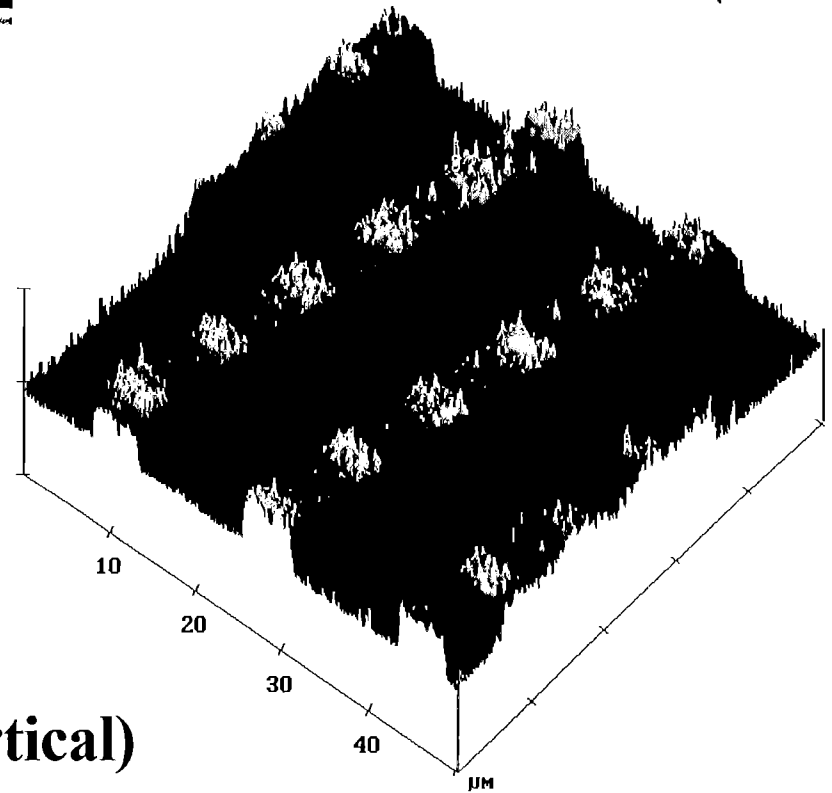
- Idea: stamping resist on underneath multilayer**
- Model resist:**



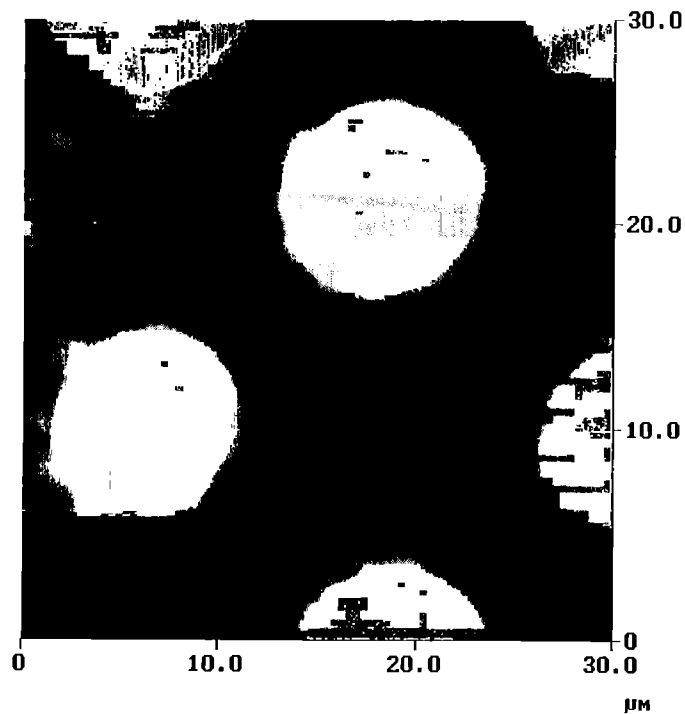
Multilevel pattern containing Ru dye -AFM



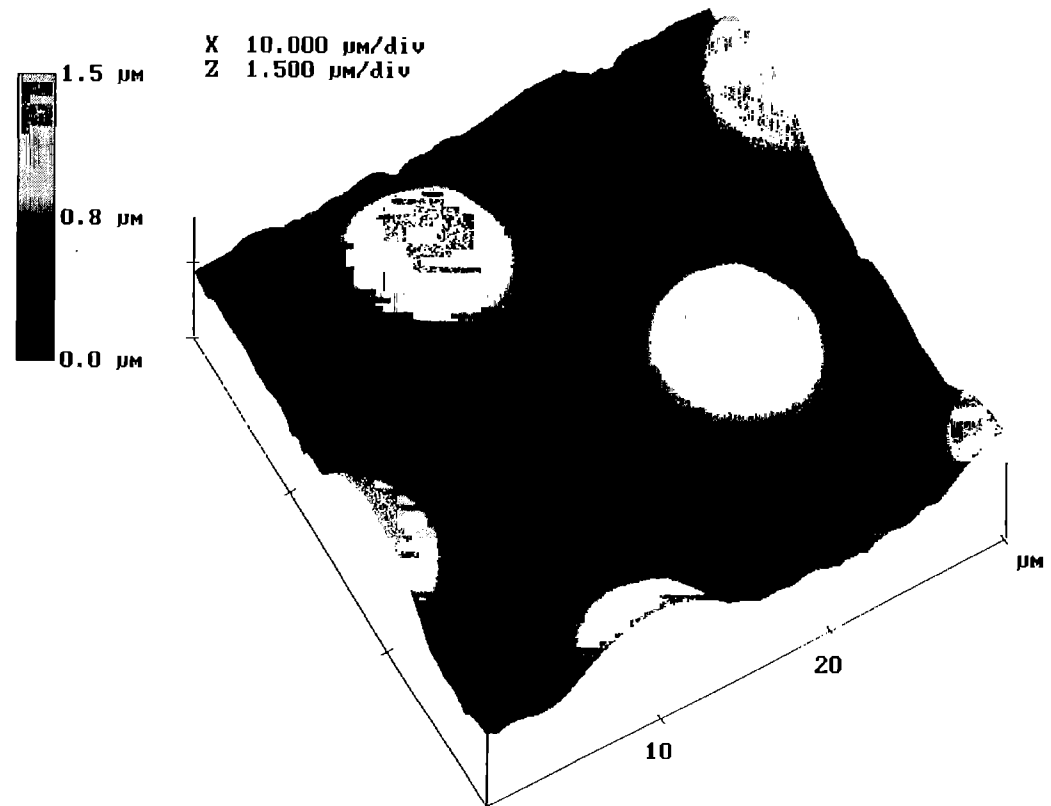
1. Adsorb multilayer system A (vertical)
2. EO-MAL stamp(horizontal)
3. Adsorb multilayer system B



EO-MAL patterning on Polystyrene Substrate (dot stamp)



(PAA/LPEI)12 at pH5/EO-MAL stamping on BPEI pH5
355b.000



(PAA/LPEI)12 at pH5/EO-MAL stamping on BPEI pH5
355b.000

1. (BPEI/PAA)4BPEI at pH5
2. Stamp EO-MAL 1hr (EO-MAL is stamped outside dots)
3. (PAA/LPEI)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**

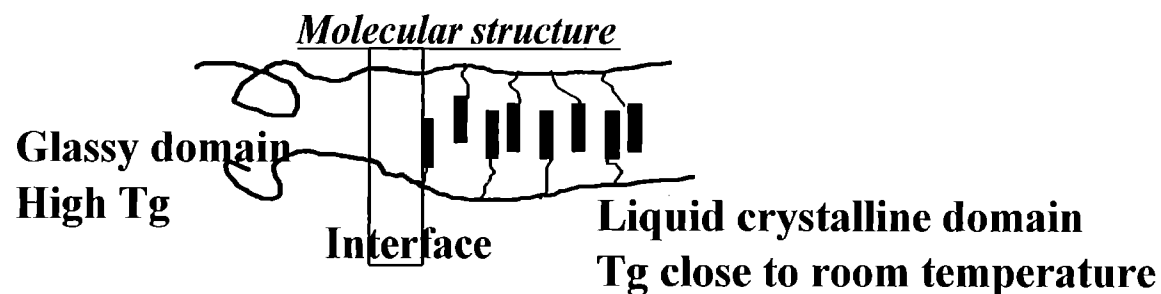
MURI Funding Level: \$50 K/yr.

Personnel

- **P.T. Hammond**
- **Aaron Moment**
- **P.T. Hammond**

ARO MURI

LC Side Chain Block Copolymers



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 T_g block to obtain “fluid” matrix
Increased kinetics for coloration, switching

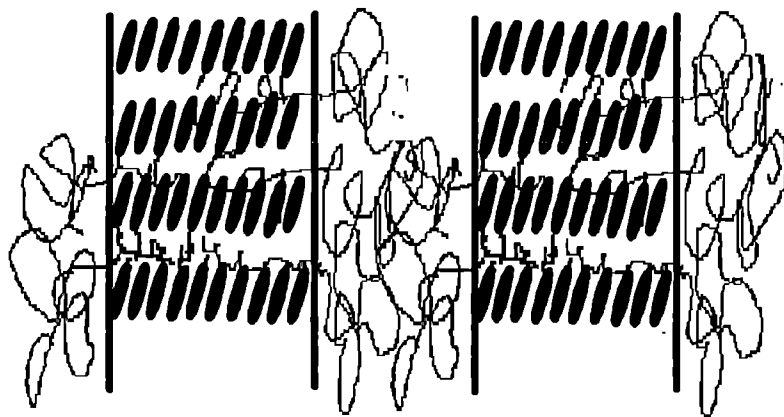


TOPS Objectives - Mesostuctured Polymers: Side Chain LC Block Copolymers

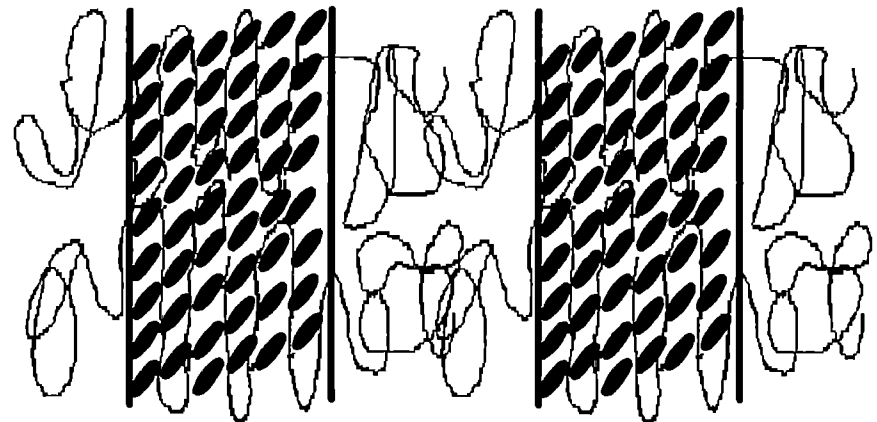
- Attach known LC's/chromophores of interest to polystyrene-vinyl siloxane backbone
 - ◎ Cholesteric LC's (reflective)
 - ◎ Merocyanine dyes
 - ◎ Salicylidenes
 - ◎ Substituted azobenzenes
- Examine chromic and spectroscopic behavior in oriented block copolymers as function of structure(**Rothberg**)
- 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.



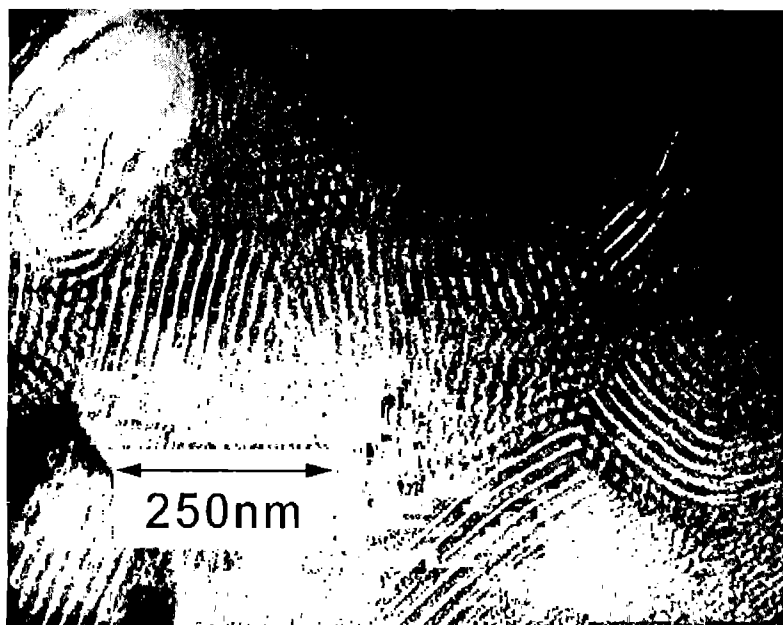
Spacer length = 6



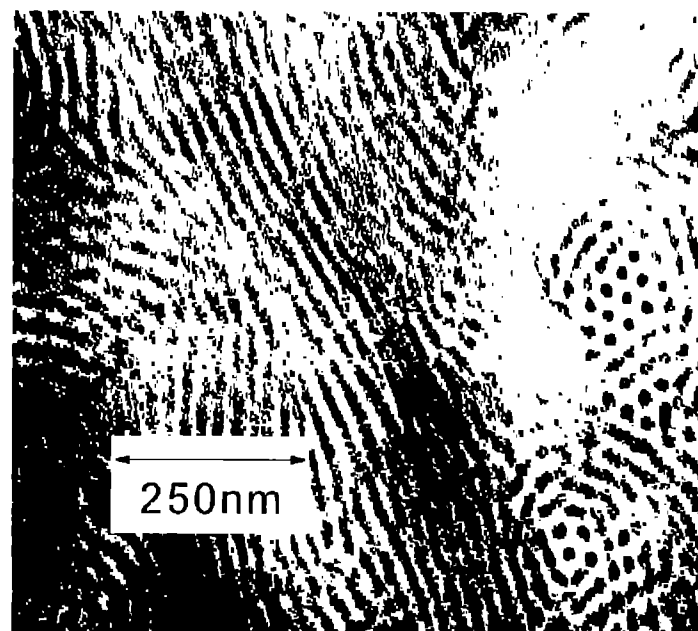
Spacer length = 10

Can use oriented blocks to obtain highly ordered, switchable chromophores

TEM images of Mesogen B polymers



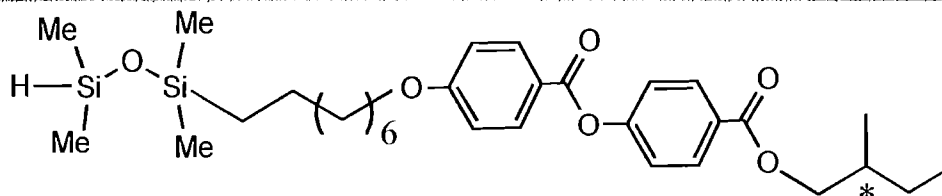
PS 12 - LCPB 8
TEM 155Å, SAXS 186Å



PS 14 - LCPB 94
TEM 257Å, SAXS 294Å

OM images of PS14K-LCP57K (A) elastomeric material on stretching

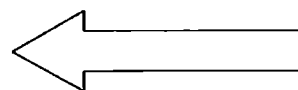
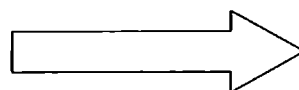
Mesogen A:



500um

Free standing film, 25 C

stretch

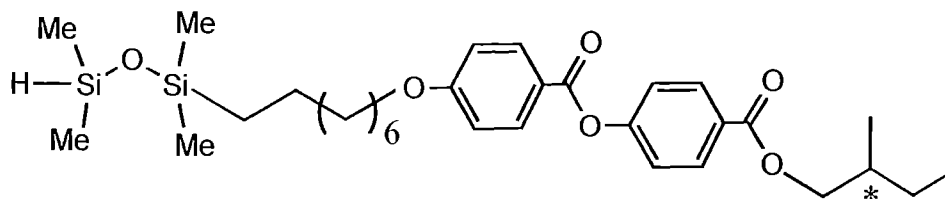


release

~ 8% strain,
1mm stretch

Summary of liquid crystalline transitions and SAXS data for block copolymers

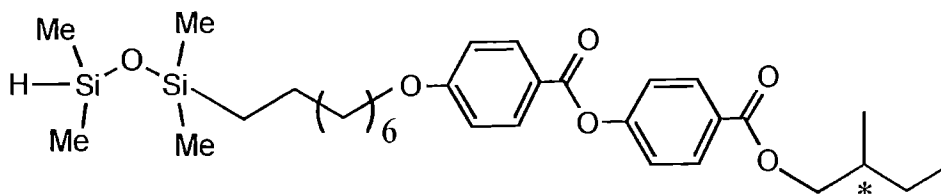
Mesogen A:



<u>Wt% PS</u>	<u>Mn</u>		<u>S-I C</u>	<u>SAXS</u>	
	<u>PS Block</u>	<u>LC Block</u>		<u>Smectic d, Å</u>	<u>Morphology d, Å</u>
0	--	34,000	89.6	37	none
43	12,000	16,000	none	none	weak
26	13,000	38,000	66.3	36	PS cylinders
20	14,000	57,057	79.4	36	PS cylinders
66	40,000	21,000	42.6	36	327/lamellar

Summary of liquid crystalline transitions and SAXS data for block copolymers

Mesogen A:



<u>Wt% PS</u>	<u>Mn</u>		<u>S-I C</u>	SAXS	
	<u>PS Block</u>	<u>LC Block</u>		<u>Smectic d, Å</u>	<u>Morphology d, Å</u>
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43	12,000	16,000	none	none	none
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66	40,000	21,000	42.6	36	327/ weak

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

Overview

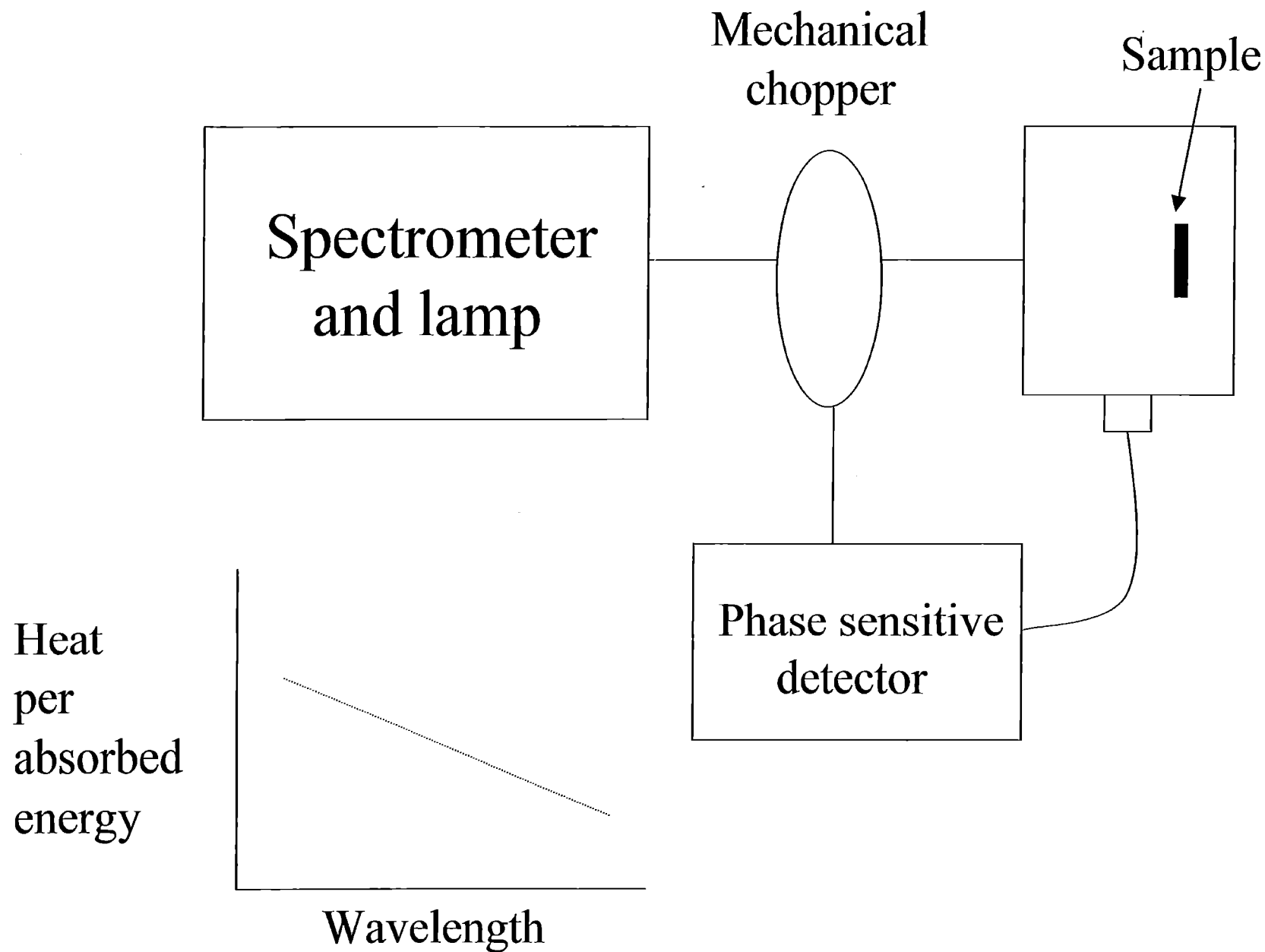
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Motivation

- 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



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

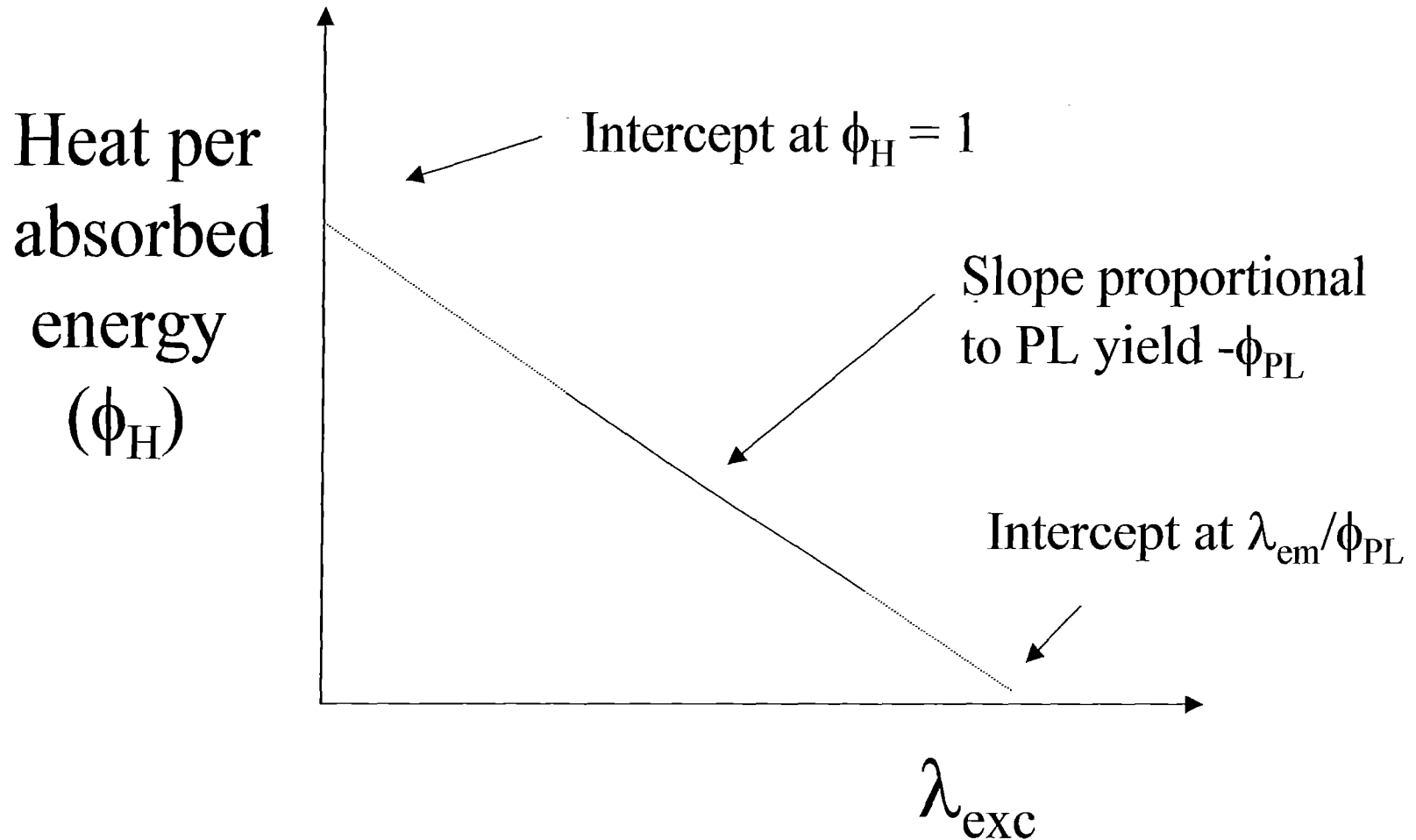
The diagram illustrates the components of the equation for heat per absorbed photon. A central box contains the equation:
$$\text{Heat per absorbed photon} = hc/\lambda_{\text{exc}} - \phi_{\text{PL}}(hc/\lambda_{\text{em}})$$
 Above the box, the word "known" has two arrows pointing to hc/λ_{exc} and hc/λ_{em} . Below the box, the word "measured" has three arrows pointing to the entire equation, hc/λ_{exc} , and $\phi_{\text{PL}}(hc/\lambda_{\text{em}})$.

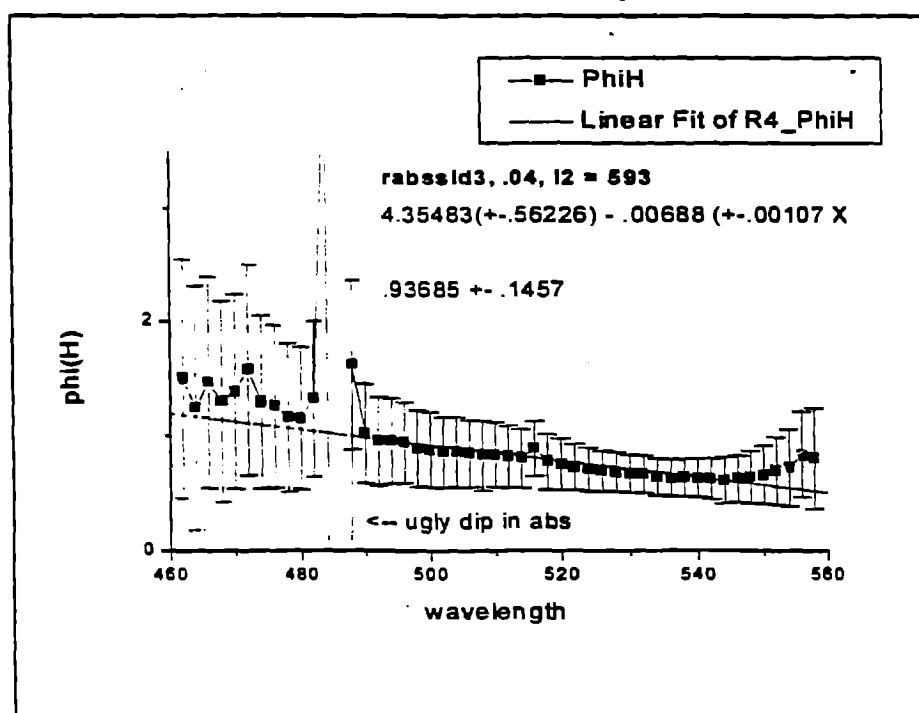
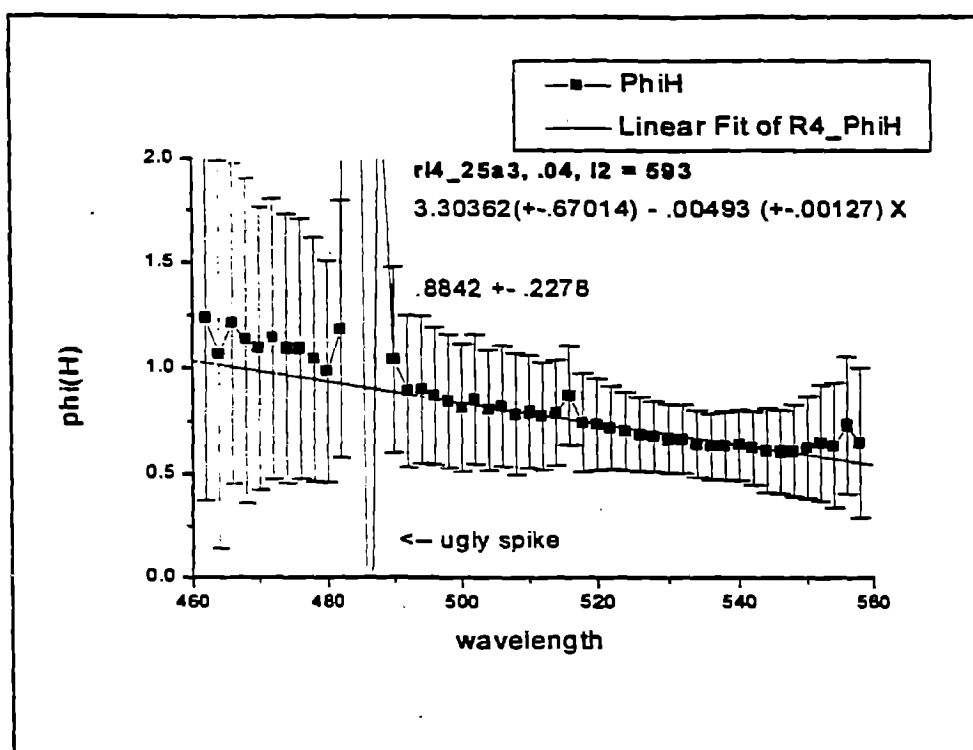
known

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

measured

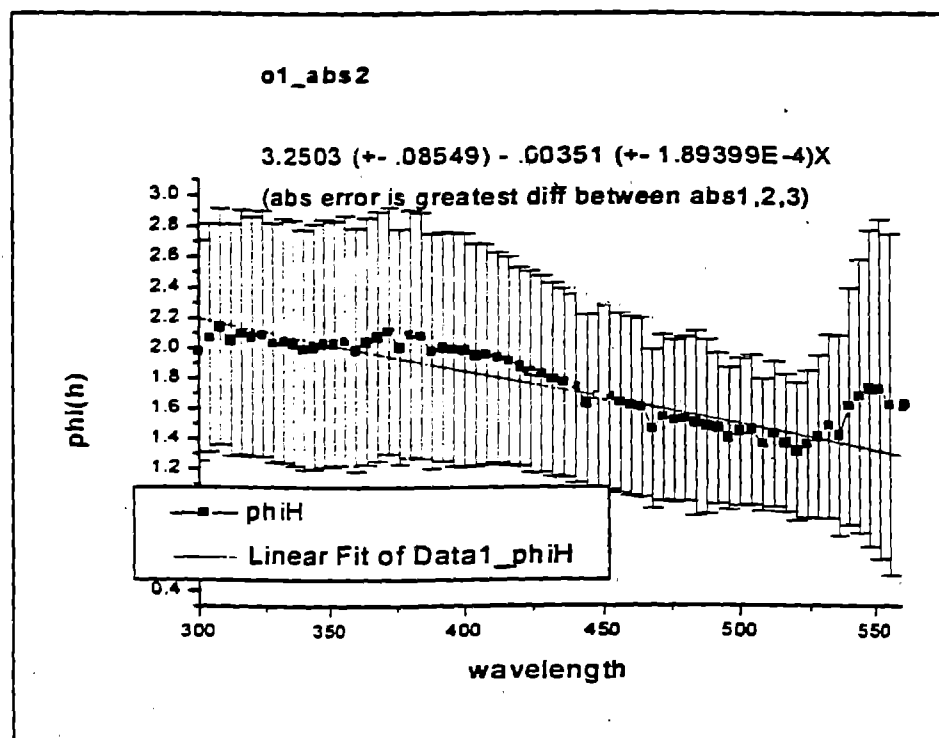
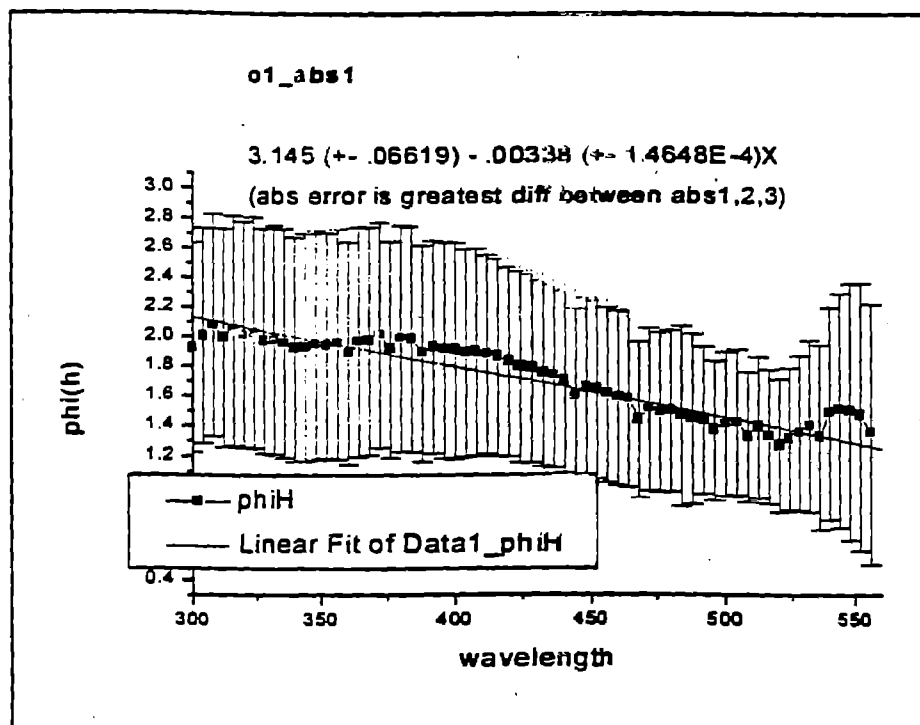
Predicted Behavior





$$\varphi_H \approx .63$$

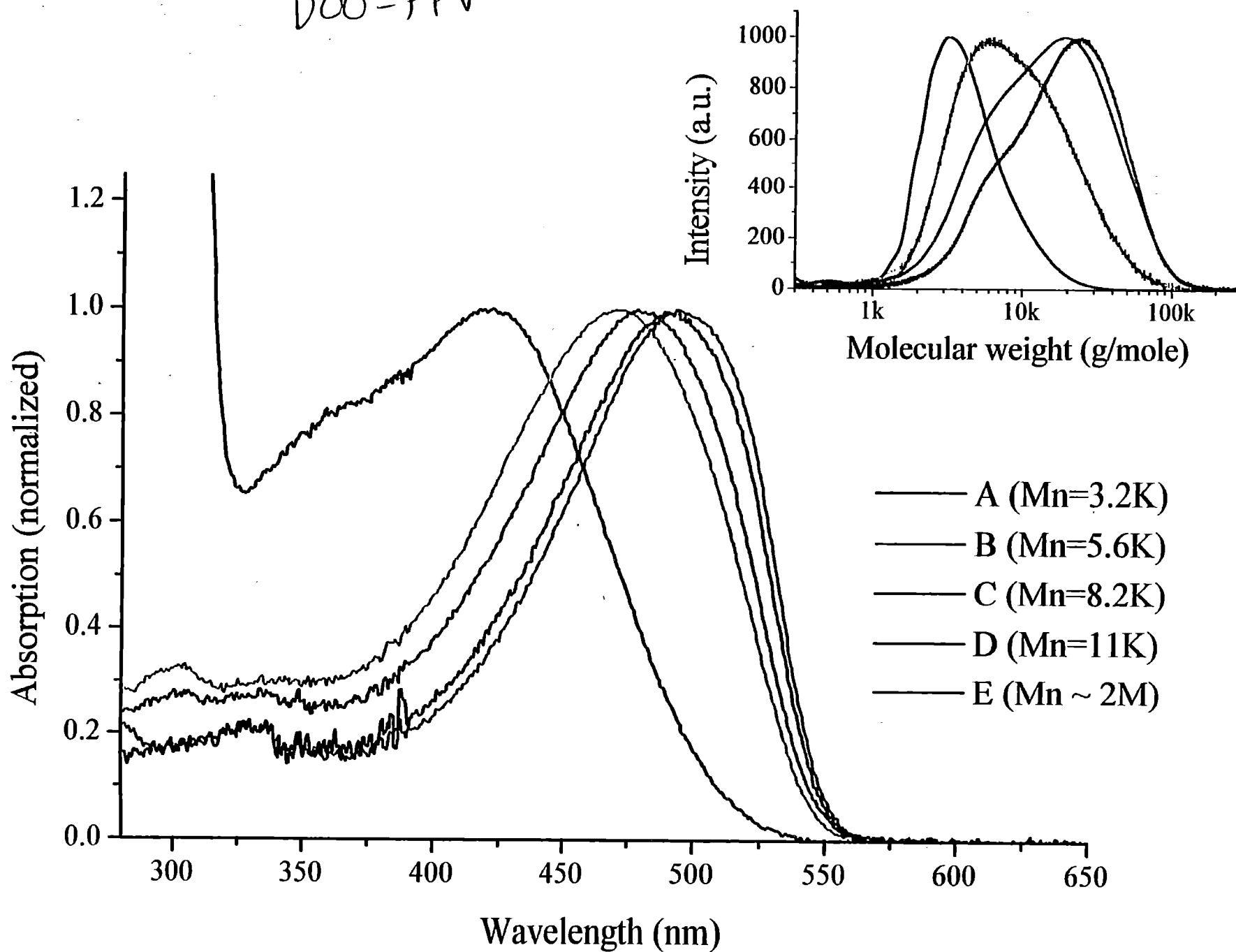
19 12 - O M_c

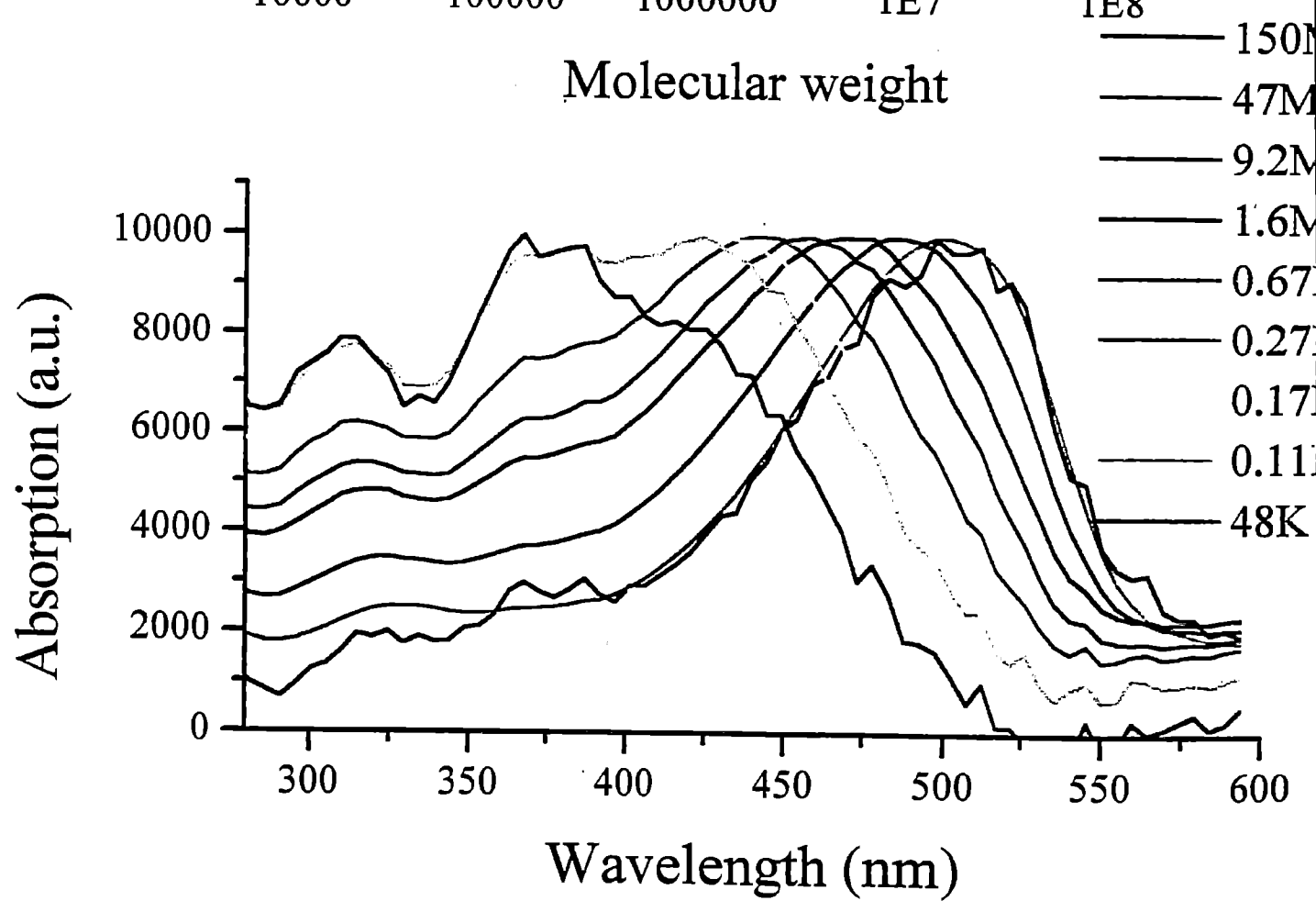
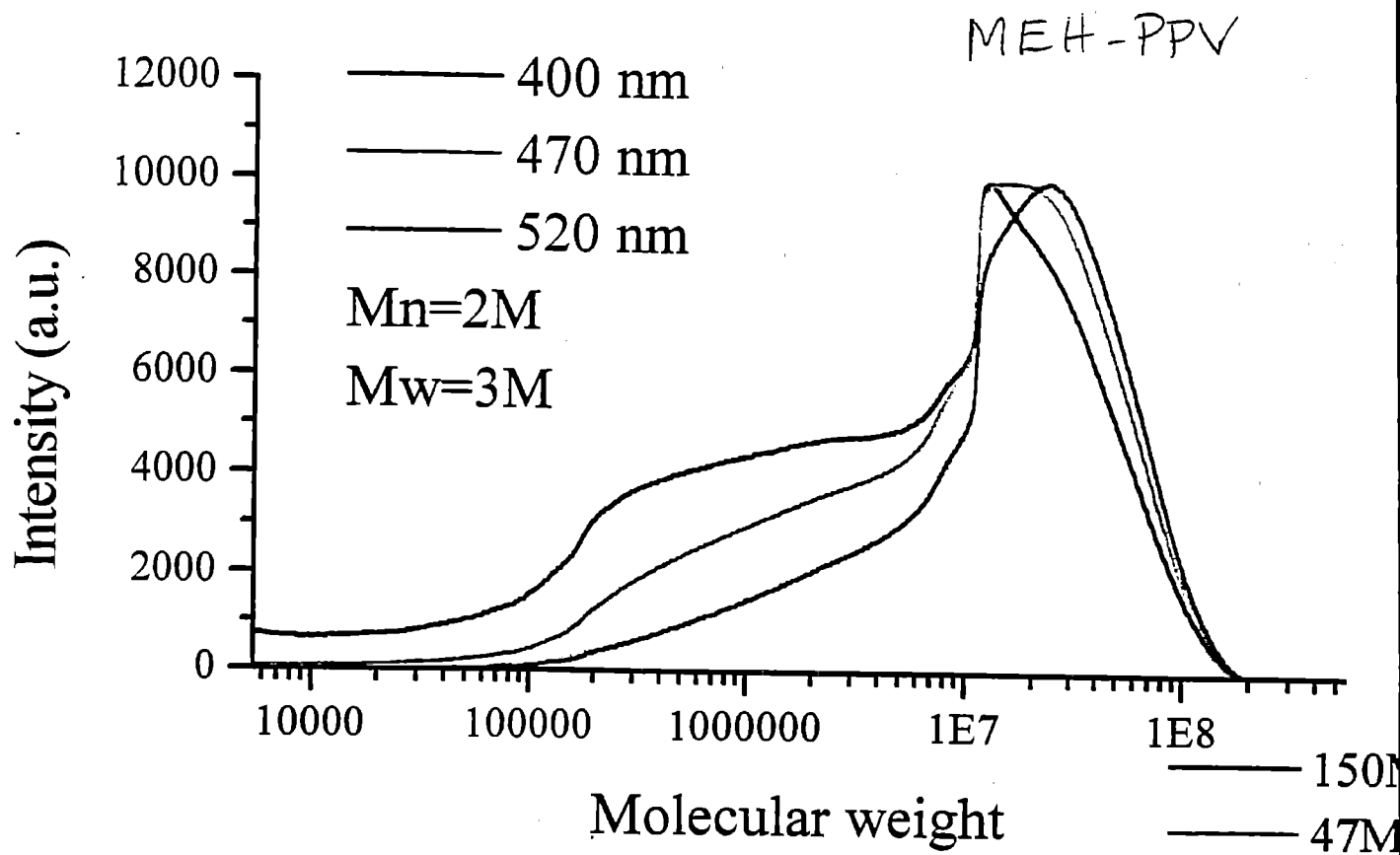


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DOO-PPV

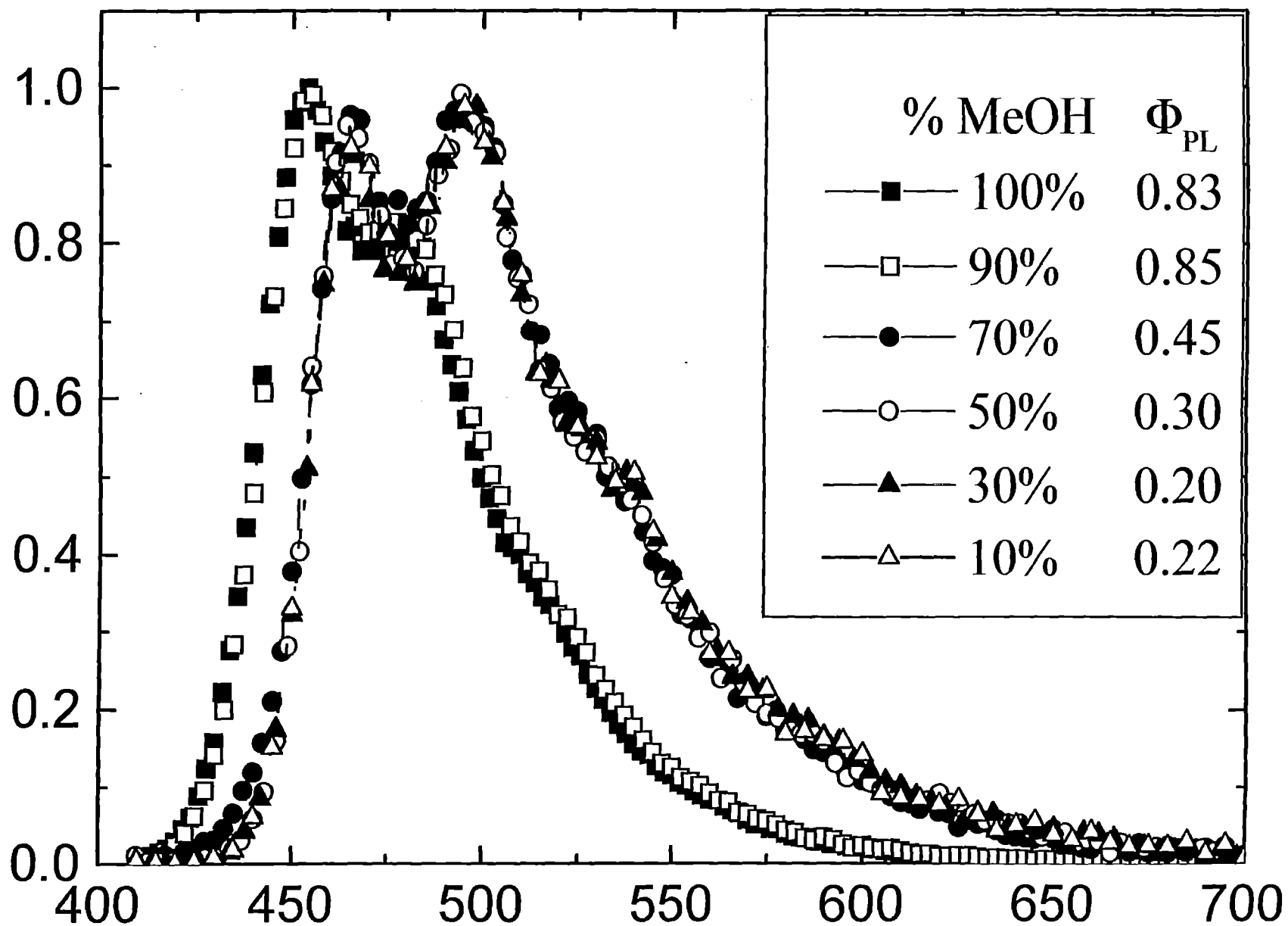




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Normalized PL



Solvent Effect Studies in the ^1H -NMR Spectroscopy

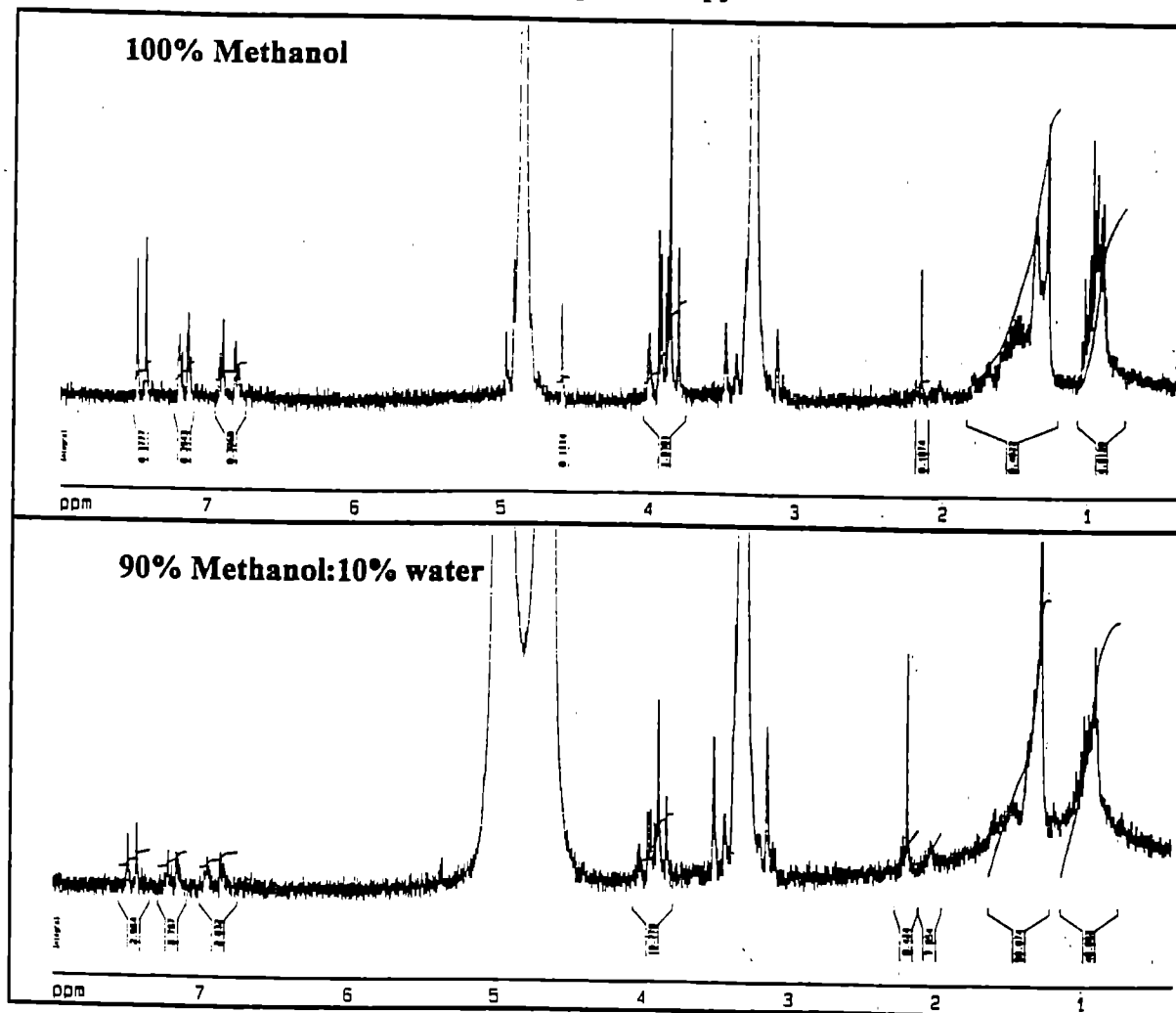


Figure 9: ^1H -NMR spectra of the Trimer of MEH-PPV in 100% methanol and 90% methanol-10% water.

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

Chemical shift (ppm)	Assignments	Integral(100%MeOH)	Integral(90%MeOH)
6.7-7.5	ring, vinylene ^1H	0.15	0.075
3.6-4.0	O-C-H ^1H	0.18	0.09
2.3-0.8	ethylhexoxy ^1H	1	1

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

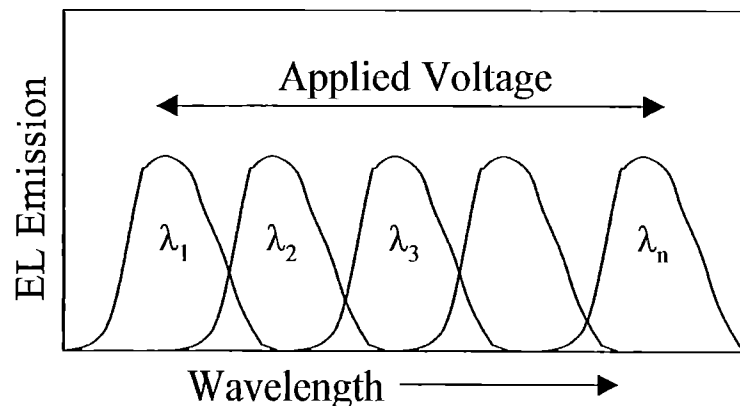
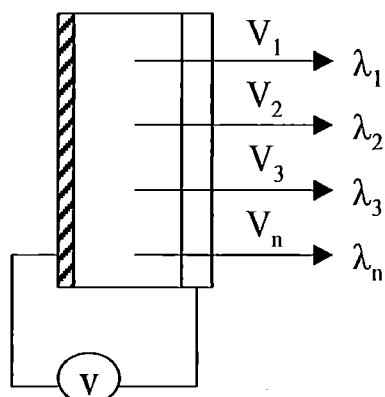
yi5099s3rep

S.A. JENEKHE

ARO TOPS MURI

TUNABLE MULTICOLOR EL POLYMERS AND DEVICES

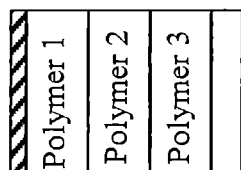
CONCEPT



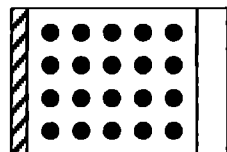
**TUNABLE
EMISSION**

POSSIBLE APPROACHES

A. Bilayer/Multilayer EL polymers



B. Phase-Separated EL Polymer Blends



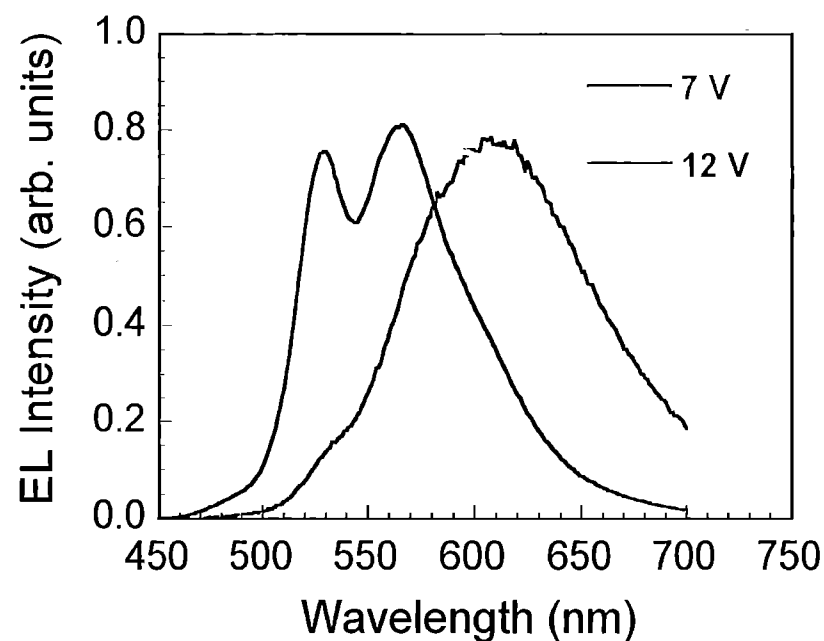
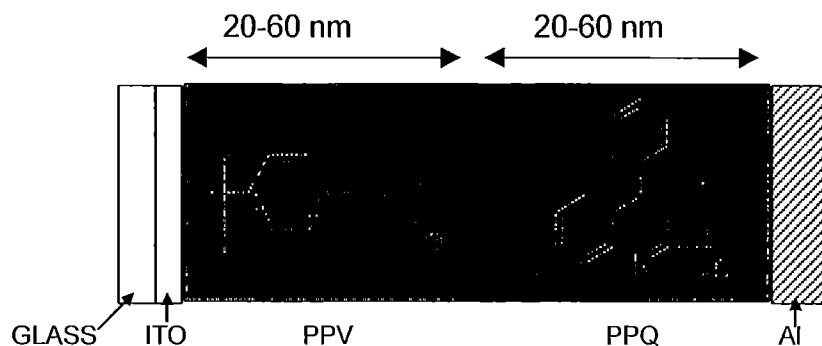
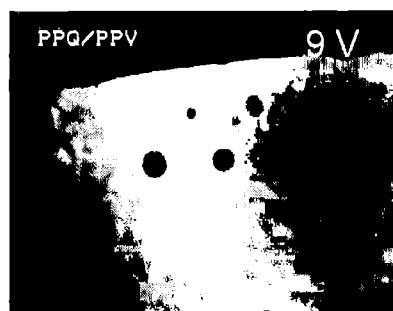
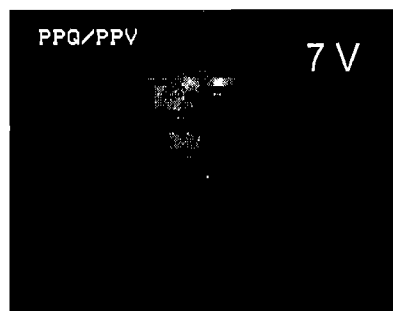
C. Microphase-Separated Block Copolymers



CHALLENGES

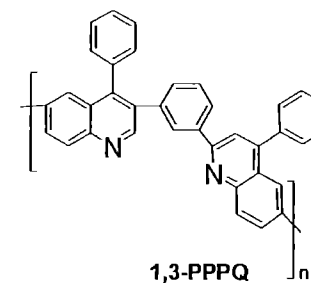
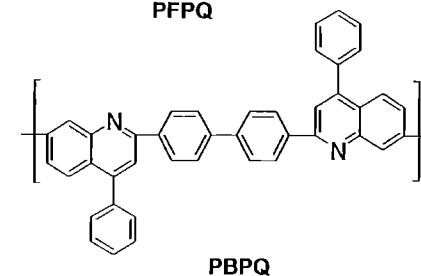
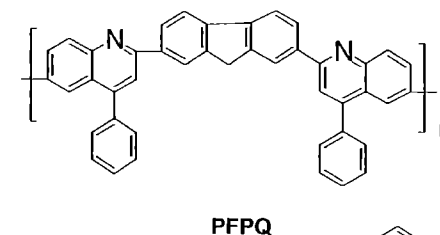
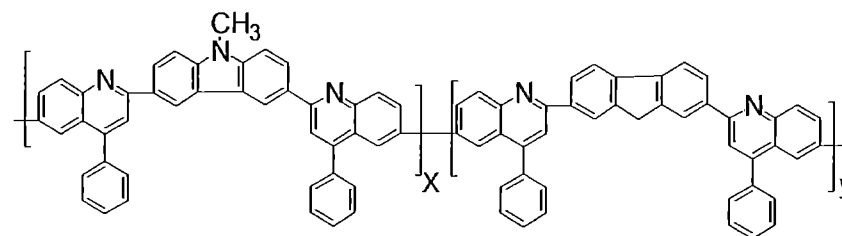
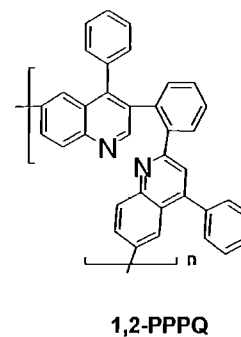
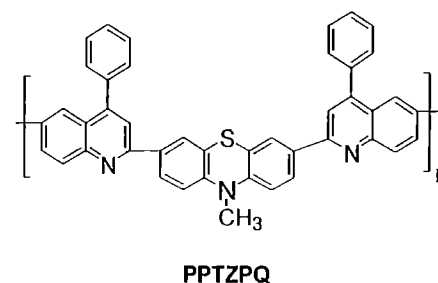
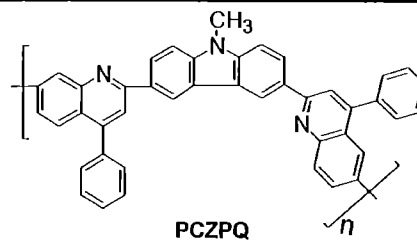
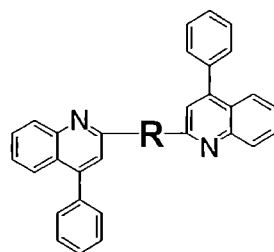
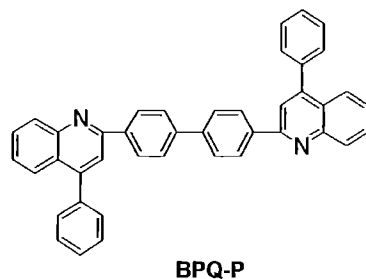
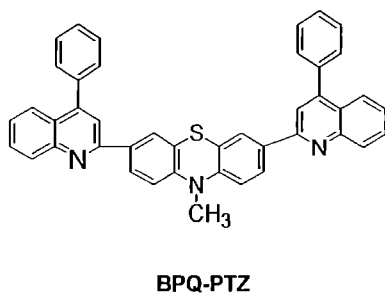
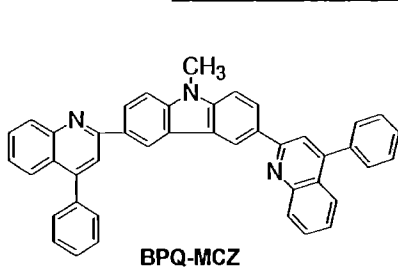
- Design of Multicomponent EL Polymers
 - Availability of R, G, B EL Polymers
 - Energy Transfer
 - Exciplex Formation
 - Photoinduced Electron Transfer
- Processing and Control of Nanophase Multicomponent EL Polymer Systems
 - Insolubility in Common Solvents
 - Solubility in Common Solvents
 - Control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

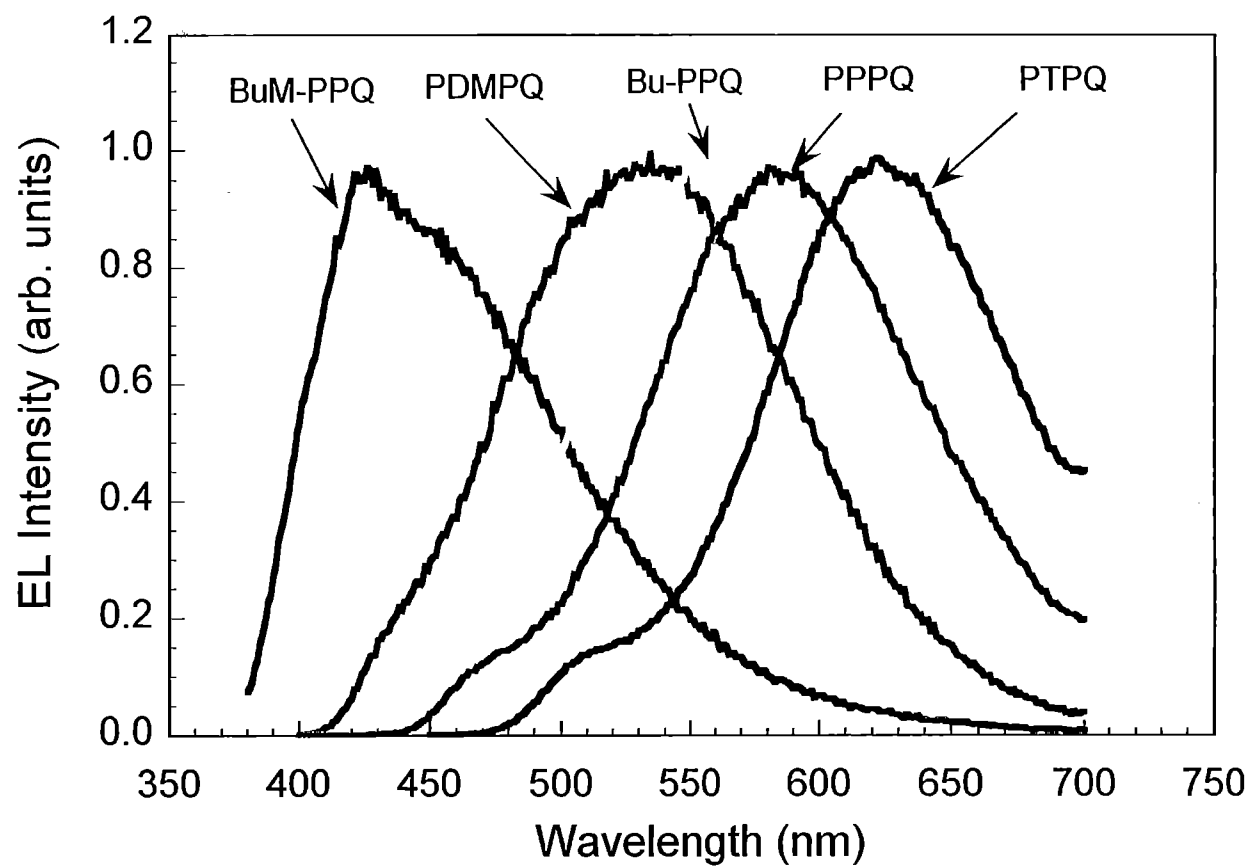
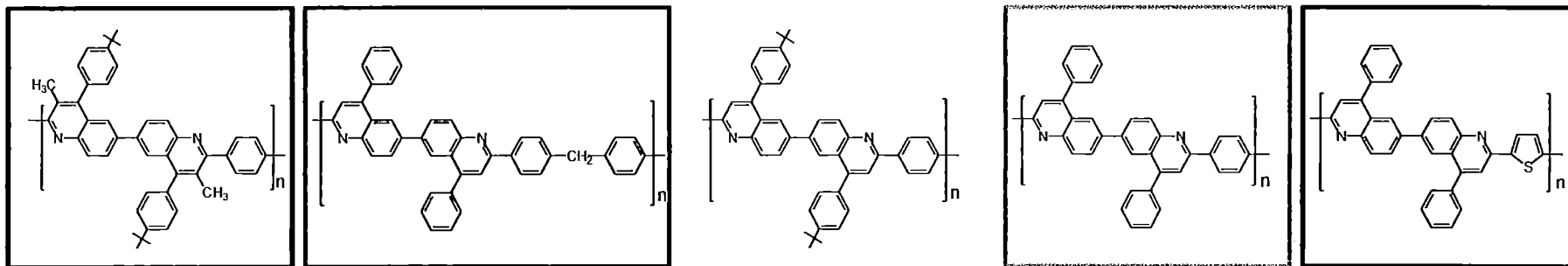
VOLTAGE-TUNABLE MULTICOLOR POLYMER LEDs



Jenekhe et al., *Chem. Mater.* **1997**, *9*, 409.
 Zhang & Jenekhe, *Macromolecules* **2000**, *33*, 2069.

New n-Type Light-emitting Polymers

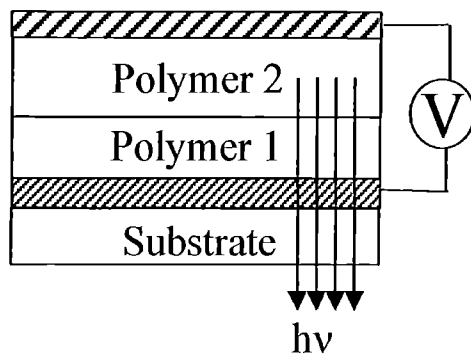




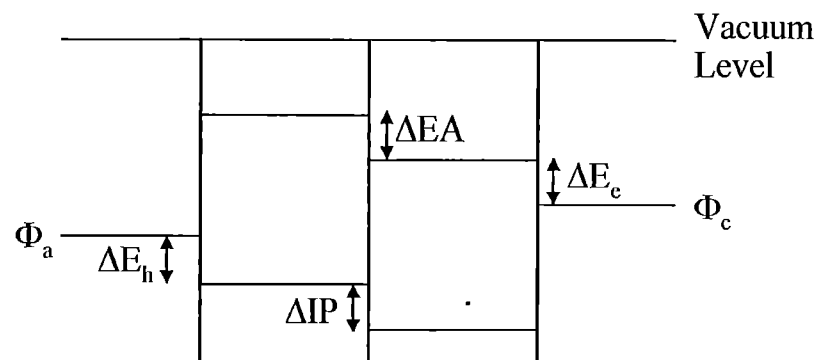
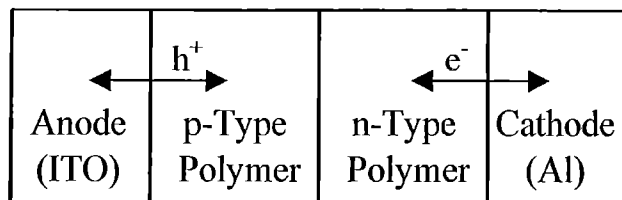
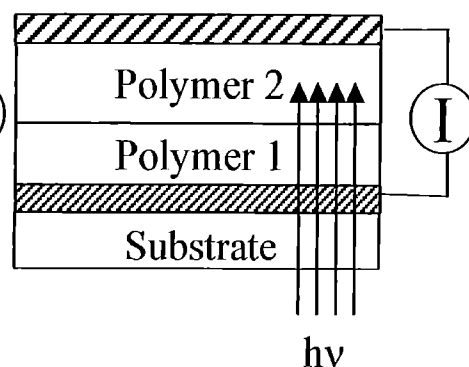
Al
Polyquinoline
TAPC/PS
ITO

POLYMER/POLYMER INTERFACES IN DEVICES

Light-Emitting
Diodes/Lasers



Photodetectors/
Photovoltaic Cells



•Role of Polymer/Polymer Interface

- (ΔIP , ΔEA)
 - Charge Depletion (Space Charge) Region?
 - Built-In Potential (Field)
 - Energy Transfer
 - Exciplex Formation
 - Photoinduced Charge Transfer
- IP = Ionization Potential (eV)
EA = Electron Affinity (eV)

•Finite Size Effects

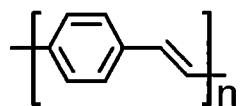
•Electrode/Polymer Interfaces

- Charge Injection Barriers (EA, IP Values)

kms0807s1

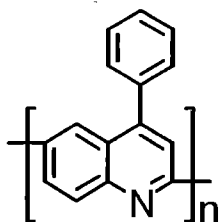
Polymer/Polymer Heterojunction LEDs

p-Type (Hole Transport)

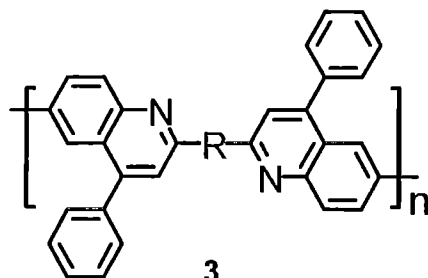


1

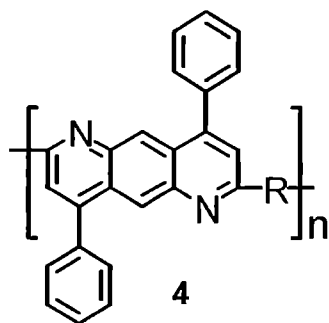
n-Type (Electron Transport)



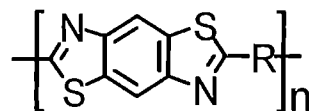
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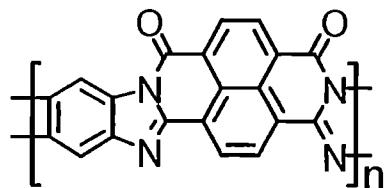
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4



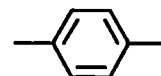
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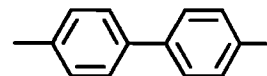
6

R

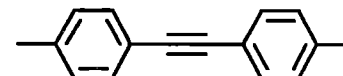
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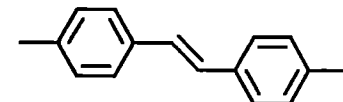
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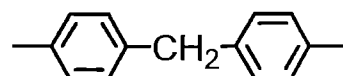
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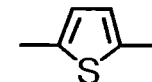
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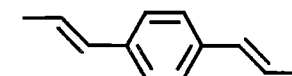
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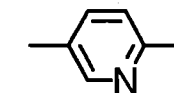
f



g



h



1. PPV

2. PPQ

3a. PPPQ

3b. PBPQ

3c. PBAPQ

3d. PSPQ

3e. PDMPQ

3f. PTPQ

4a. PPDA

4b. PBDA

4c. PBADA

4d. PSDA

4e. PDMDA

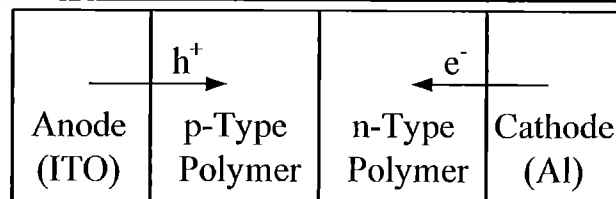
4f. PTDA

5g. PBTPV

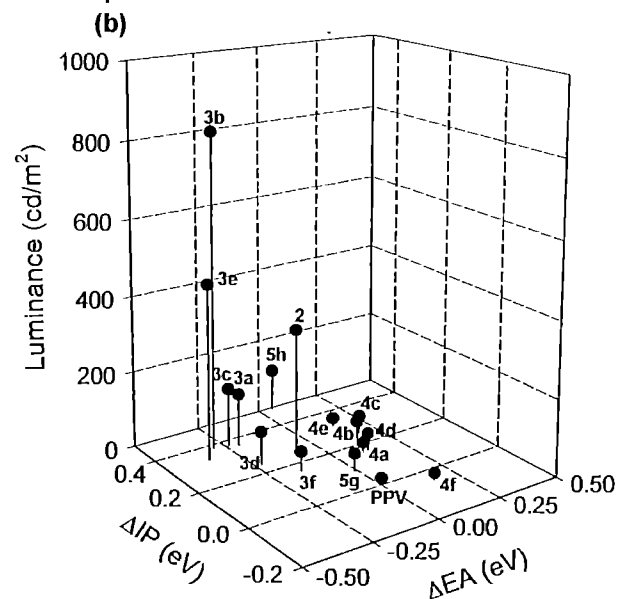
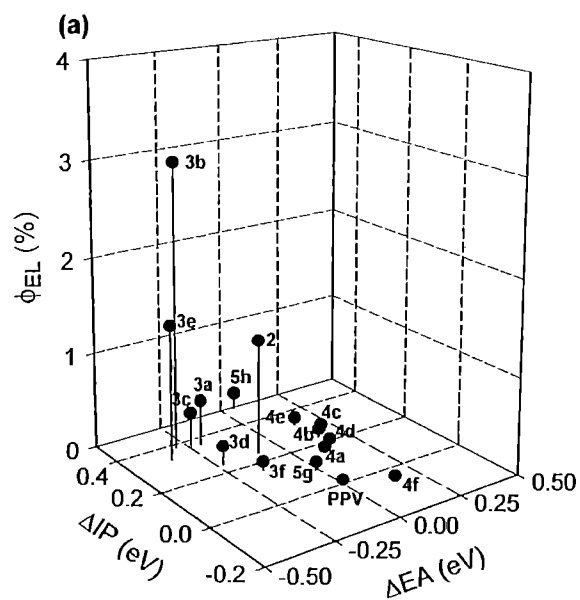
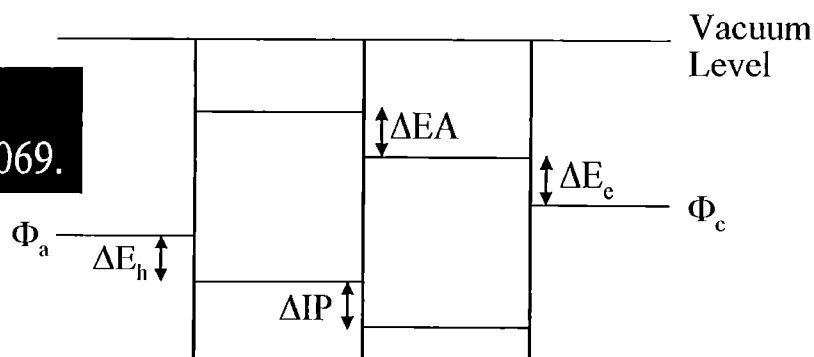
5h. PPyBT

6. BBL

POLYMER/POLYMER INTERFACES IN HETEROJUNCTION LEDS



Zhang and Jenekhe,
Macromolecules 2000, 33, 2069.



Efficient LEDs From Polymer/Polymer Heterojunctions

POLYMER/POLYMER INTERFACES IN DEVICES

- **Can Be More Important than Injection Barriers at Electrodes**
- **ΔEA and ΔIP 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**
(ϕ_{PL} , ΔEA , ΔIP)

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**

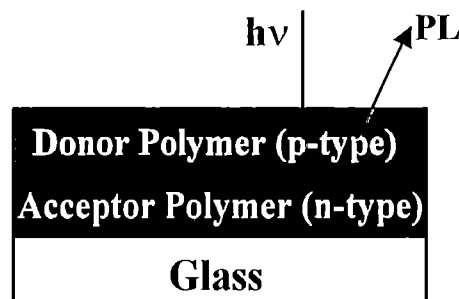
PROBING POLYMER/POLYMER INTERFACES

Investigate the Photophysical and Charge transfer Processes of Novel Donor/Acceptor Heterojunctions of π -conjugated Polymers

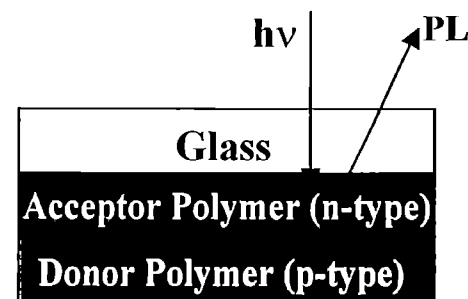
- Photophysical and Charge Transfer Processes at Polymer/Polymer Interfaces play a Critical Role in the Efficiency and Performance of LEDs.
- Charge Transfer and Separation at Polymer/Polymer Interfaces are Key to Efficient Photovoltaic Devices.

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



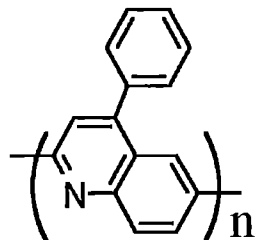
1) Front Face Geometry



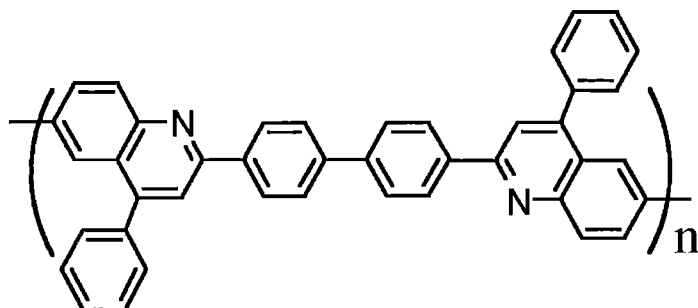
2) Inverted Face Geometry

Electroluminescent Conjugated Polymers

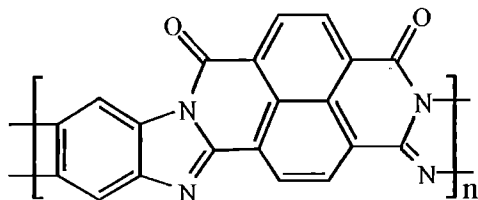
Acceptor Polymers



PPQ: poly(2,6-(4-phenylquinoline))

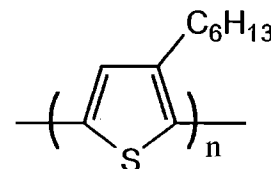


PBPQ: poly(2,2'-(*p,p'*-biphenylene)-6,6'-bis(4-phenylquinoline))

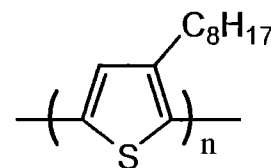


BBL: poly(benzimidazobenzo phenanthroline ladder)

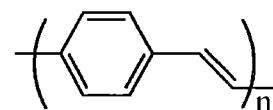
Donor Polymers



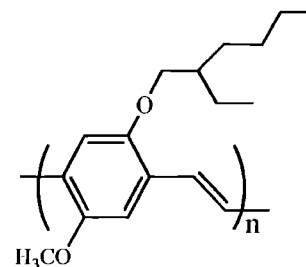
PHT: poly(3-hexylthiophene)



POT: poly(3-octylthiophene)



PPV: poly(*p*-phenylene vinylene)

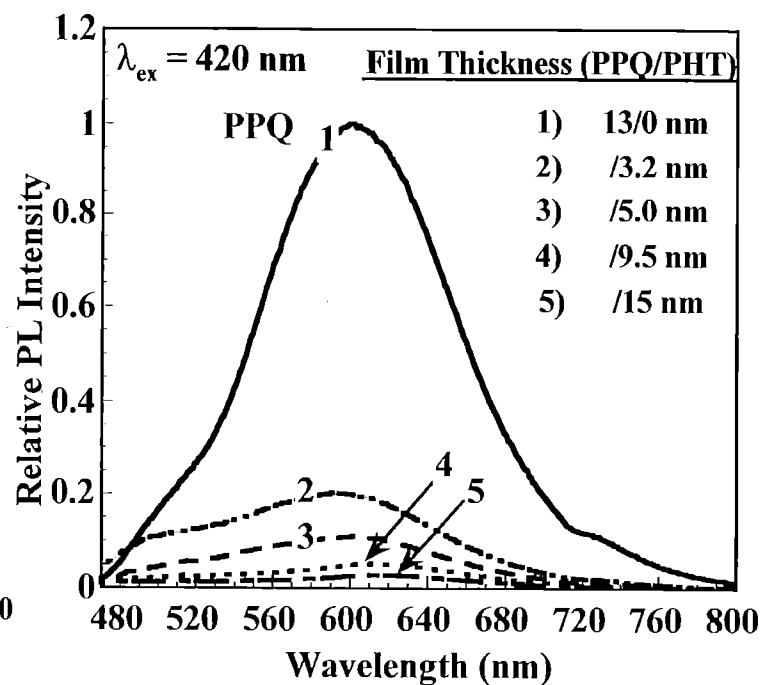
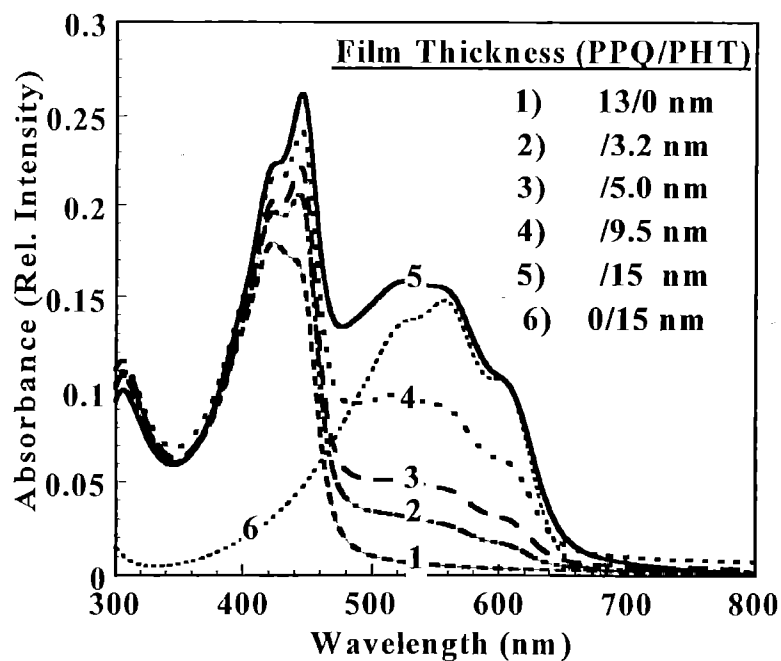
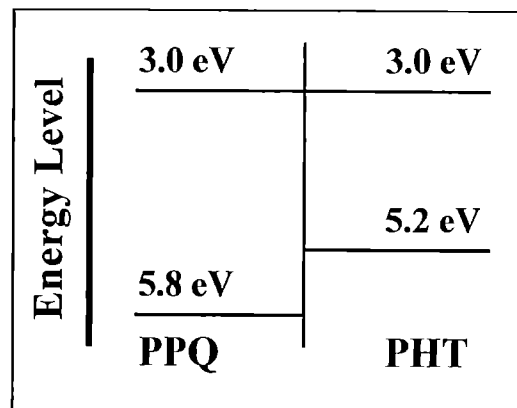
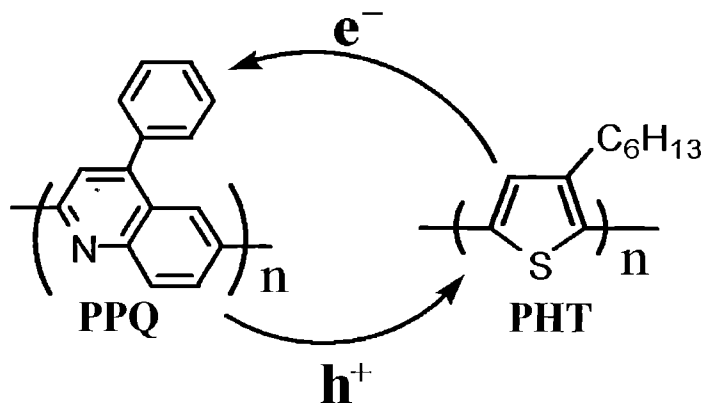


MEH-PPV: poly(2-methoxy-5-(2'ethylhexyloxy)-1,4-phenylene vinylene)

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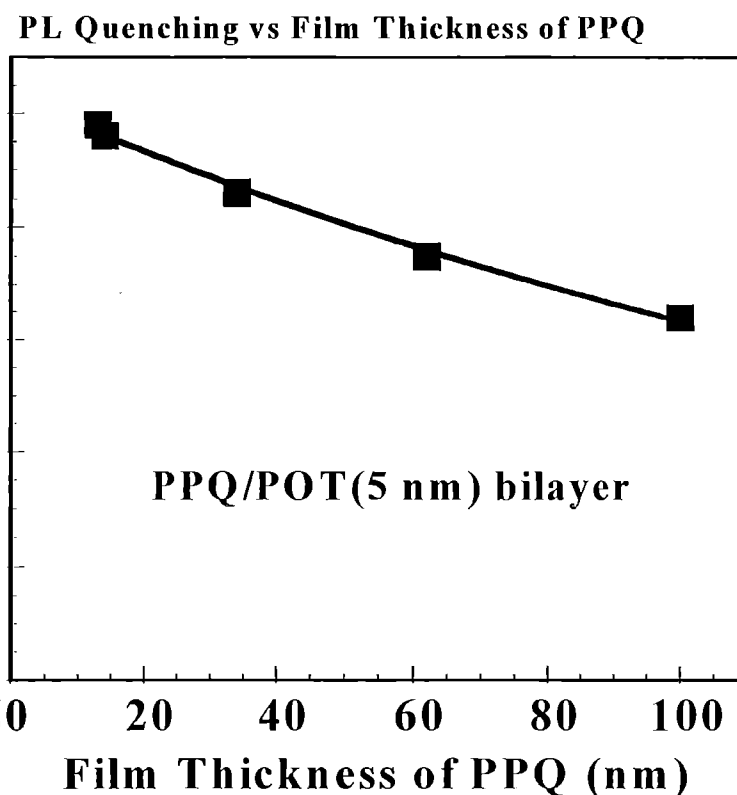
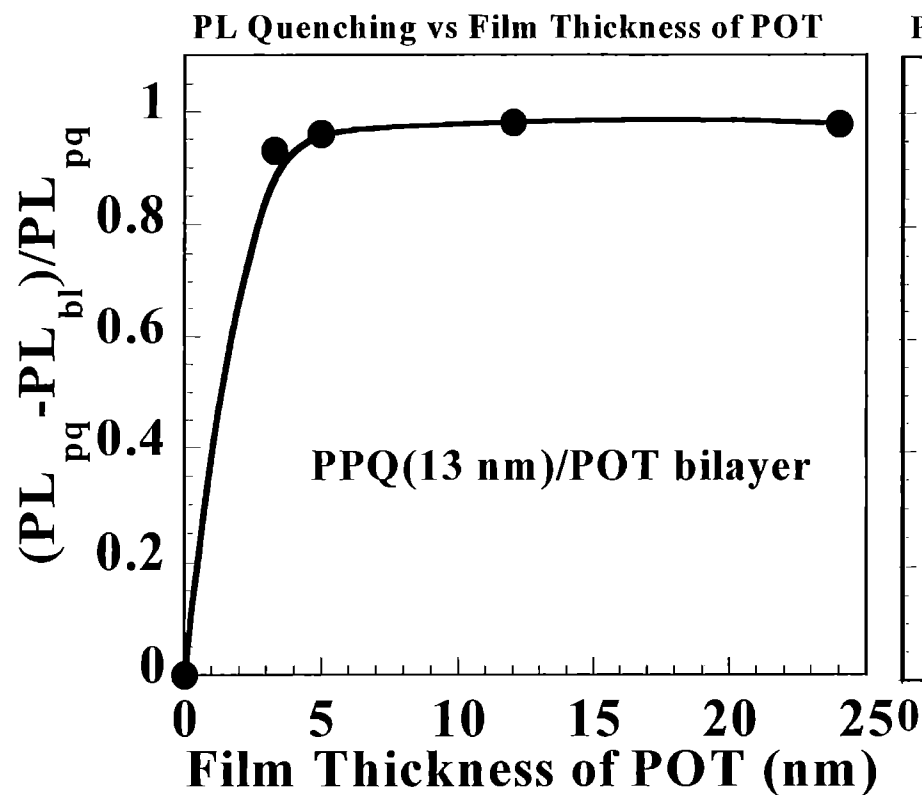
S. A. JENEKHE

Photoinduced Charge Transfer in Polyquinoline/Polythiophene Heterojunctions



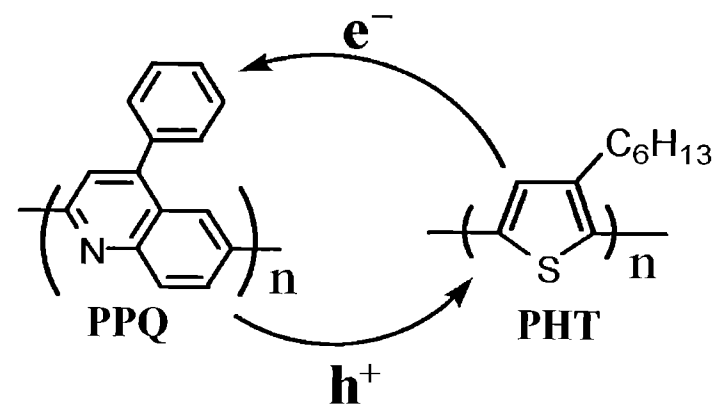
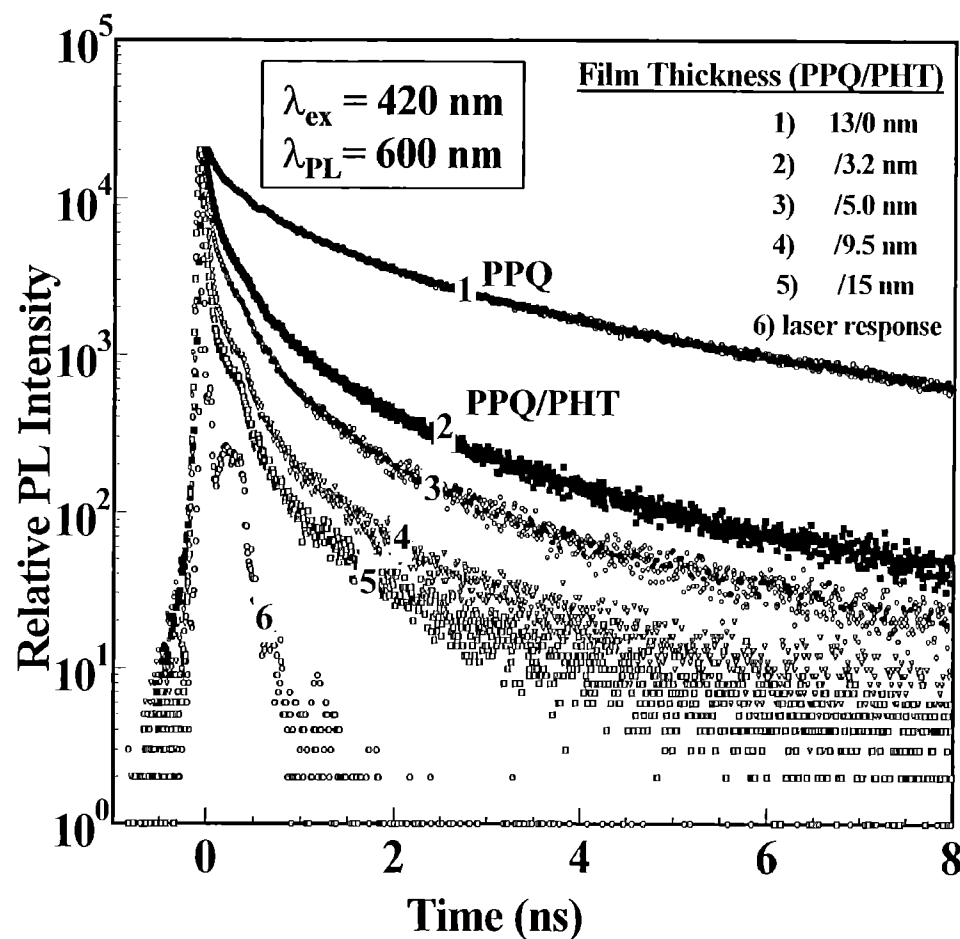
PL Quenching in Polyquinoline/Polythiophene Heterojunctions

— *Effect of Film Thickness*



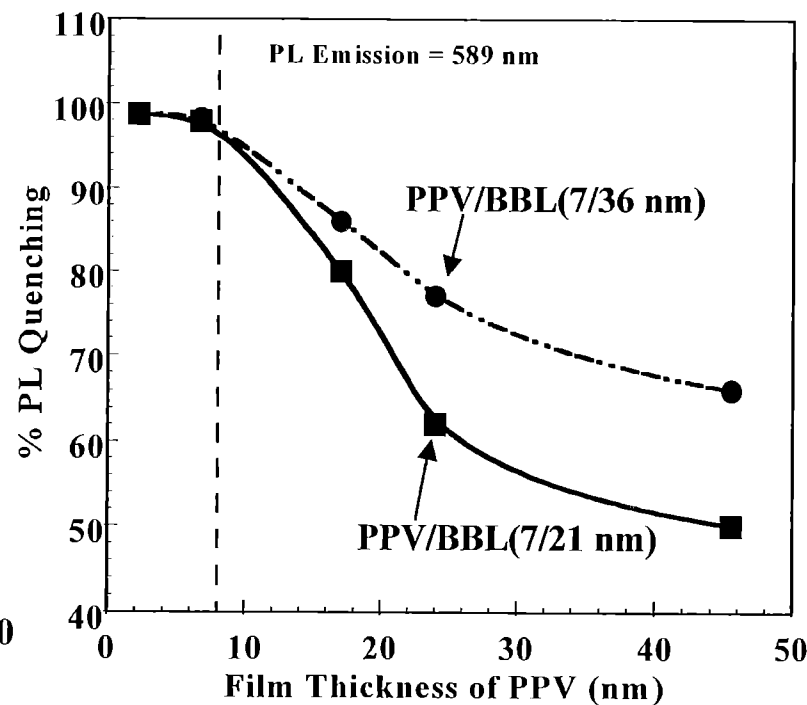
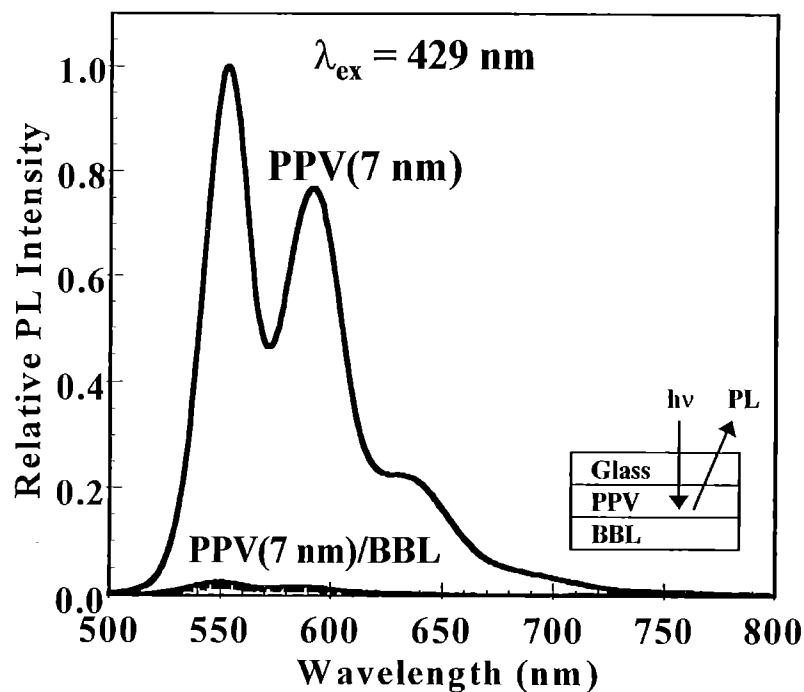
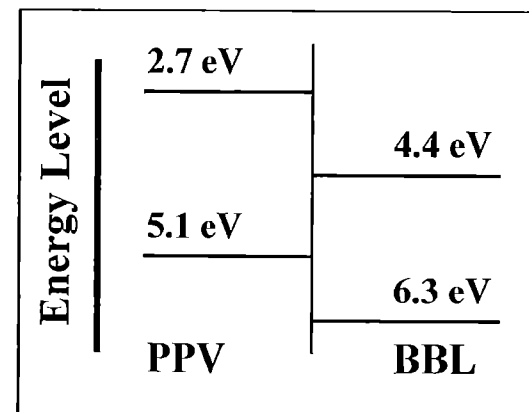
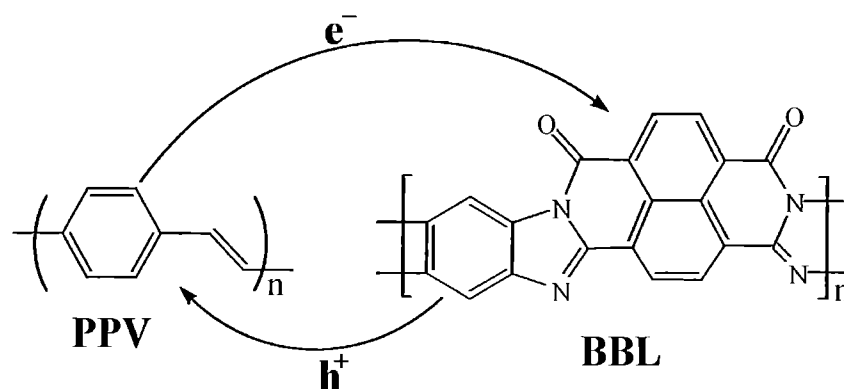
— Exciton Diffusion Length estimated to be 15 - 20 nm for Polyquinolines

Photoinduced Charge Transfer in Polyquinoline/Polythiophene Heterojunctions

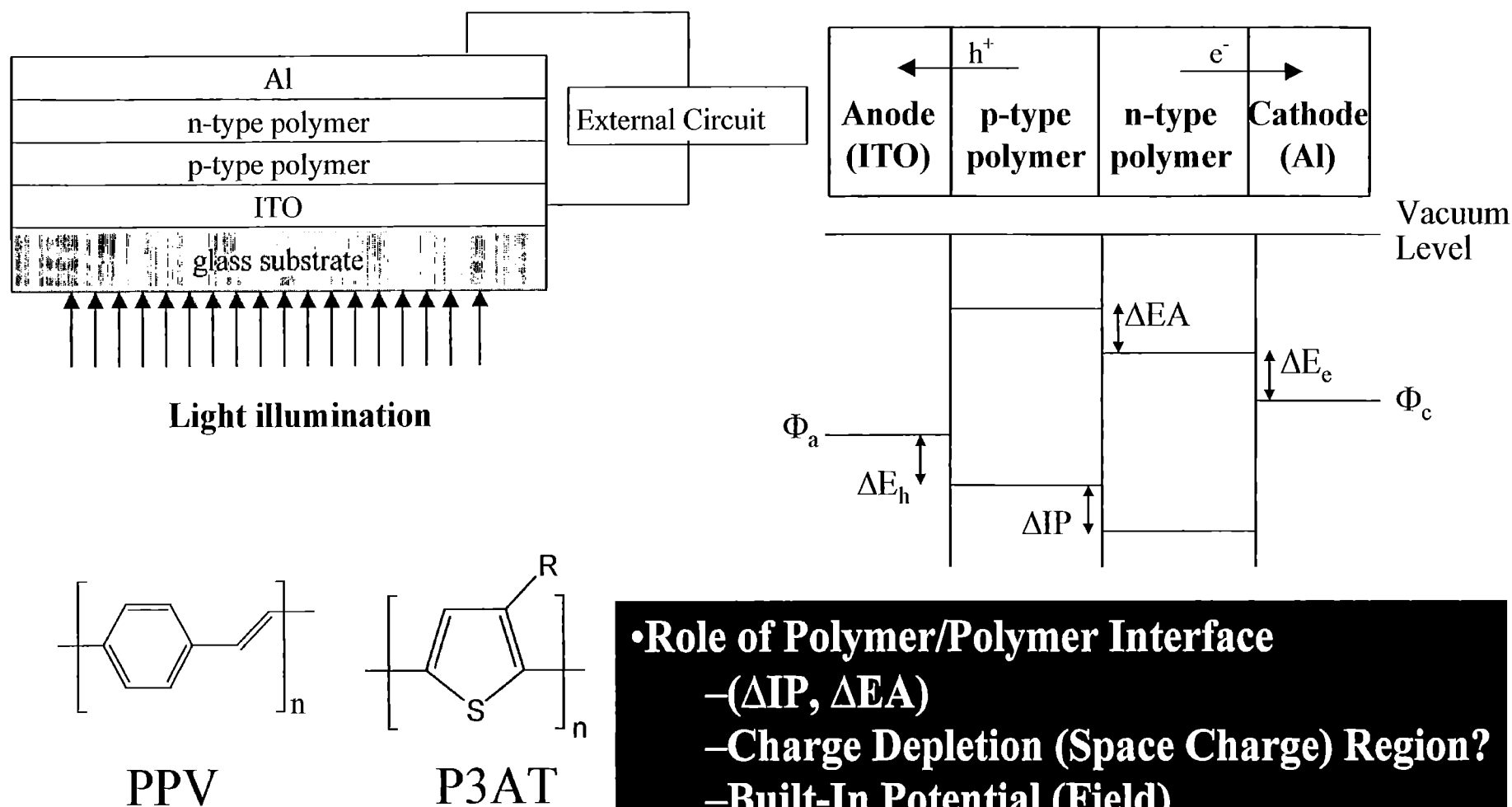


- PPQ Thin Film
 PL Lifetime, $\tau = 4.4 \text{ ns}$
- PPQ/PHT(13/15 nm) bilayer
 PL lifetime, $\tau = 29 \text{ ps}$.
- A factor of 150 reduction in PL lifetime.

Photoinduced Charge Transfer at PPV/BBL Heterojunctions

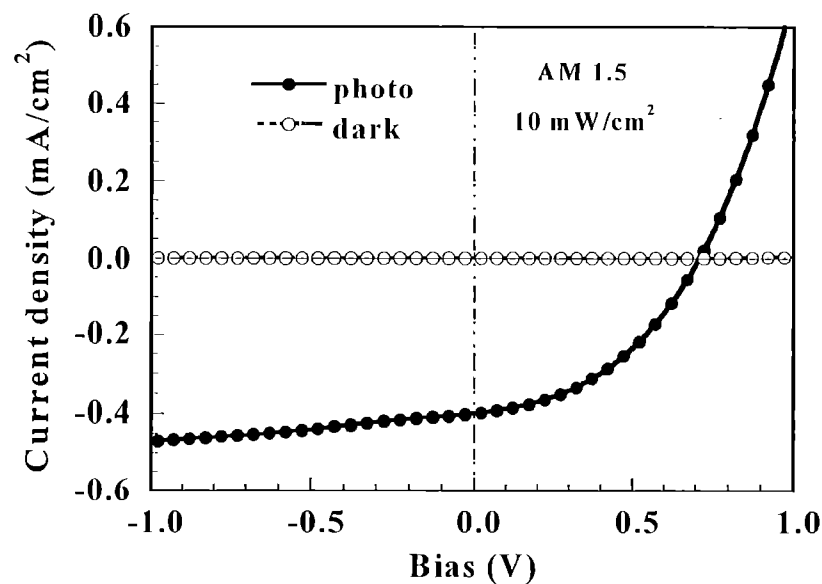
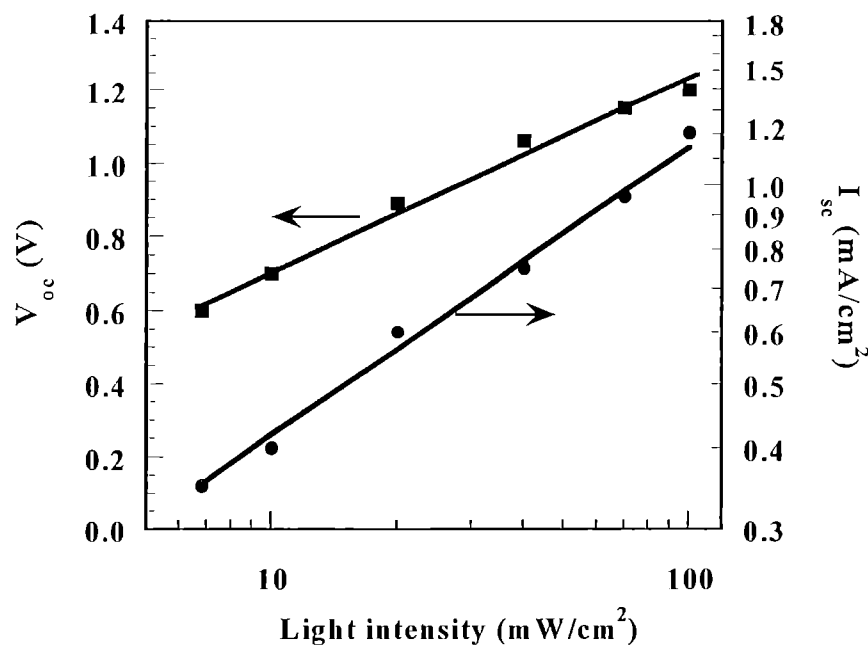
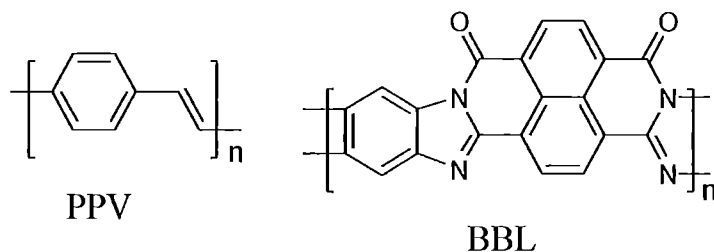


PHOTOVOLTAIC PROPERTIES OF SEMICONDUCTING POLYMER HETEROJUNCTIONS



- Role of Polymer/Polymer Interface
 - $(\Delta IP, \Delta EA)$
 - Charge Depletion (Space Charge) Region?
 - Built-In Potential (Field)
- Finite Size Effects
- Ohmic Contacts

PPV/BBL SOLAR CELLS



$$I_{sc} = 0.4 - 1.2 \text{ mA/cm}^2$$

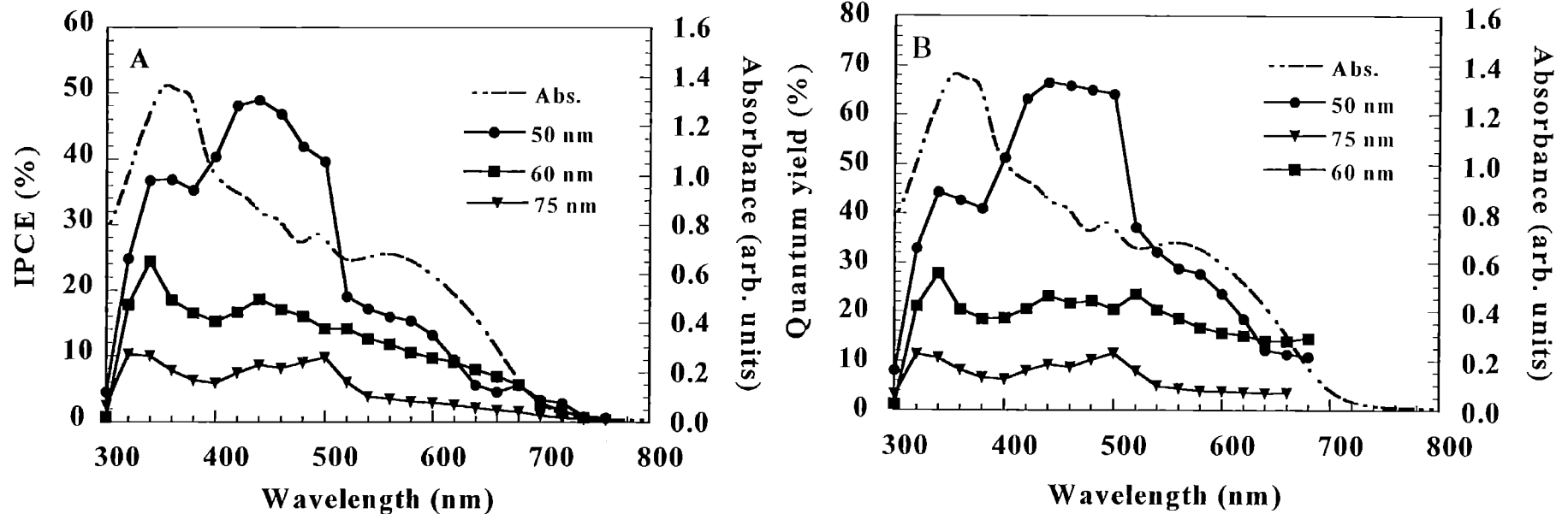
$$V_{oc} = 0.7 - 1.2 \text{ V}$$

$$\text{Fill Factor (FF)} = \frac{(IV)_{\max}}{V_{oc} I_{sc}} = 0.41 - 0.43$$

$$\text{Power Conversion Efficiency } \eta_p = 1.4 - 2.0 \%$$

CHARGE COLLECTION FROM PPV/BBL SOLAR CELLS

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



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

Solar Cells From Polymer/Polymer Heterojunctions

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

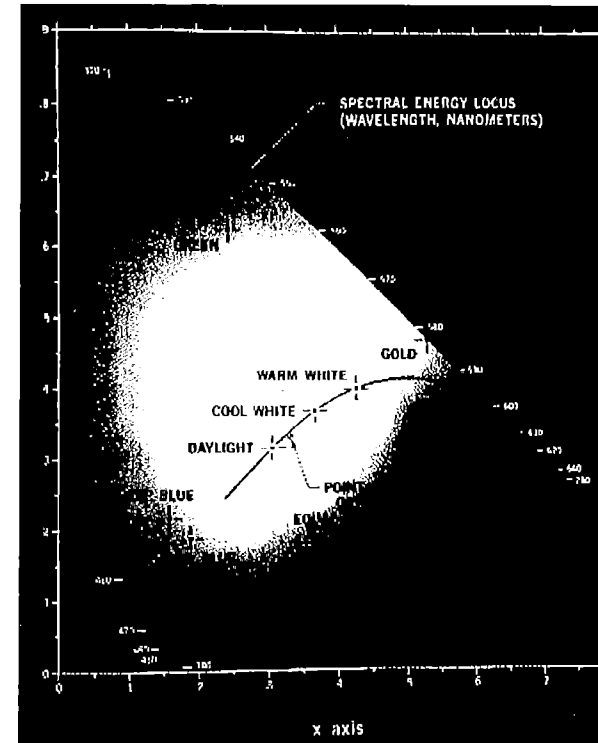
Outline

- Goals and Background
- Bilayer Tunable Photoluminescence
- Bilayer Tunable Electroluminescence
 - PPV/PCZPQ
 - PPV/Ru(bpy)₃²⁺
- 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

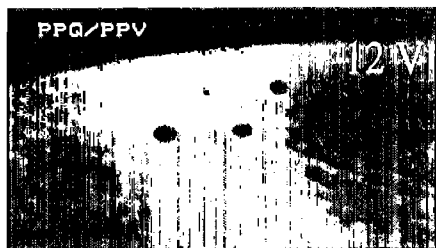


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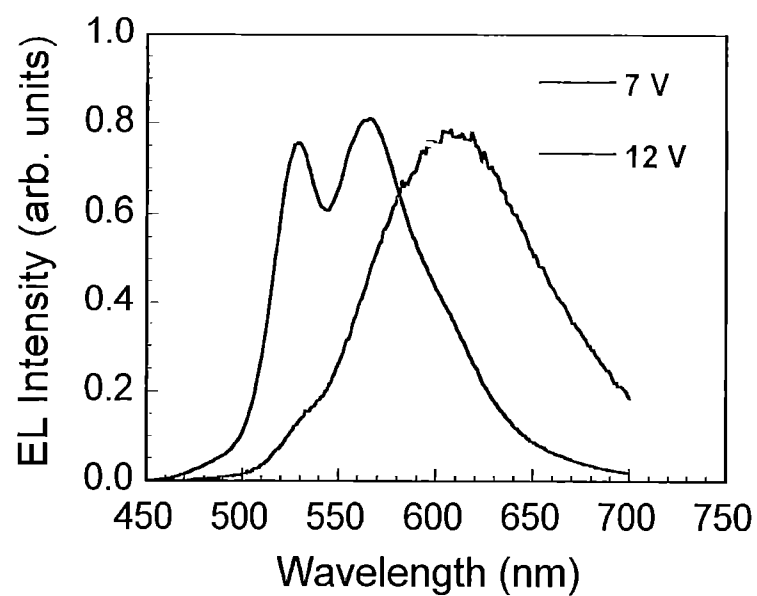
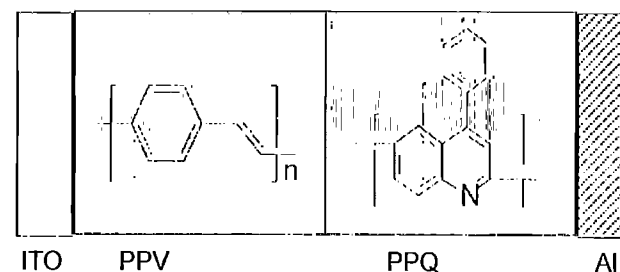
KATHLEEN MEEKER

km0807sl

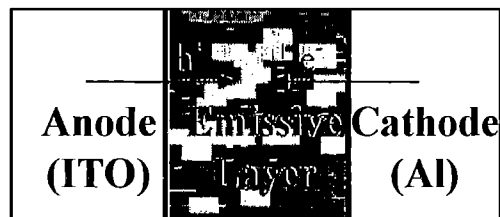
Background: Tunable EL in Polymer Heterojunctions



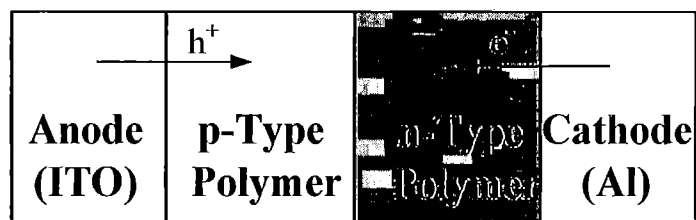
Zhang and Jenekhe, *Macromolecules*
2000, 2069-2082.



Approaches to Tunable Electroluminescence



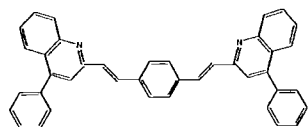
Emissive layers comprised of polymer blends can potentially provide tunable EL; each polymer contributes its emission spectrum.



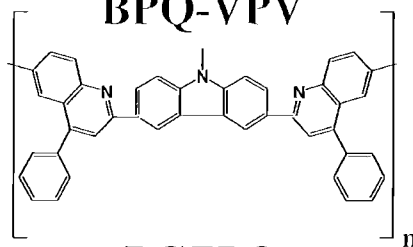
Two polymer layers can improve charge injection/transport and provide for selective excitation.

Materials Explored

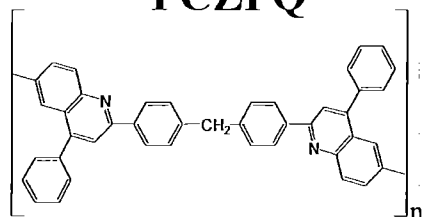
Poly- and oligoquinolines



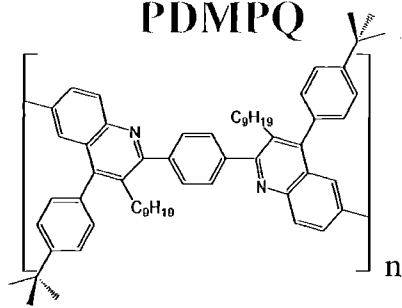
BPQ-VPV



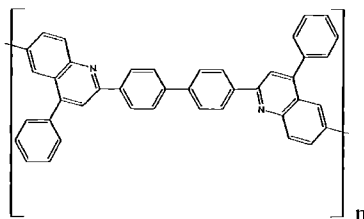
PCZPQ



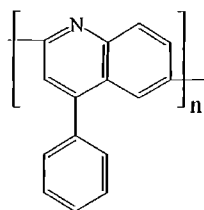
PDMPQ



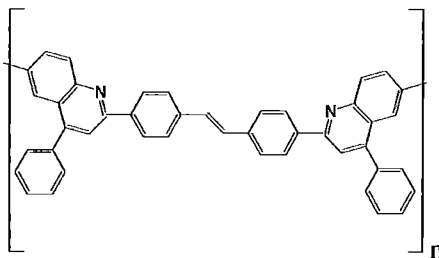
BuN-PPQ



PBPQ

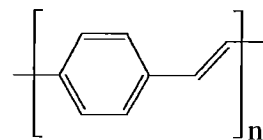


PPQ

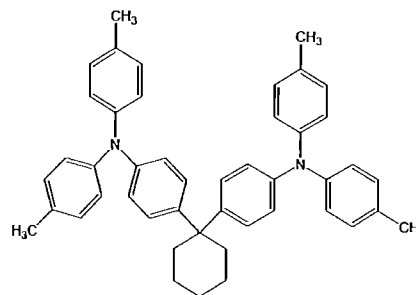


PSPQ

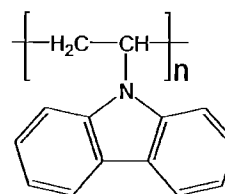
p-type materials



PPV

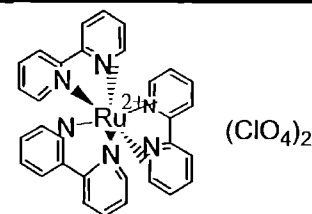


TAPC



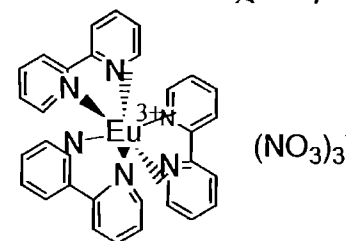
PVK

Metal Complexes



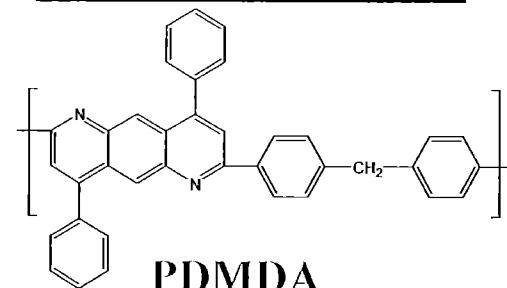
$\text{Ru(bpy)}_3(\text{ClO}_4)_2$

From the Bard group



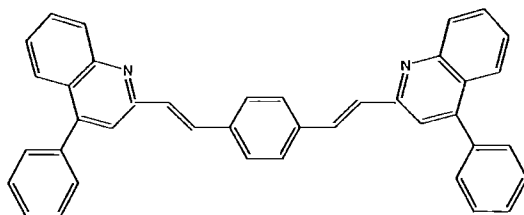
$\text{Eu(bpy)}_3(\text{NO}_3)_3$

Polyanthrazolines

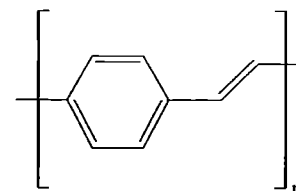


PDMDA

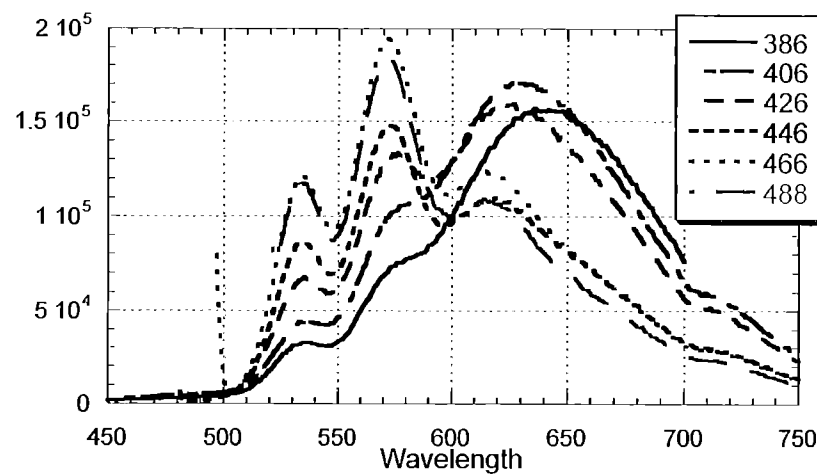
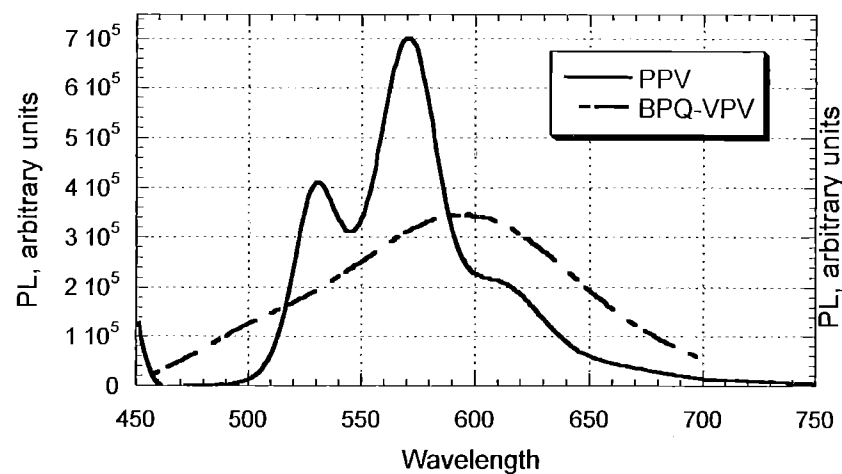
Tunable Bilayer Photoluminescence



BPQ-VPV



PPV

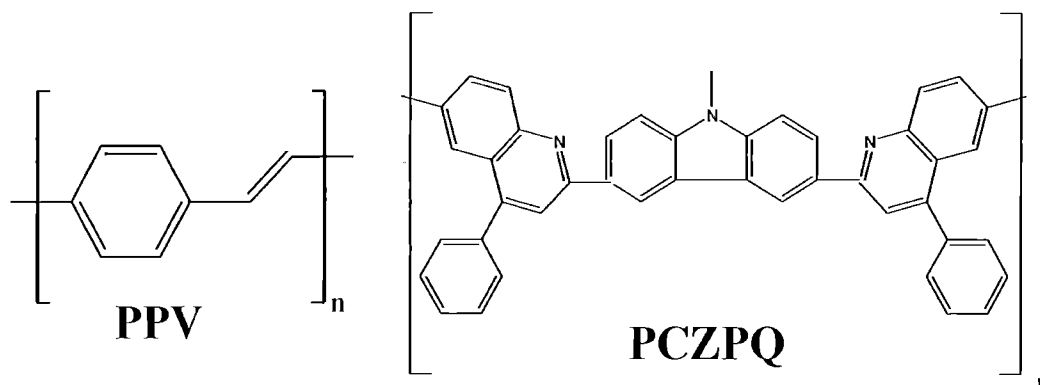


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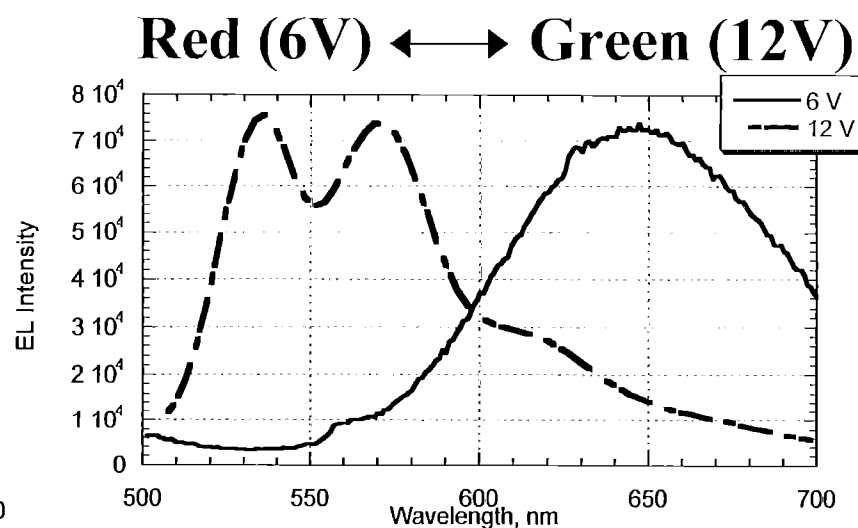
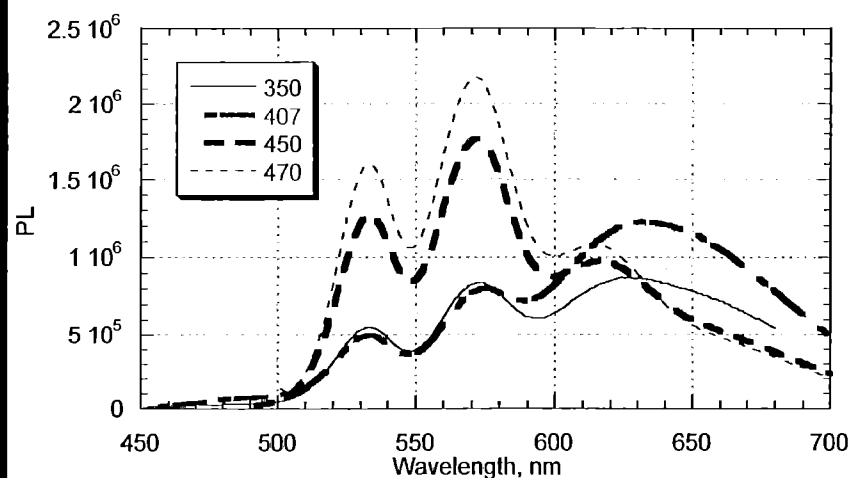
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km0807s3

Voltage-Tunable EL from PPV/PCZPQ Bilayers

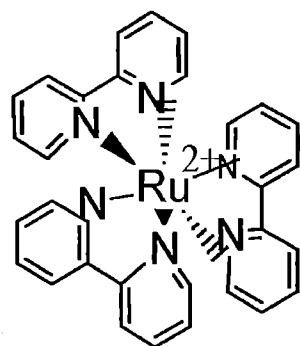


ITO/PPV/PCZPQ/Al

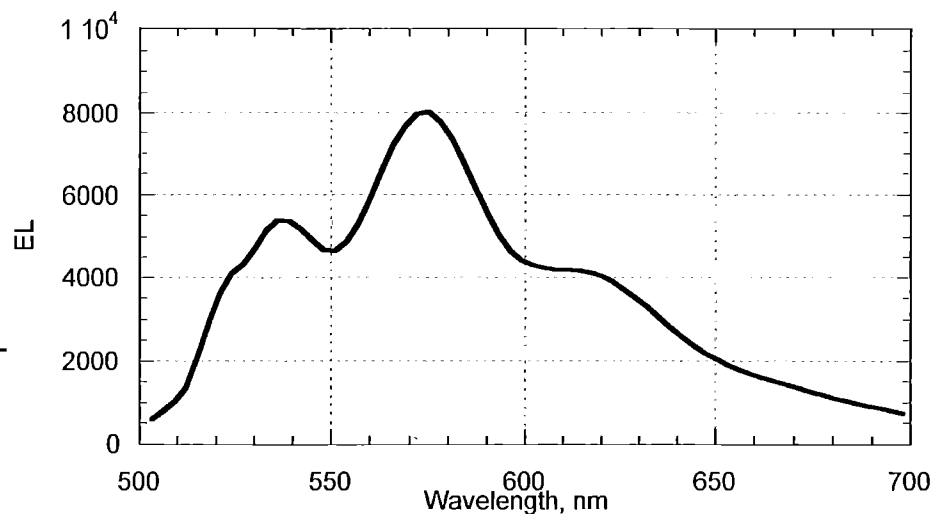


Effects of Film Thickness on Bilayer EL Color

ITO/PPV (70 nm)/ Ru(bpy)₃(ClO₄)₂ (30 nm) /Al

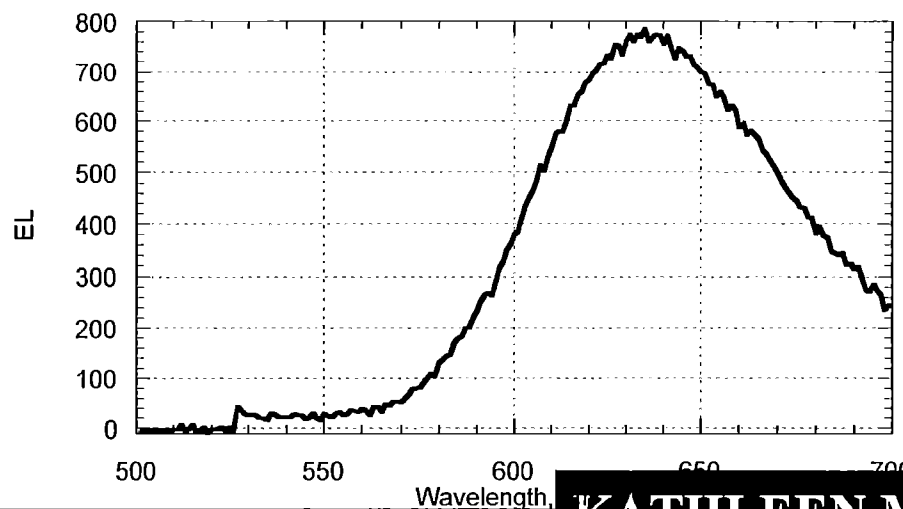


(ClO₄)₂⁻



80 Cd/m²
turn on at 6 V

ITO/PPV (30 nm)/ Ru(bpy)₃(ClO₄)₂ (50 nm)/Al



200 Cd/m²
turn on at 6 V

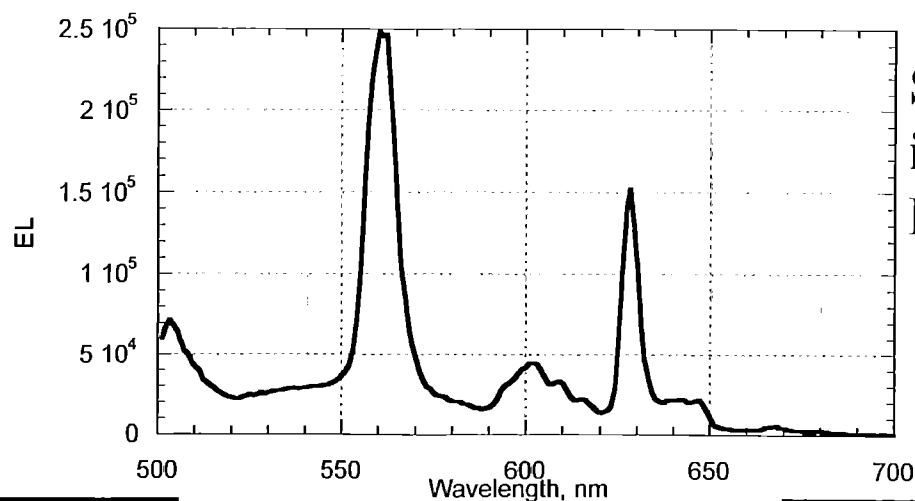
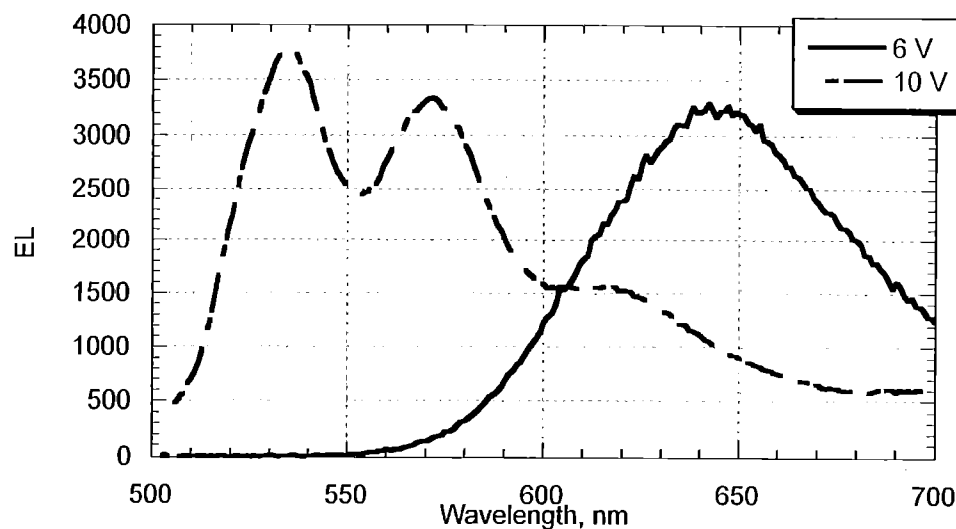
ARO TOPS MURI

KATHLEEN MEEKER

km0807s6

Tunable EL: ITO/PPV/Ru(bpy)₃(ClO₄)₂/Al

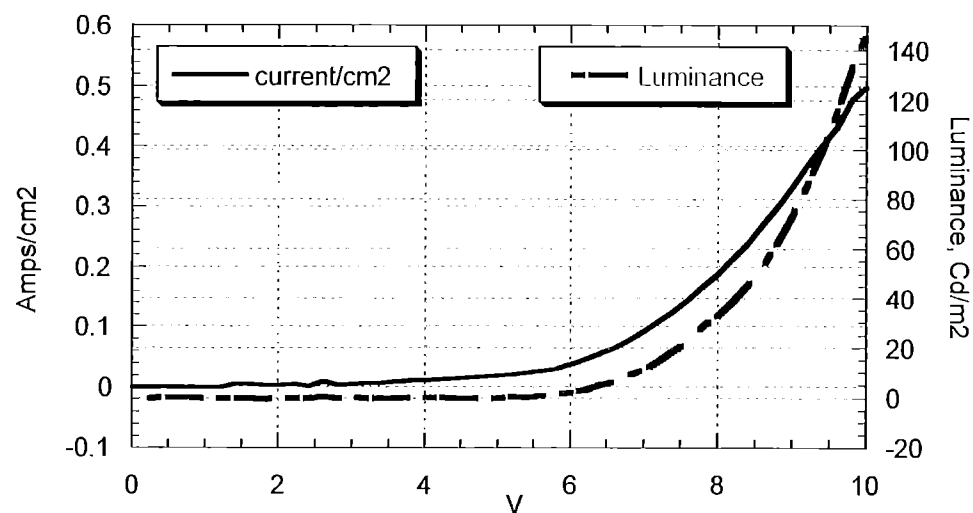
ITO/ PPV (40 nm) / Ru(bpy)₃(ClO₄)₂ (50 nm)/Al



Spectrum acquired at intermediate voltage. Microcavity effects?

Bilayer LED Performance

ITO/PPV (40 nm)/Ru(bpy)₃(ClO₄)₂ (50 nm)/Al

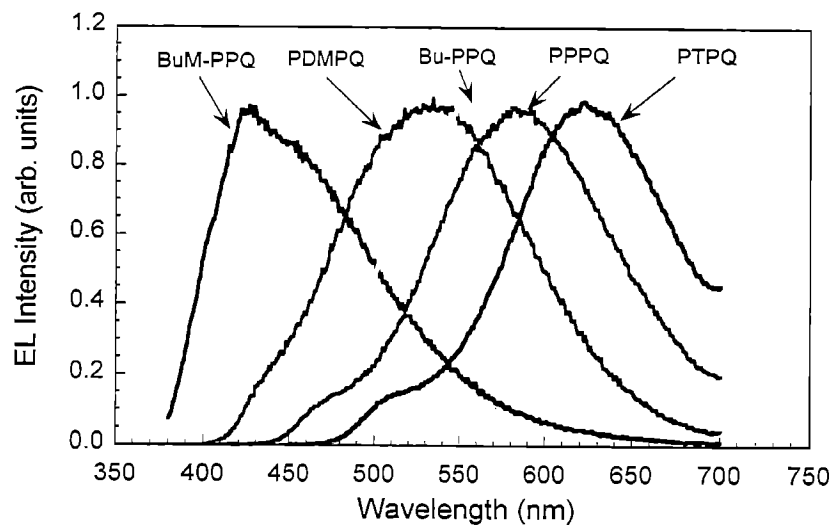
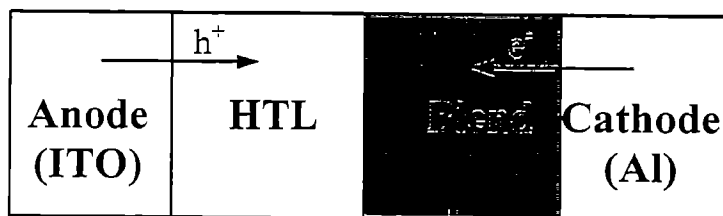
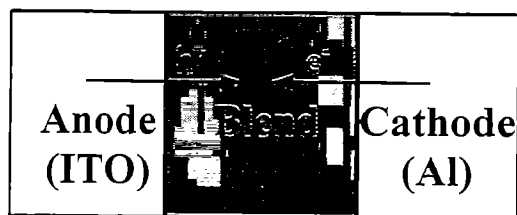


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km0807s9

EL of Polymer Blends



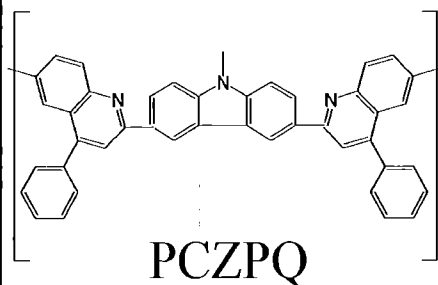
Possible Problems

A. Photophysical Processes

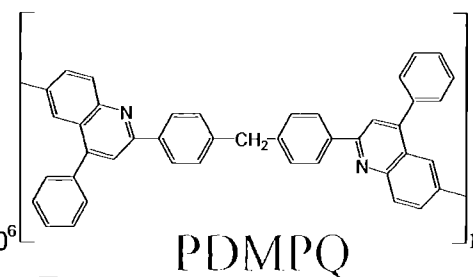
- Energy Transfer
- Exciplex Formation
- Photoinduced Electron Transfer

B. Control of Phase Separation

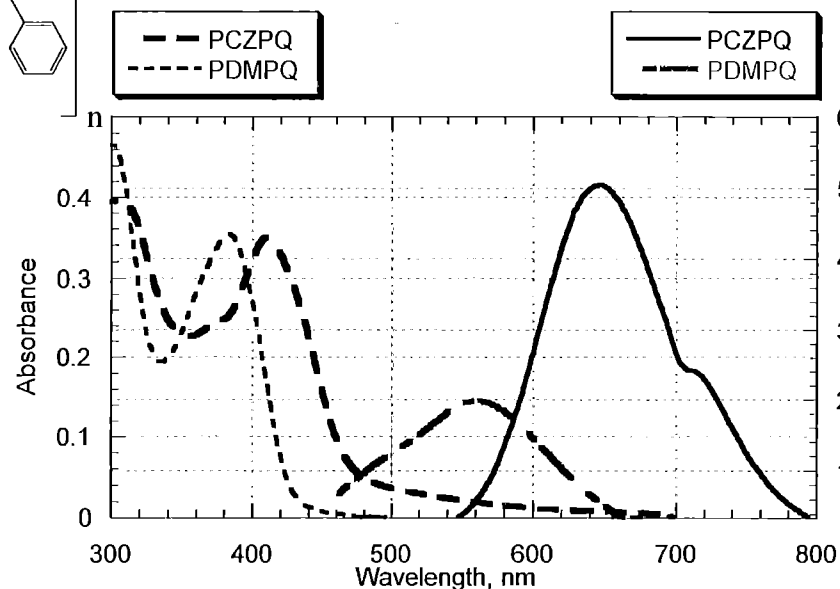
Polymer Blends



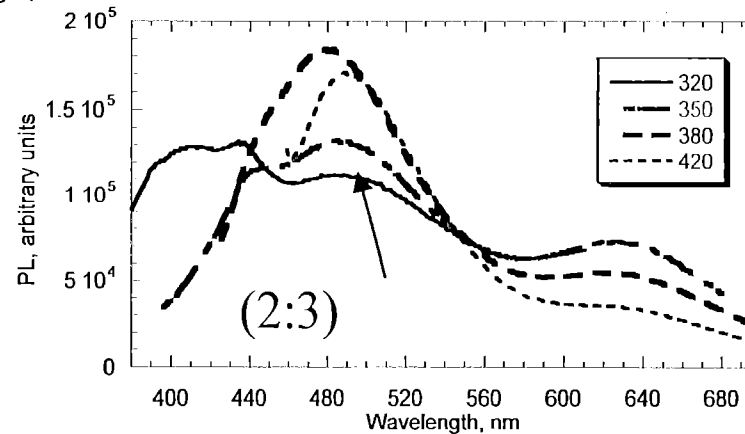
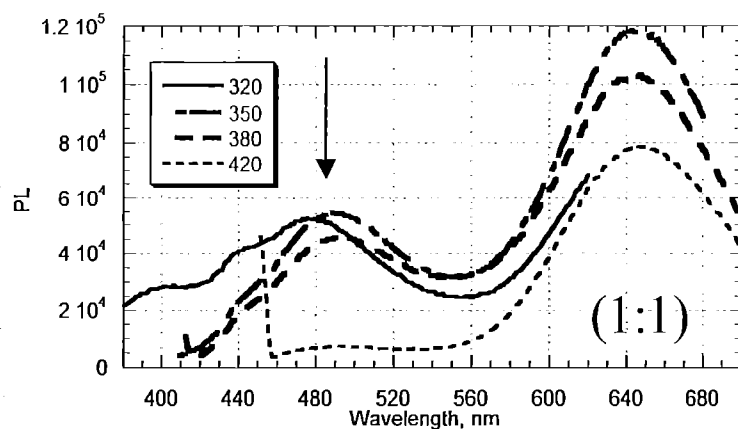
PCZPQ



PDMPQ



PL intensity, arbitrary units

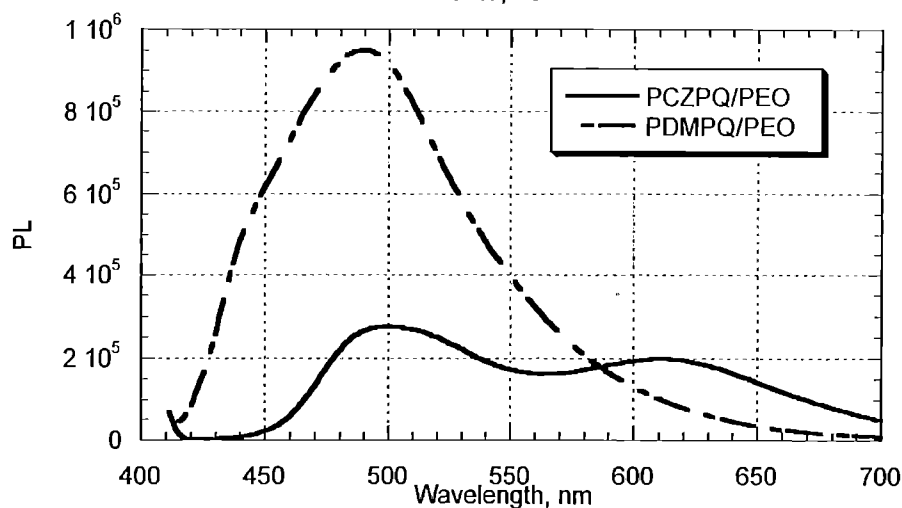
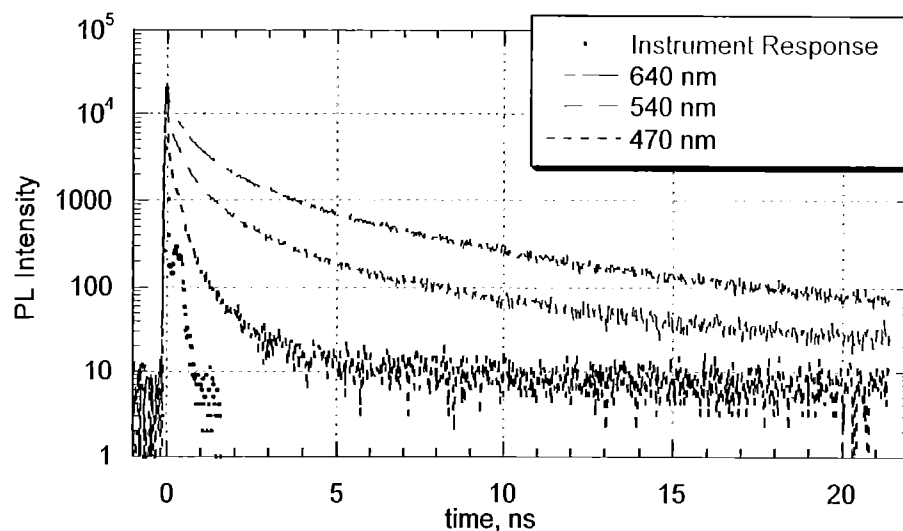


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Rm0807s15

Origin of New Blue Peak in Blends



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

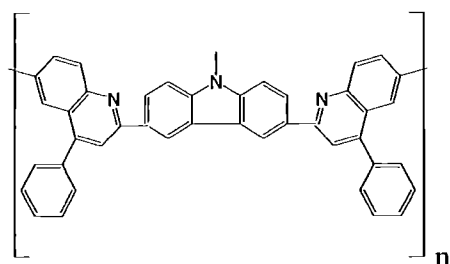
48.5 ps 85%

0.57 ns 12%

7.9 ns 3%

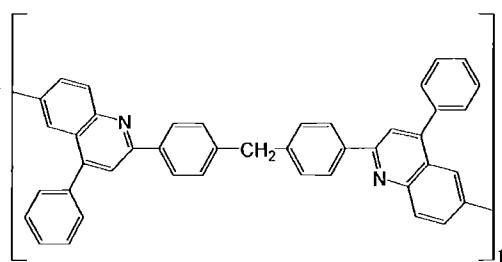
- Intrachain Excitons
- Excimers in Pure Films

EL of Binary Blends

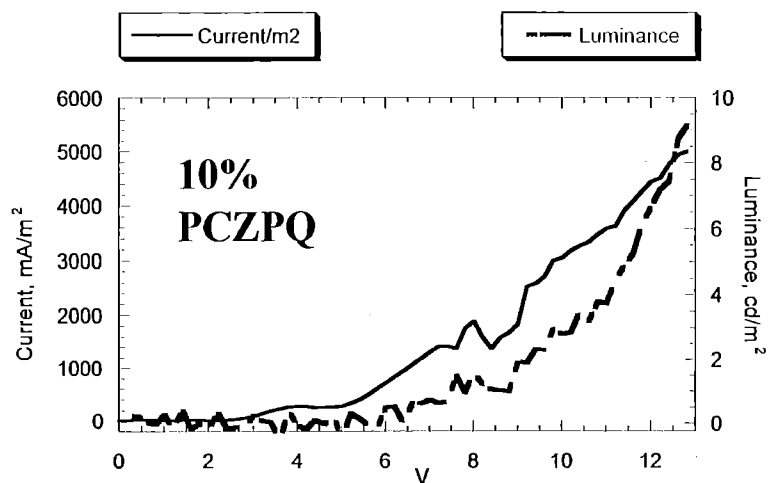
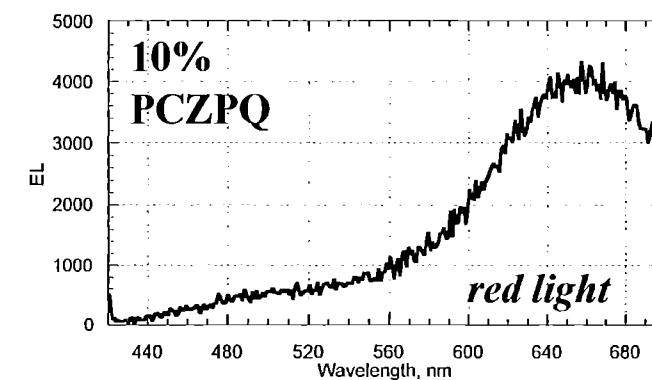
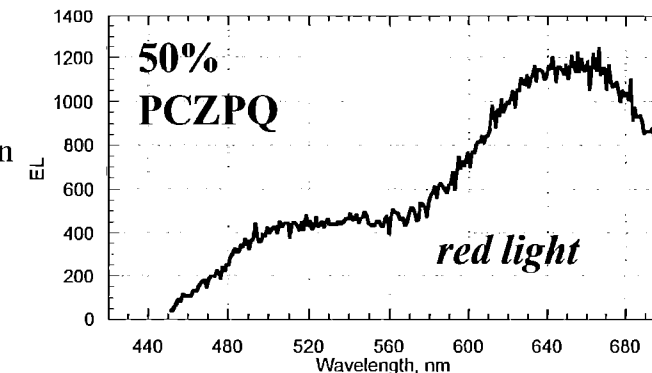
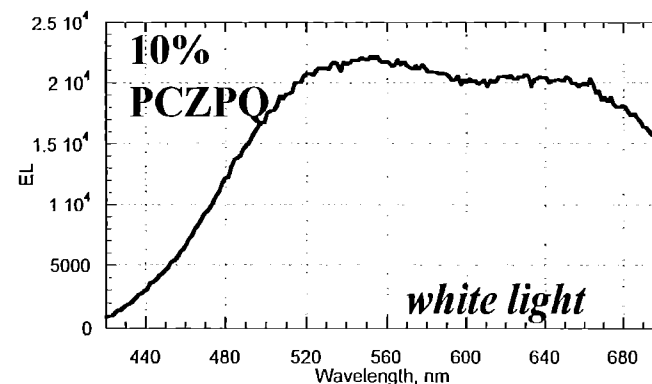


PCZPQ

ITO/Blend/Al



PDMPQ

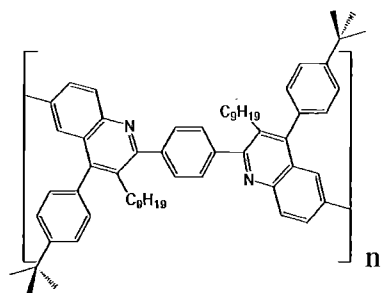
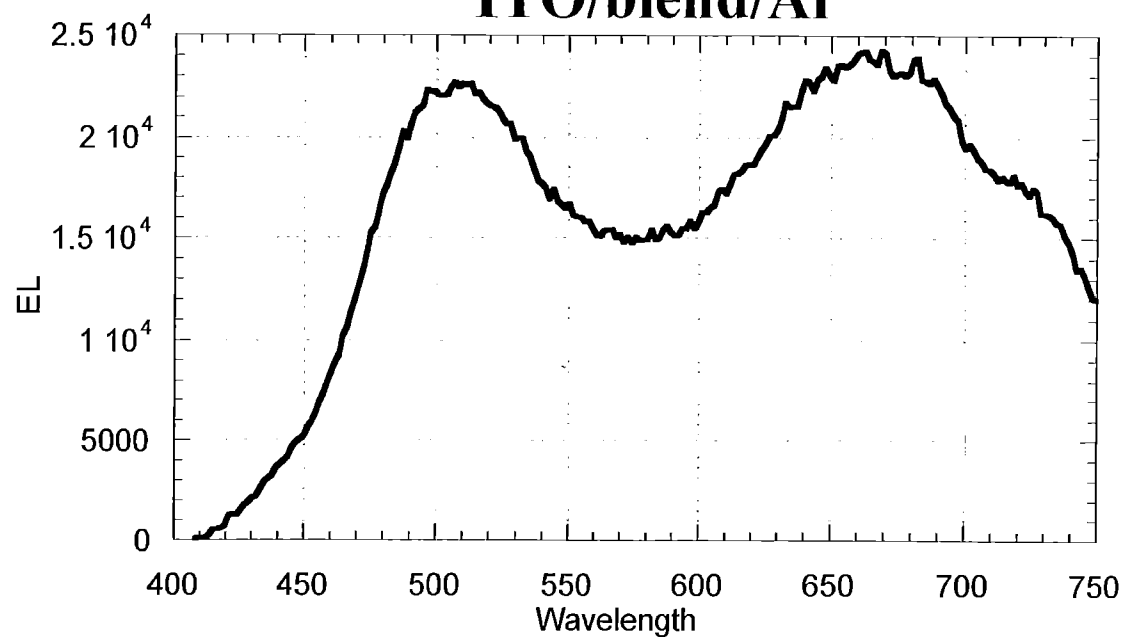


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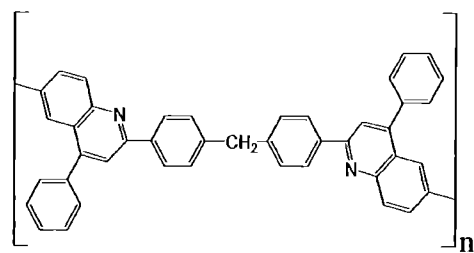
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Electroluminescence of Ternary Blends: BuN-PPQ, PDMPQ, PCZPQ (2:2:1)

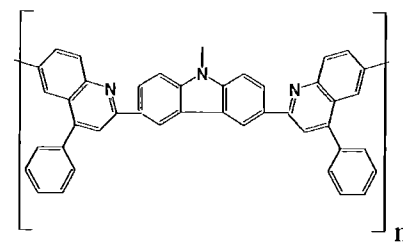
ITO/blend/Al



BuN-PPQ



PDMPQ



PCZPQ

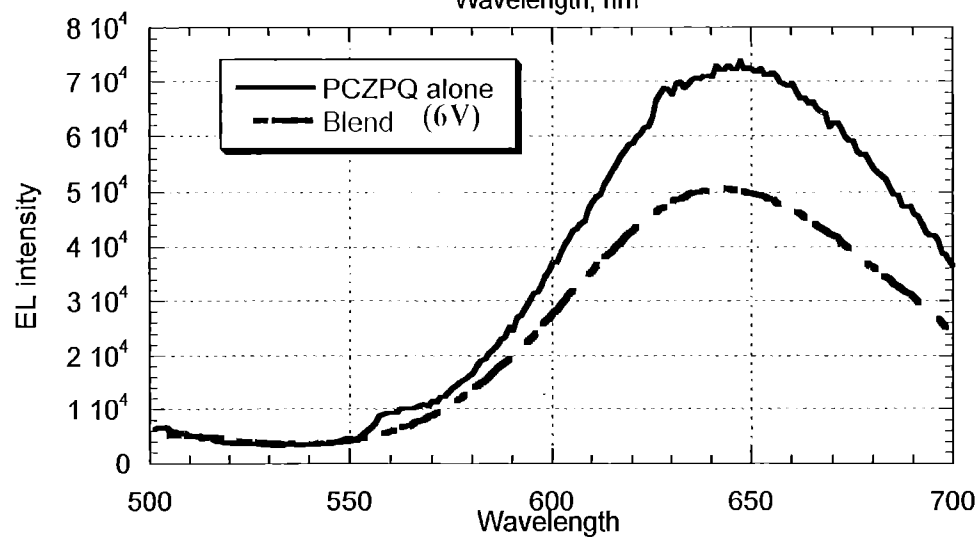
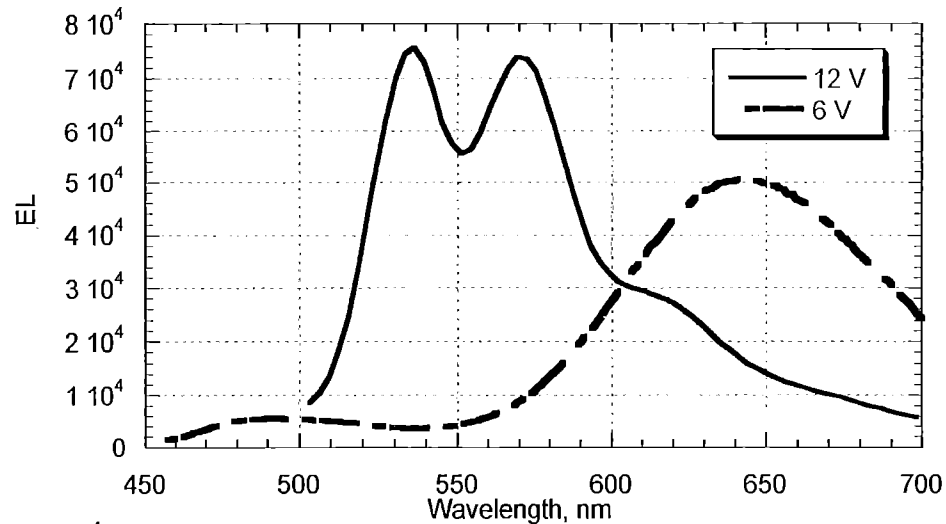
Tunable EL: Ternary Blends

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*

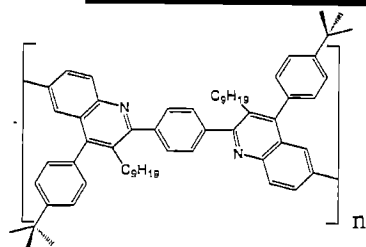


ARO TOPS MURI

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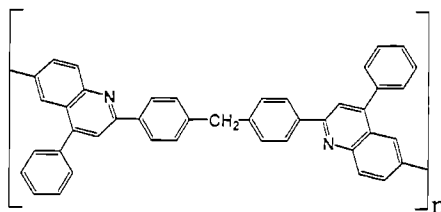
km0807s26

Selective Emission from Ternary Blends



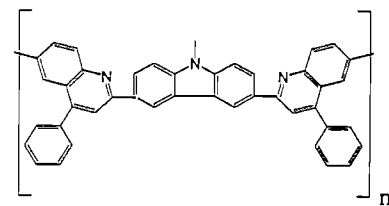
BuN-PPQ

$\lambda_{EL} = 424 \text{ nm}$
IP = 5.71 eV



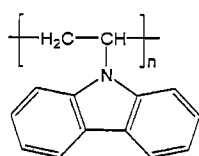
PDMPQ

$\lambda_{EL} = 540 \text{ nm}$
IP = 5.44 eV

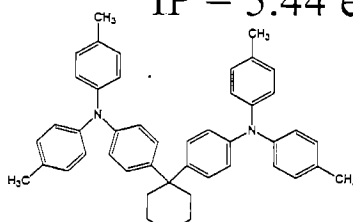


PCZPQ

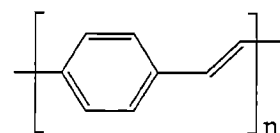
$\lambda_{EL} = 640 \text{ nm}$
IP = 5.27 eV



PVK
5.8 eV



TAPC:PS
5.3 eV



PPV
5.11 eV

Ionization
potential?

Emission
from blend?

Selective
emission?

Tunability?

blue

red

red

yes

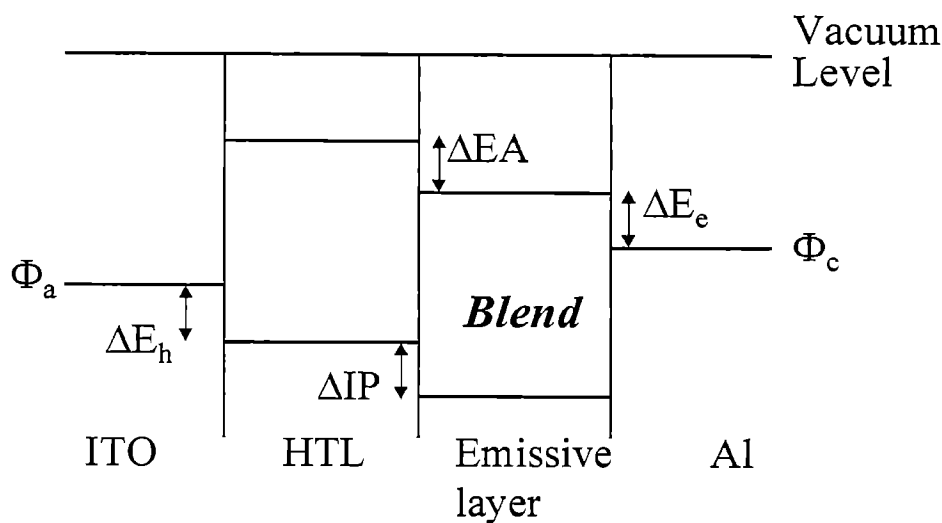
yes

yes

no

no

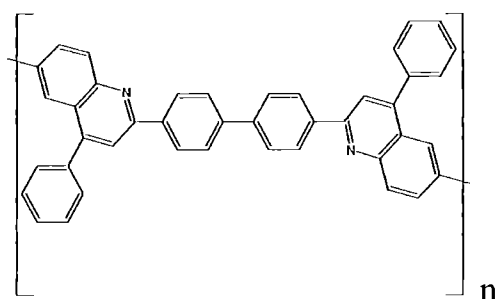
yes



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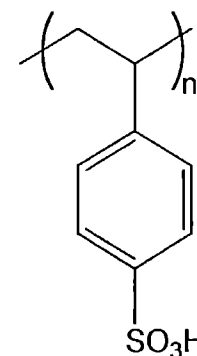
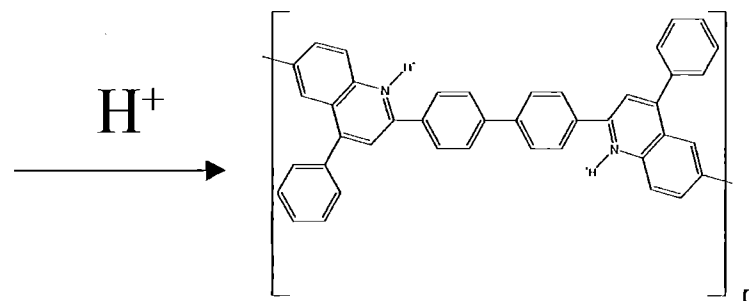
KATHLEEN MEEKER

Environmentally Responsive Light Emitting Polymers

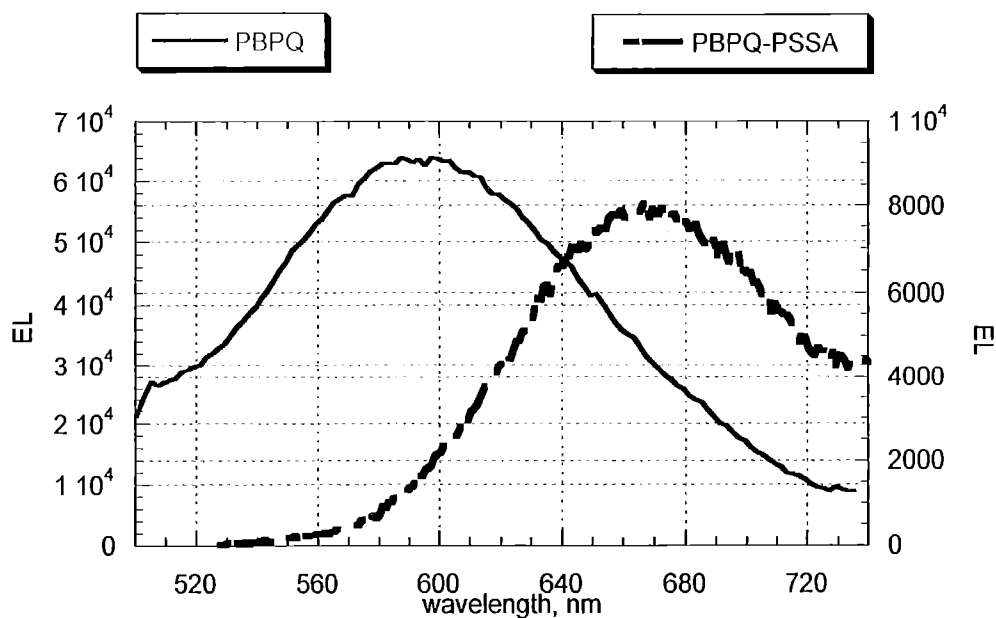


PBPQ

yellow-orange EL



PSSA



70-80 nm red shift
red EL

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km0807s29

Conclusions

- 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

ARO TOPS MURI

KATHLEEN MEEKER

km0807s3

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.

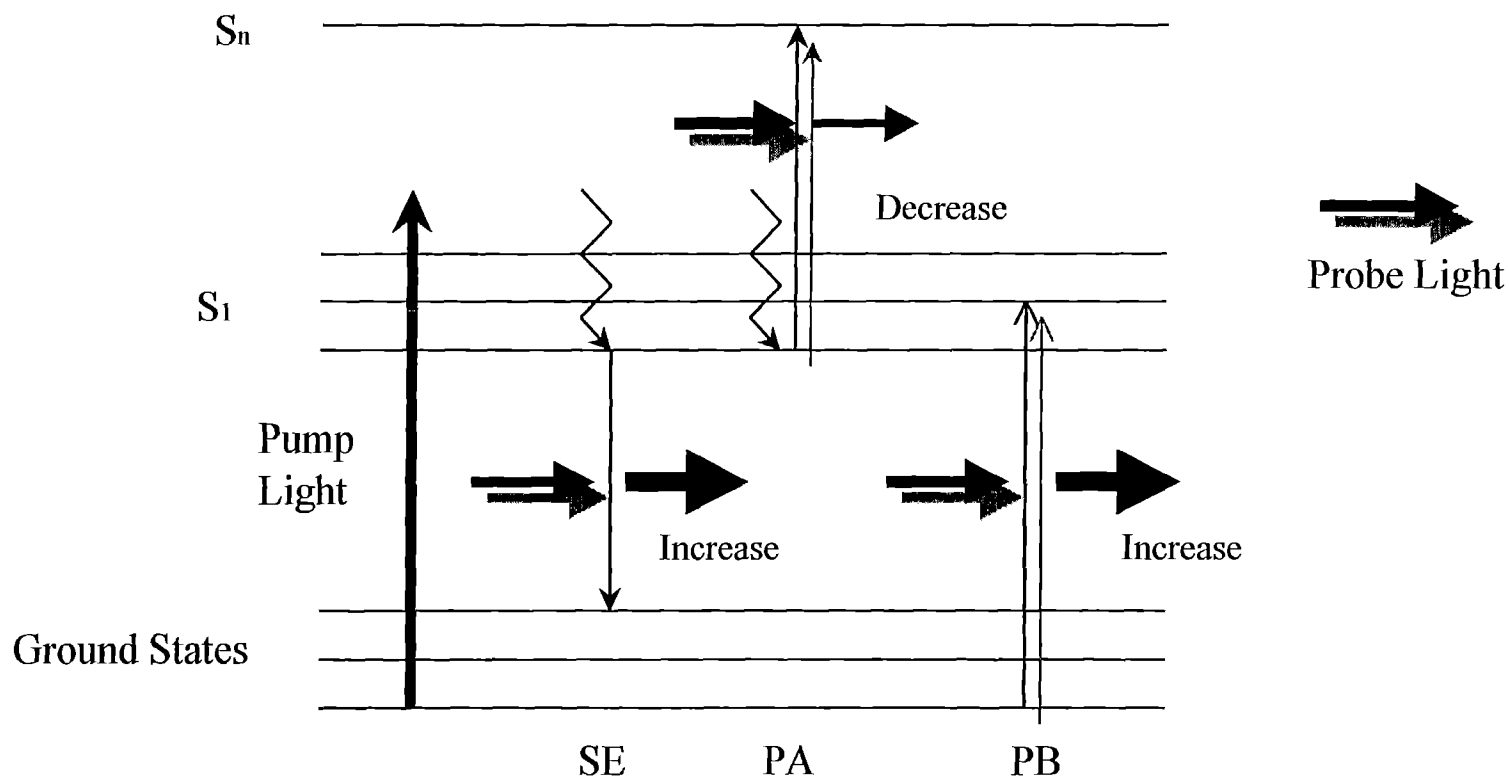
Electroluminescent polymer: MEH-PPV
(Poly(2-methoxy, 5-(2-ethylhexoxy)-
paraphenylenevinylene))

L.Rothberg, Rochester

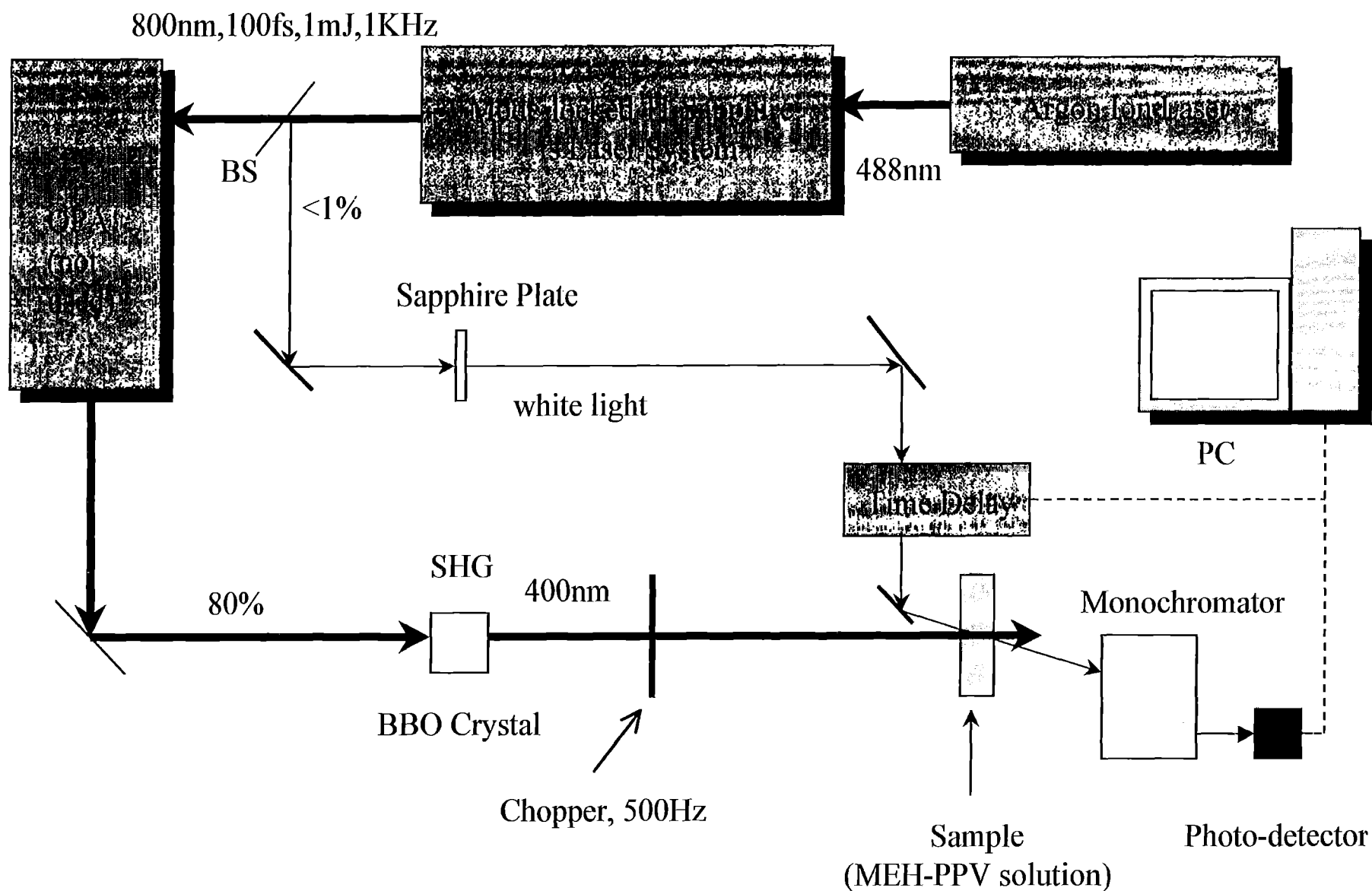
ARO MURI

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.



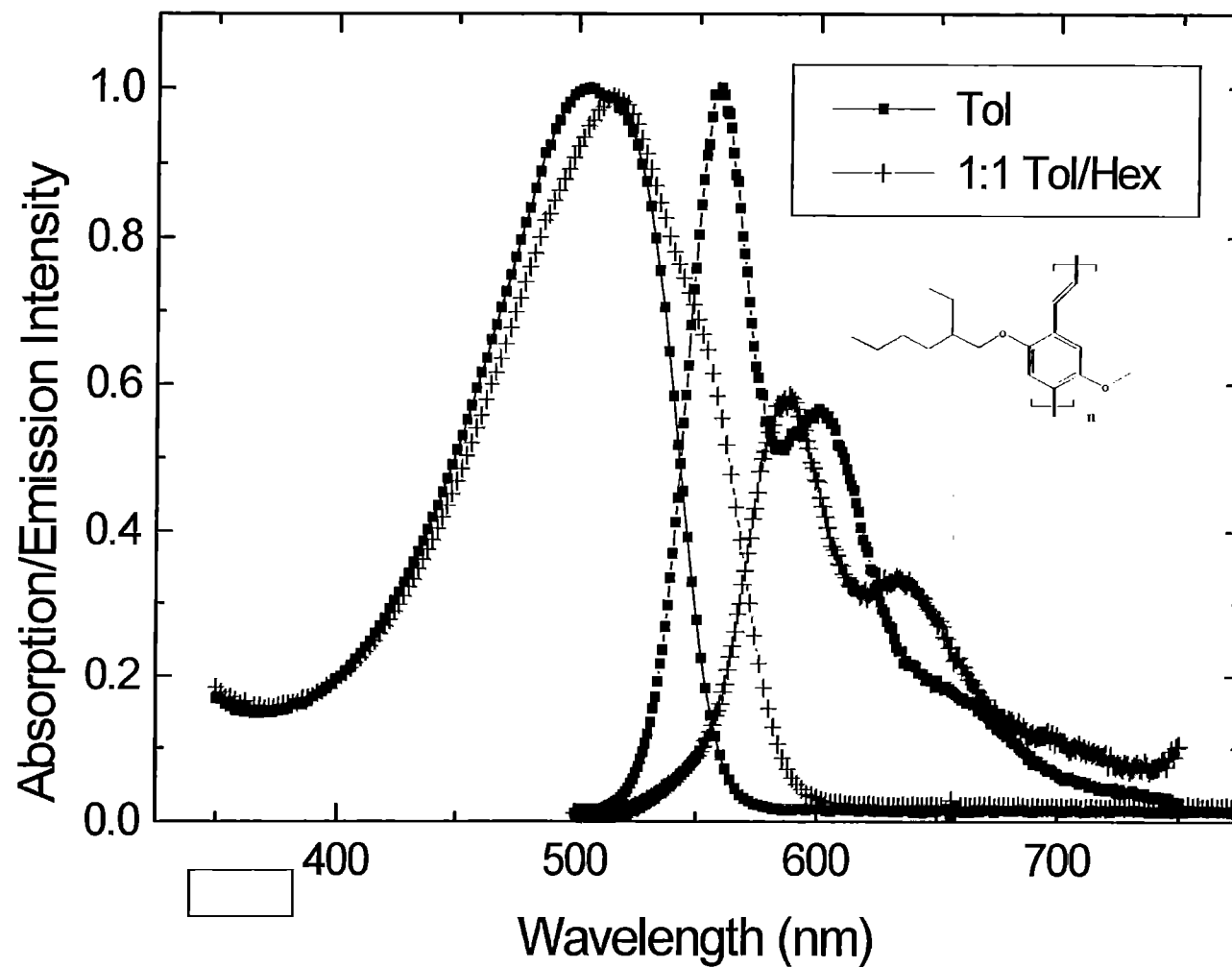
Experimental Set-up



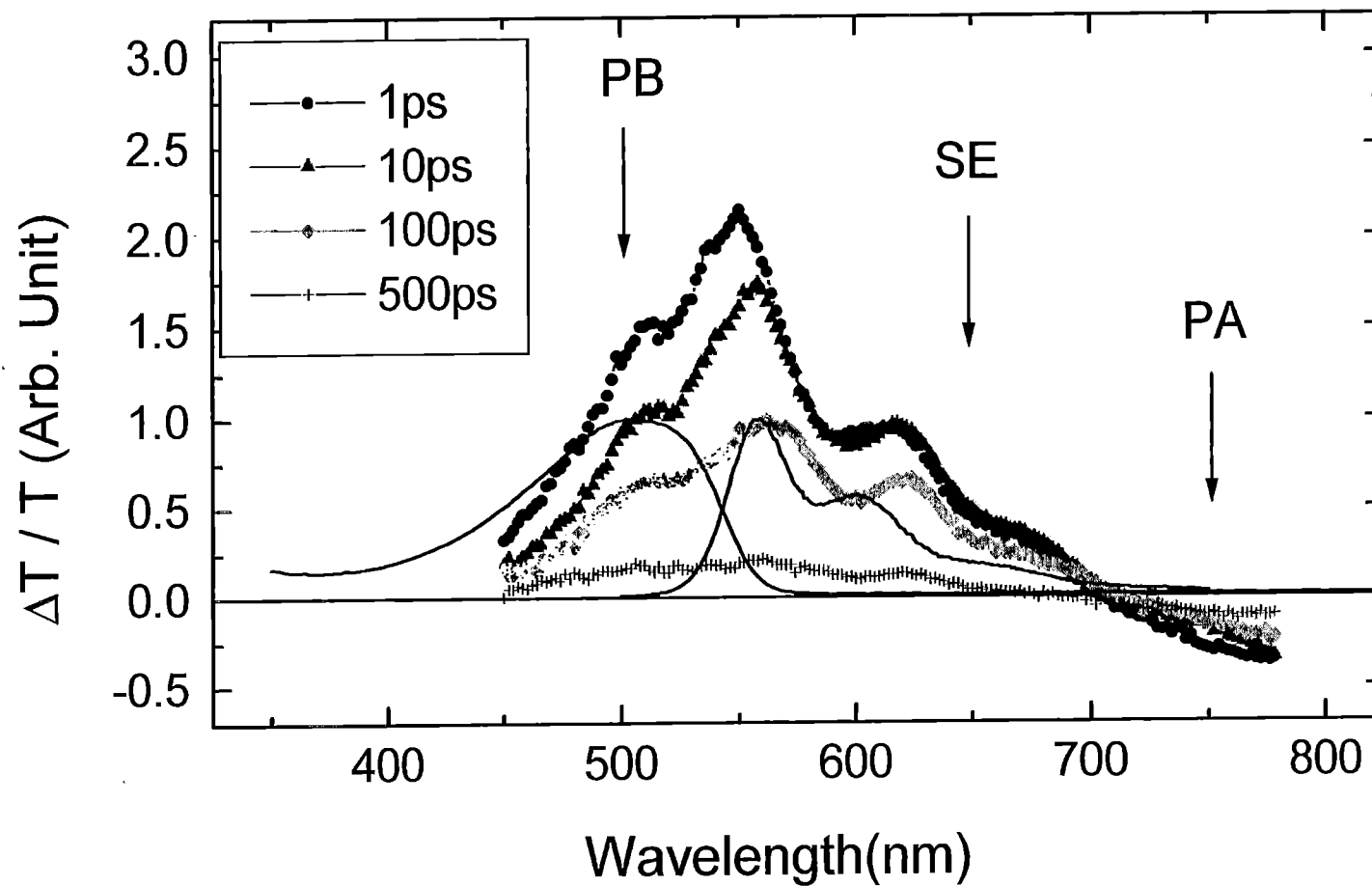
L.Rothberg, Rochester

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Solvatochromism in MEH-PPV



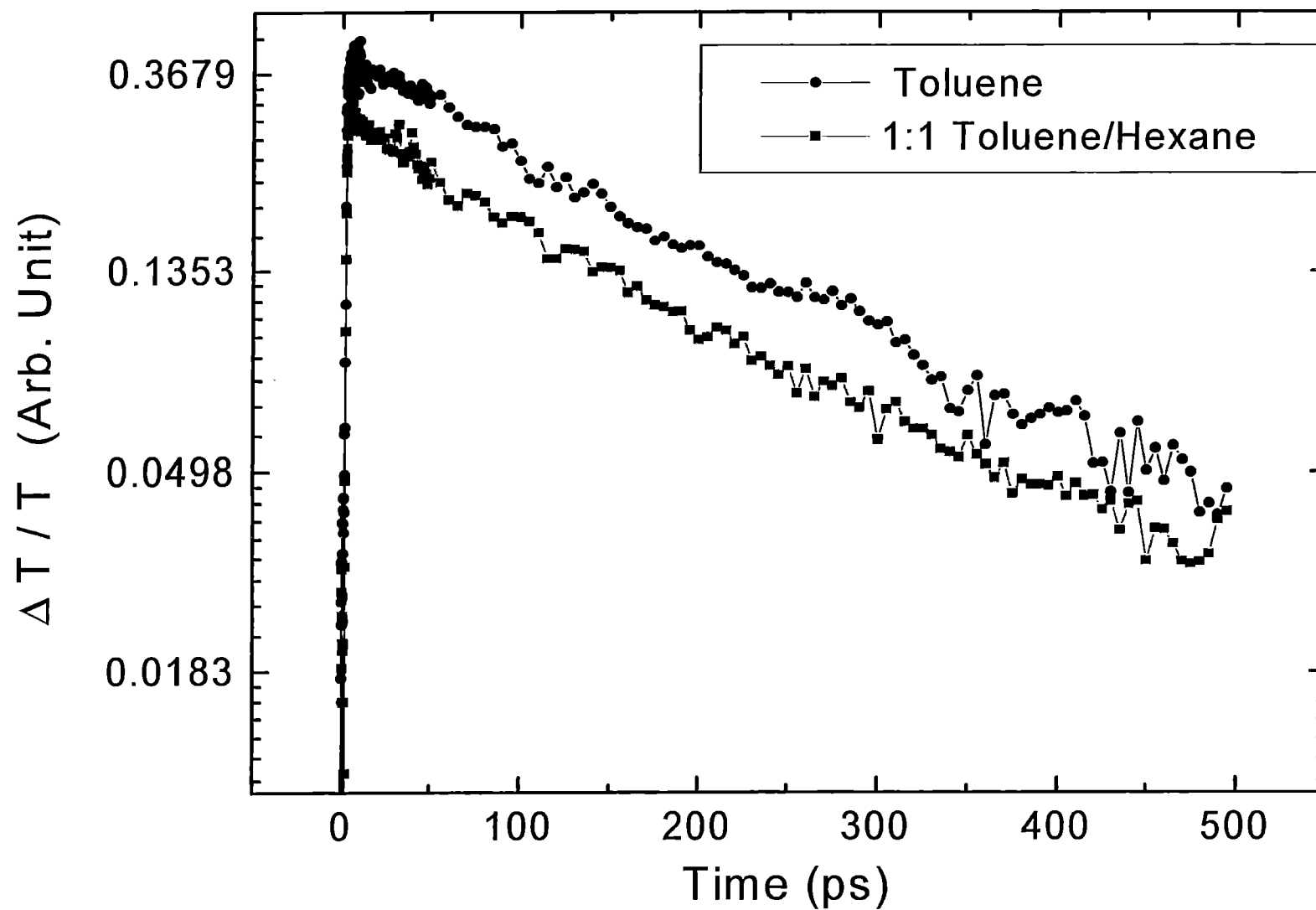
Transient Absorption (MEH-PPV/toluene)



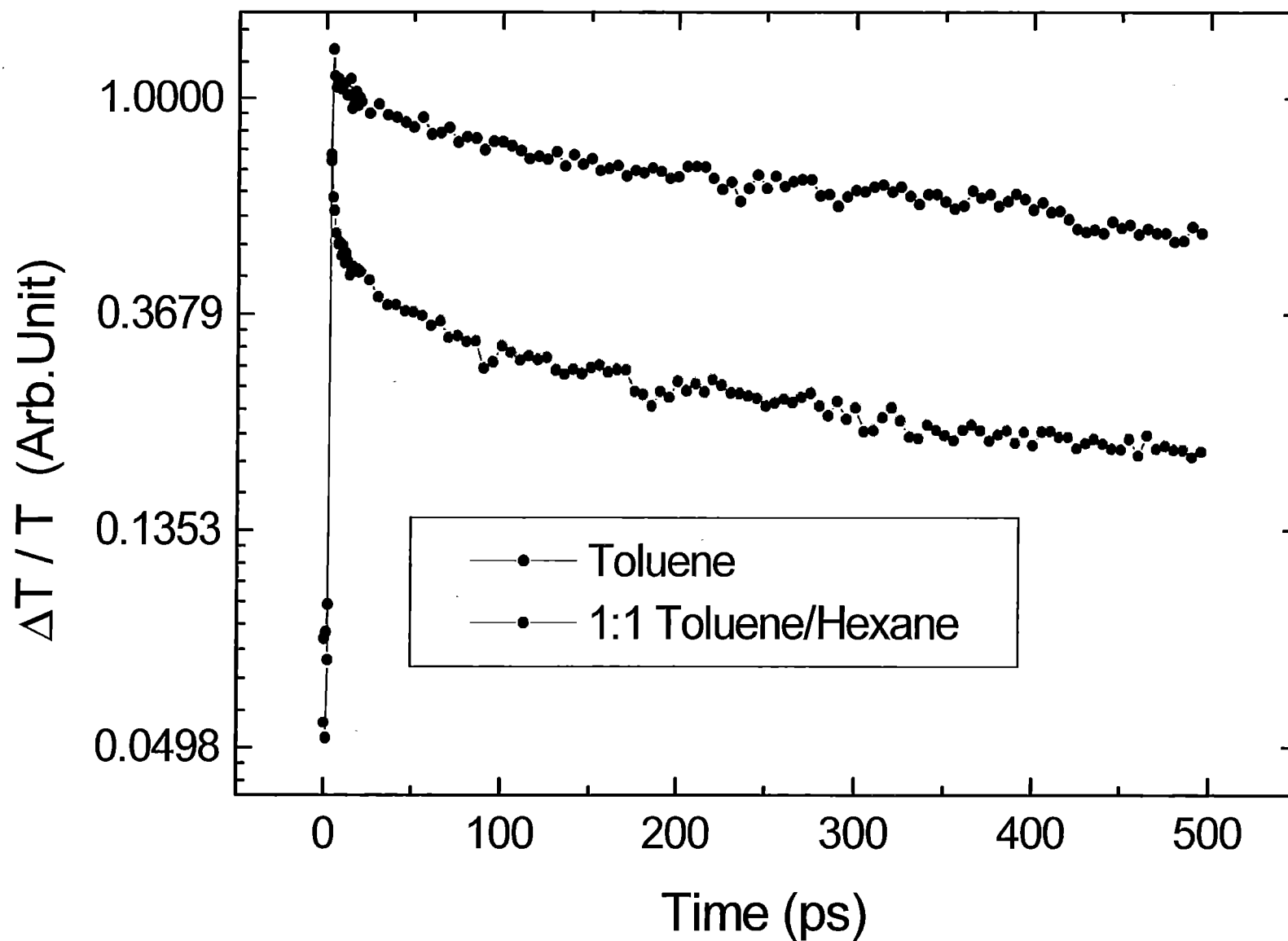
L.Rothberg, Rochester

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MEH-PPV Dynamics at 650 nm



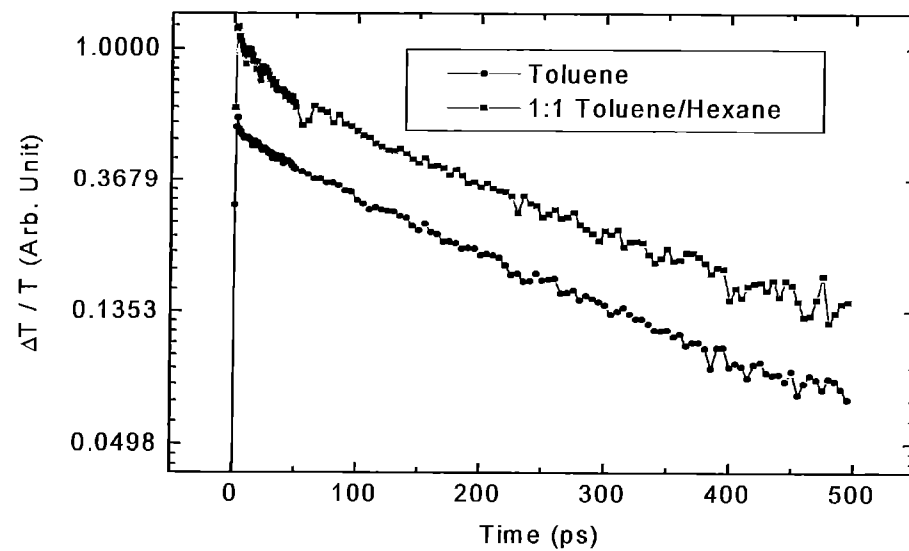
MEH-PPV Photoinduced Absorption (750 nm)



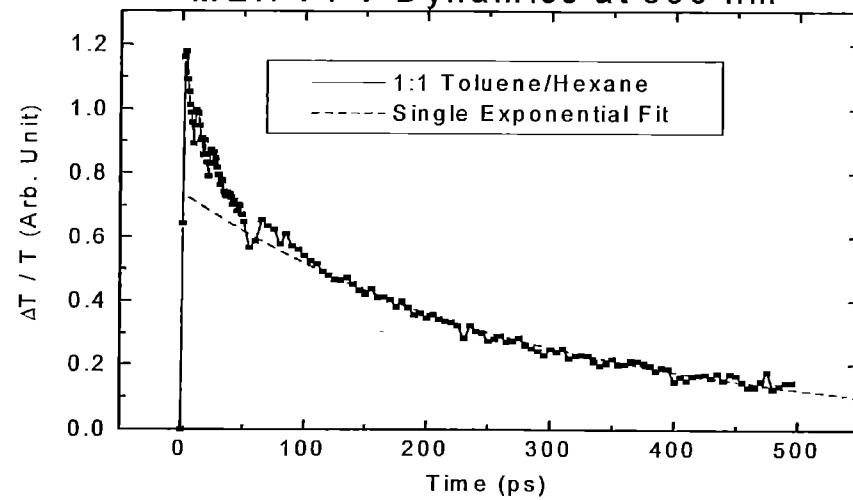
L.Rothberg, Rochester

ARO MURI

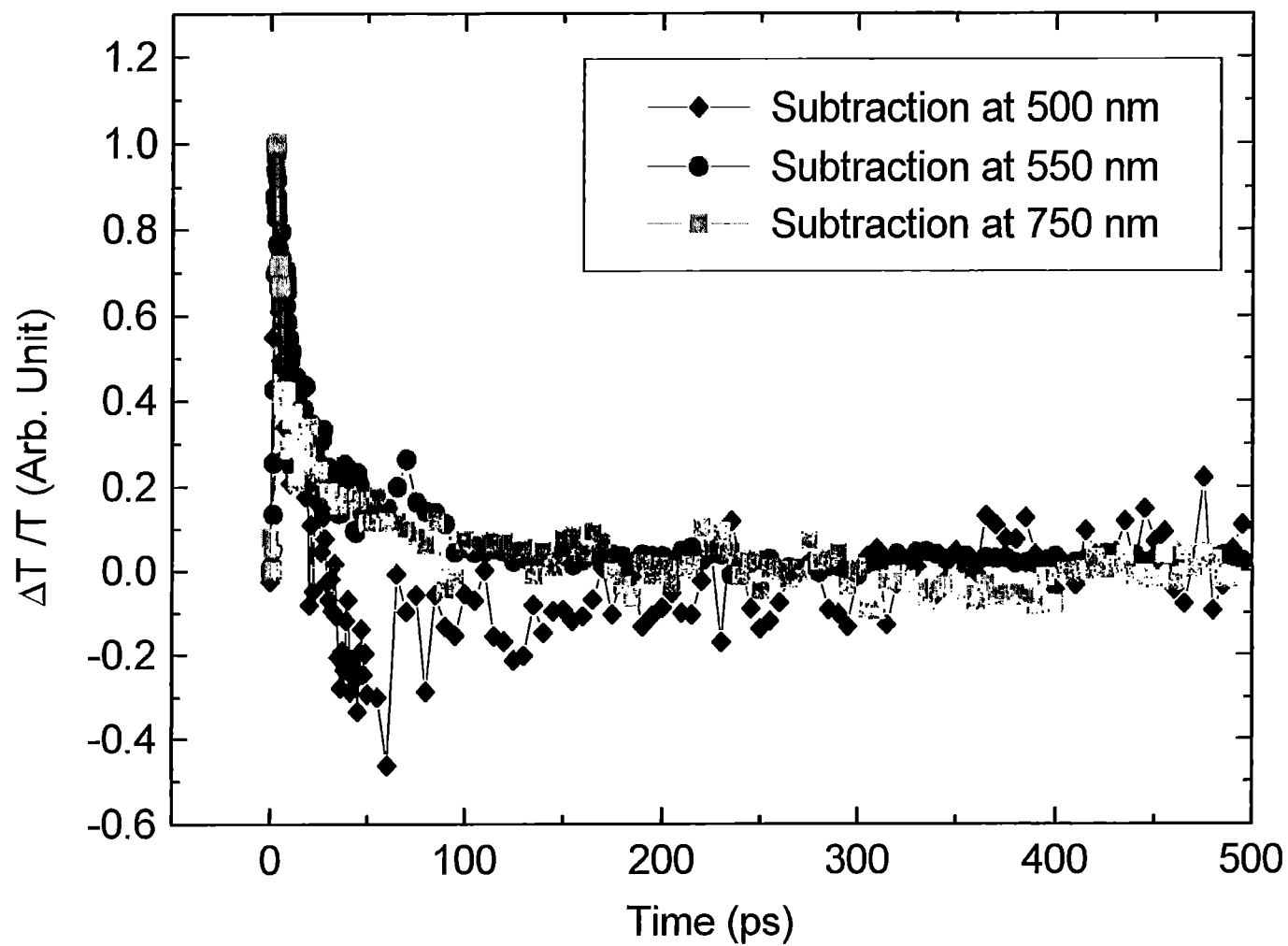
MEH-PPV Dynamics at 550 nm



MEH-PPV Dynamics at 550 nm



Comparison of Good and Bad Solvent Dynamics



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
- Electrogenenerated Chemiluminescence (ECL)
- Organic EL (Polymer, Alq)
- Hybrid Systems
- Applications
 - Displays
 - Lasers
 - Analytical Devices

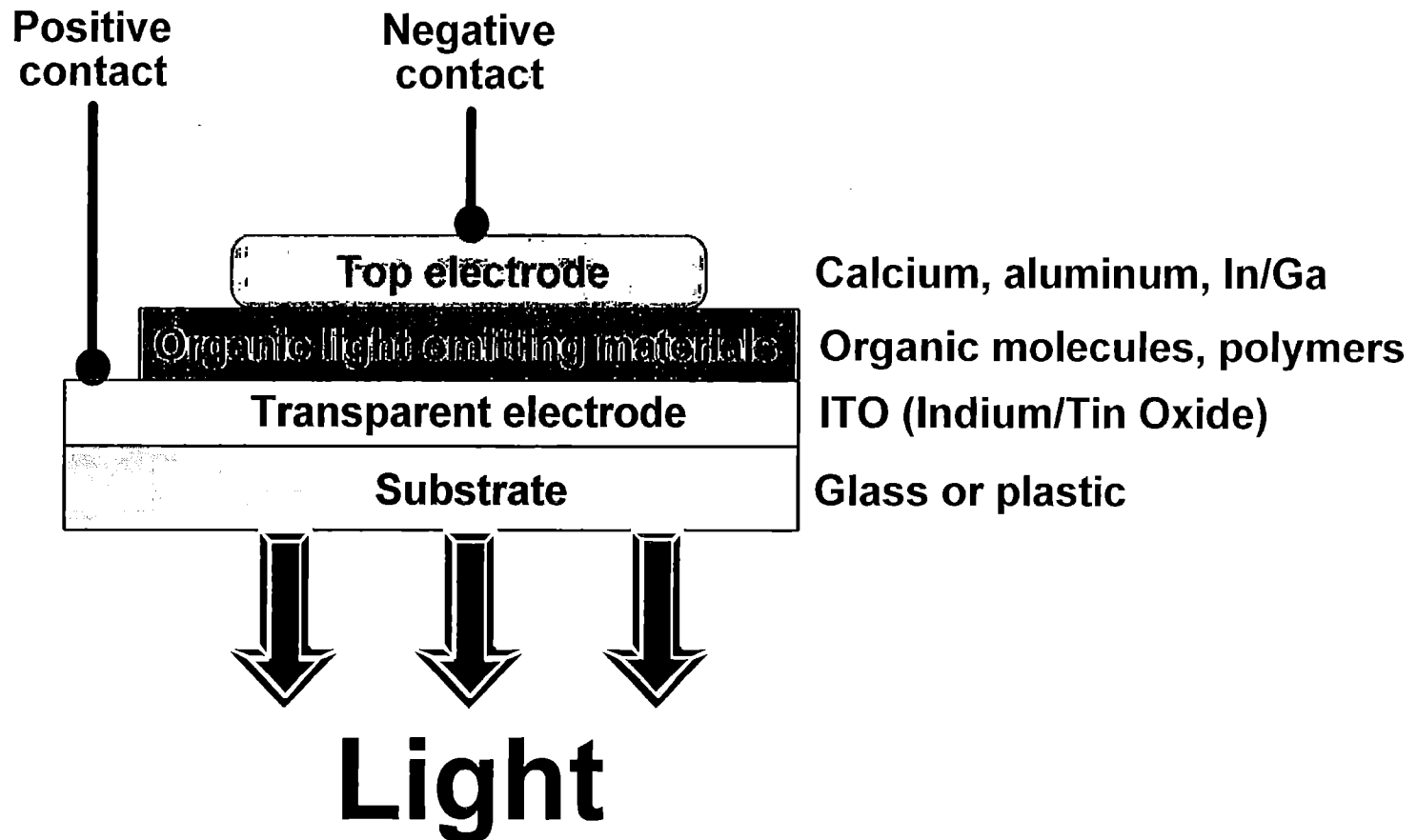
Key Issues - Devices

- Efficiency
- Stability (Life)
- Cost
- Manufacturability

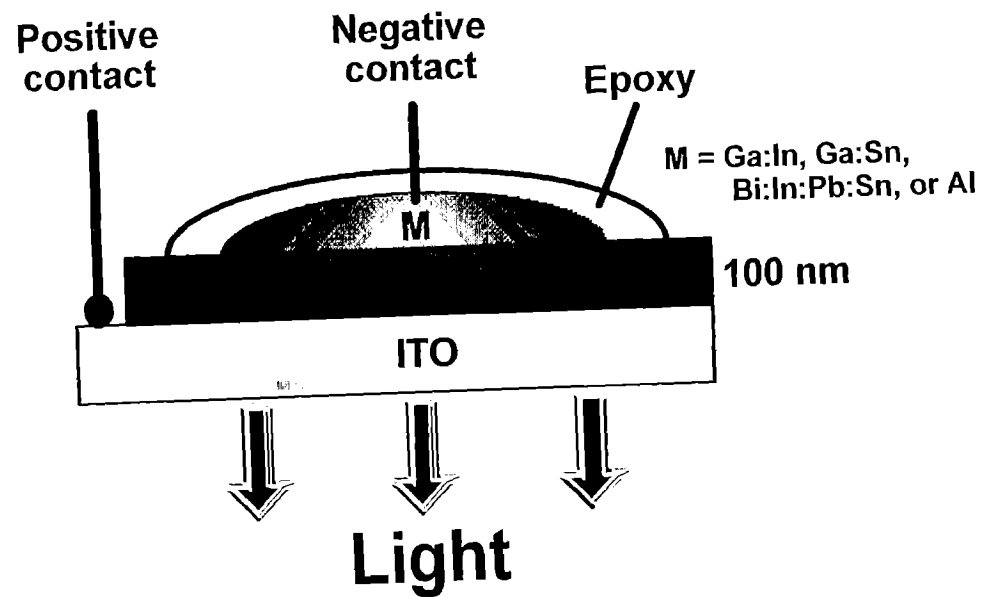
Key Issues - Science

- Degradation mechanisms
 - ⑧ 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)



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

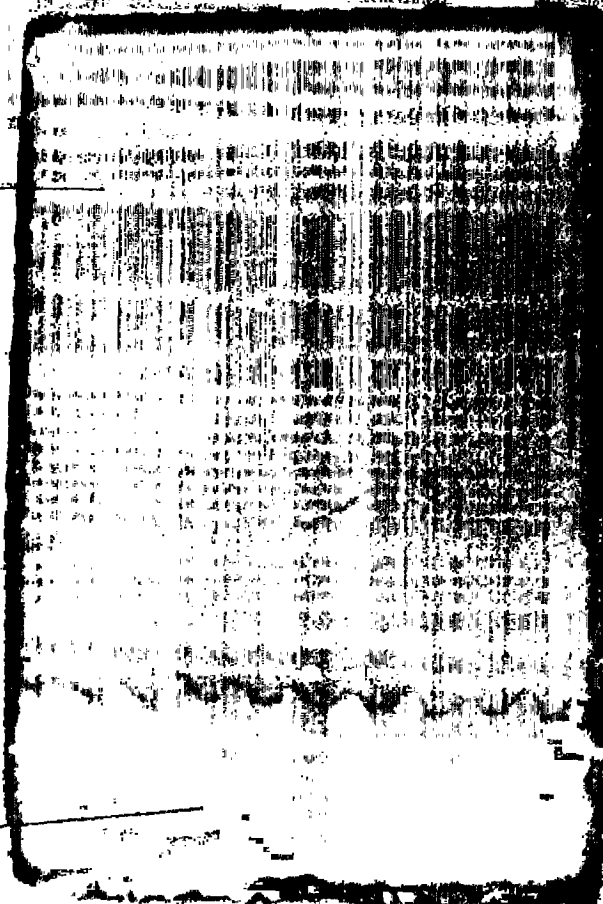


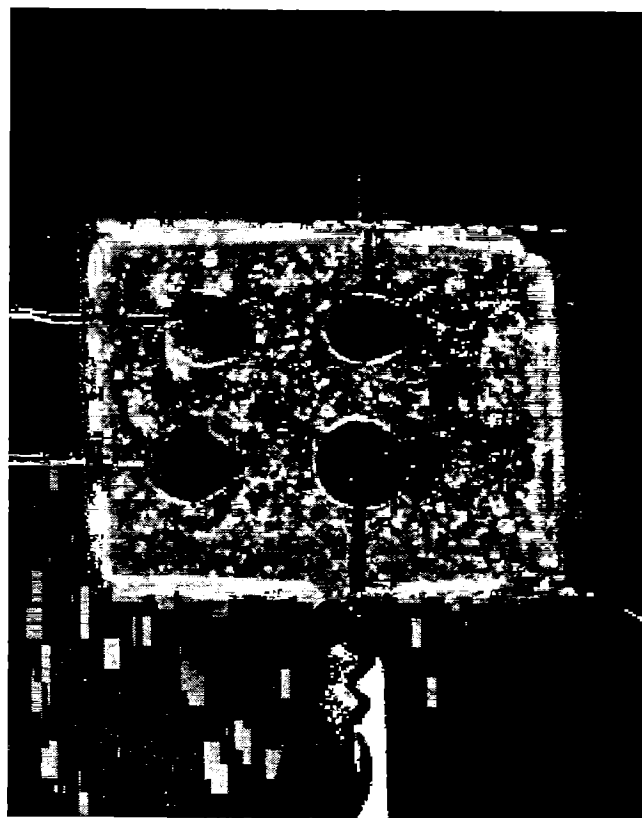
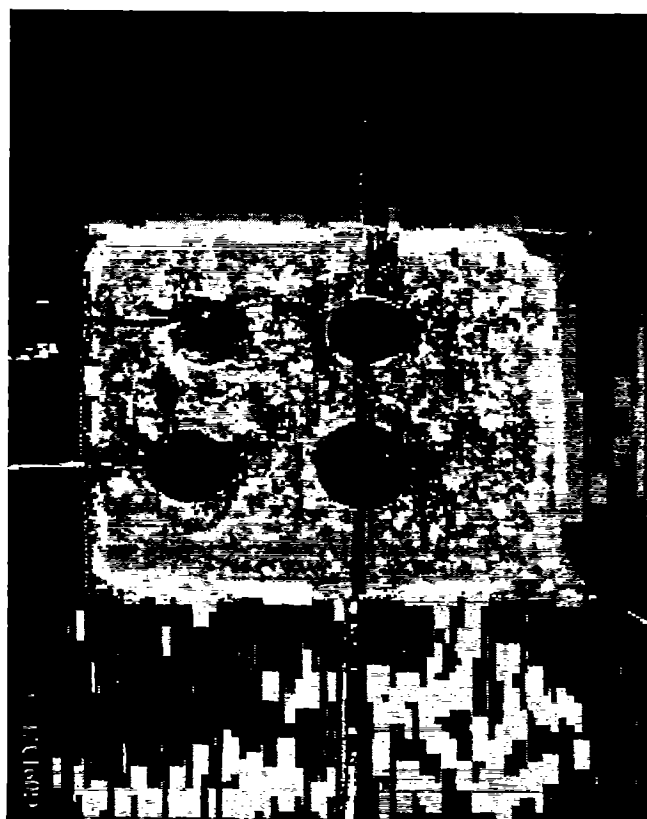
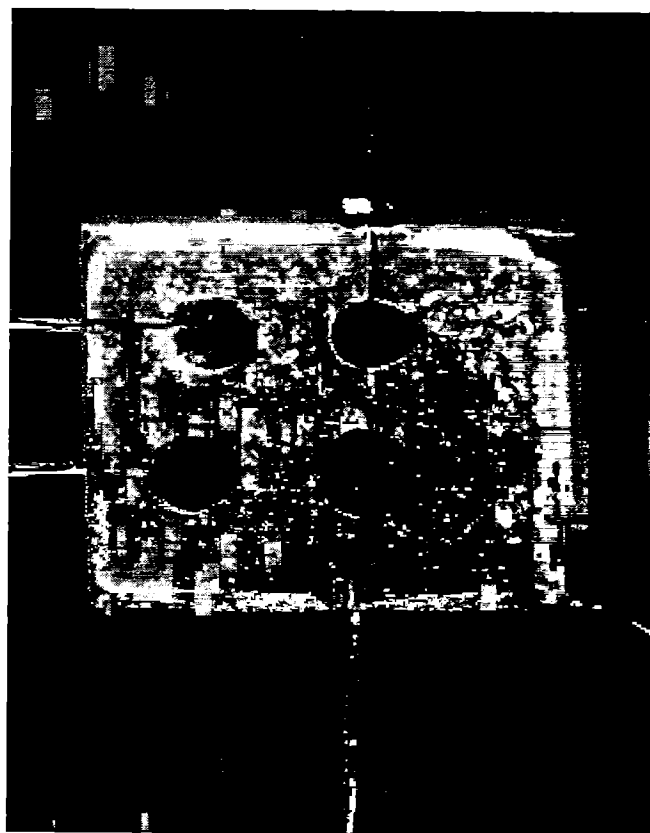
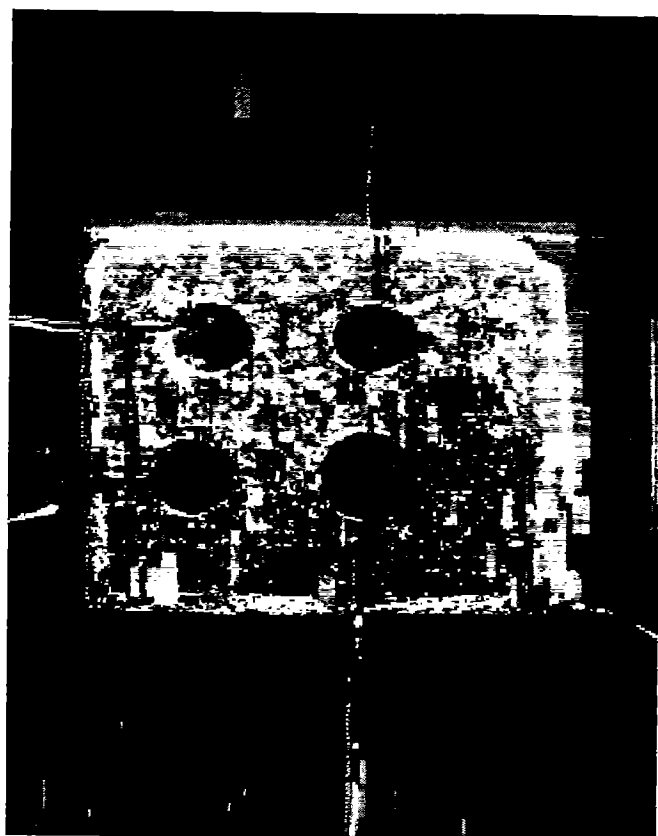
Thin Film of 3 Layers Spin-Coated On ITO

G091820

Film

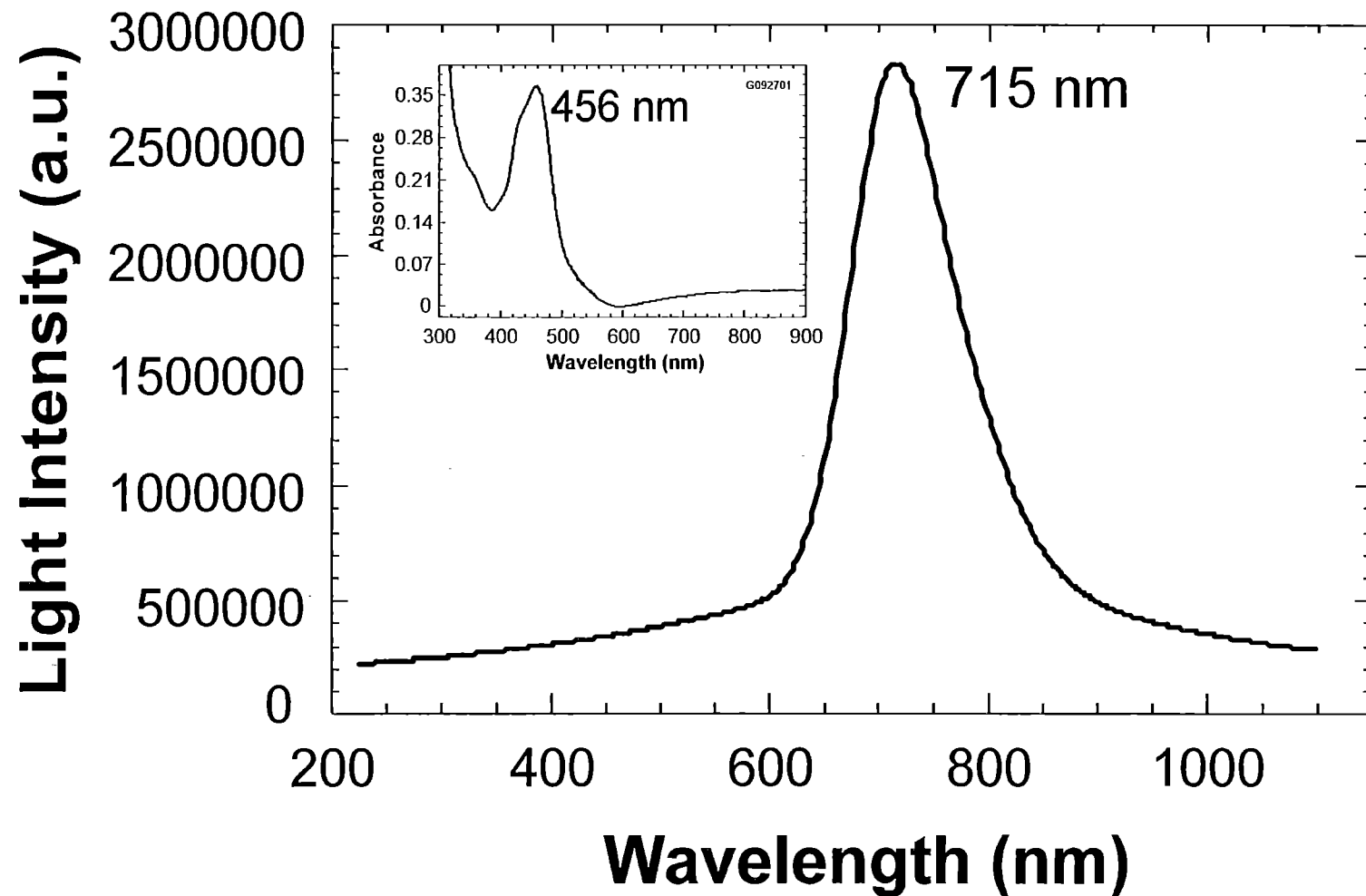
Bare ITO



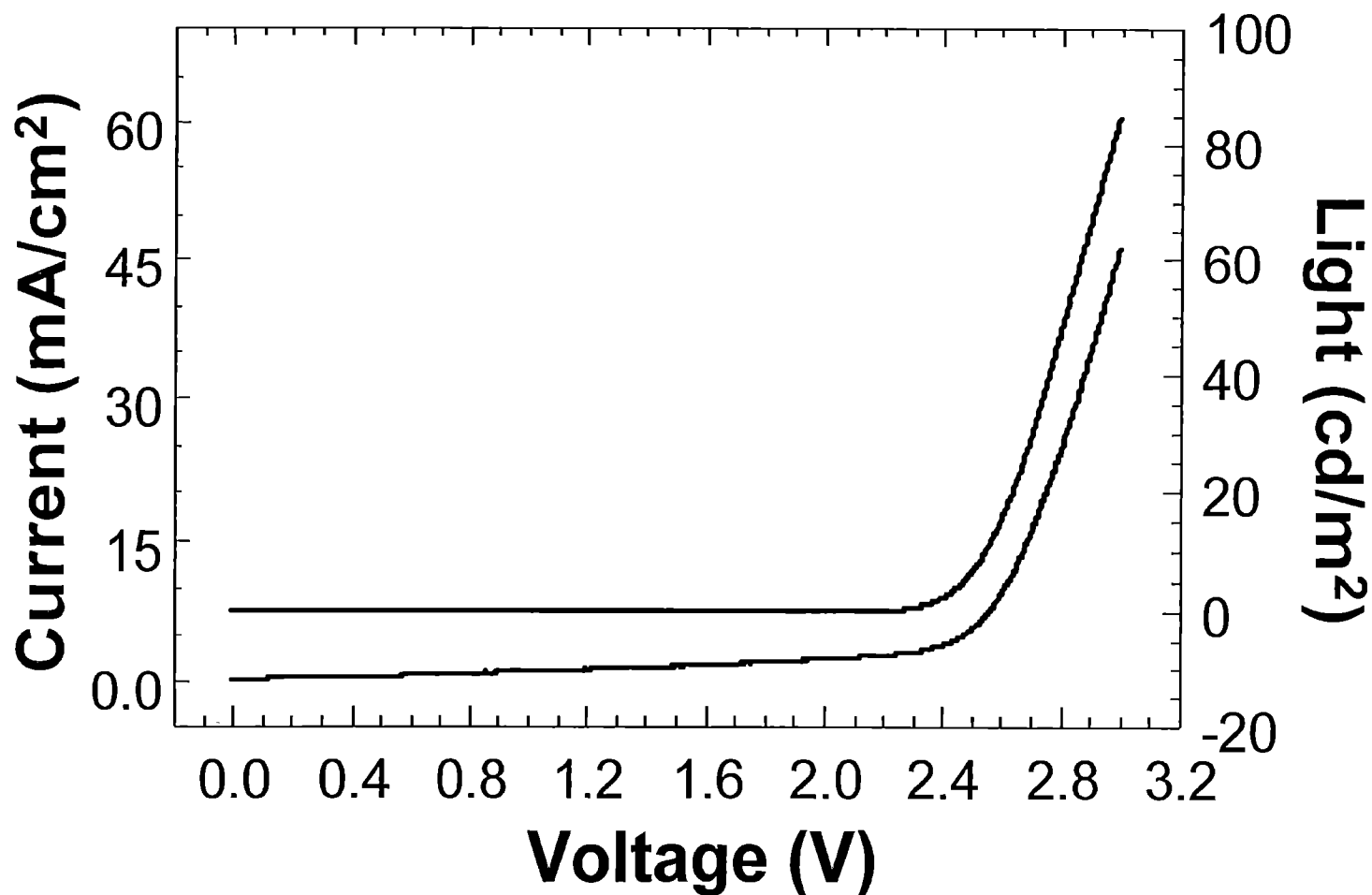


Luminescence Spectrum of An OLED

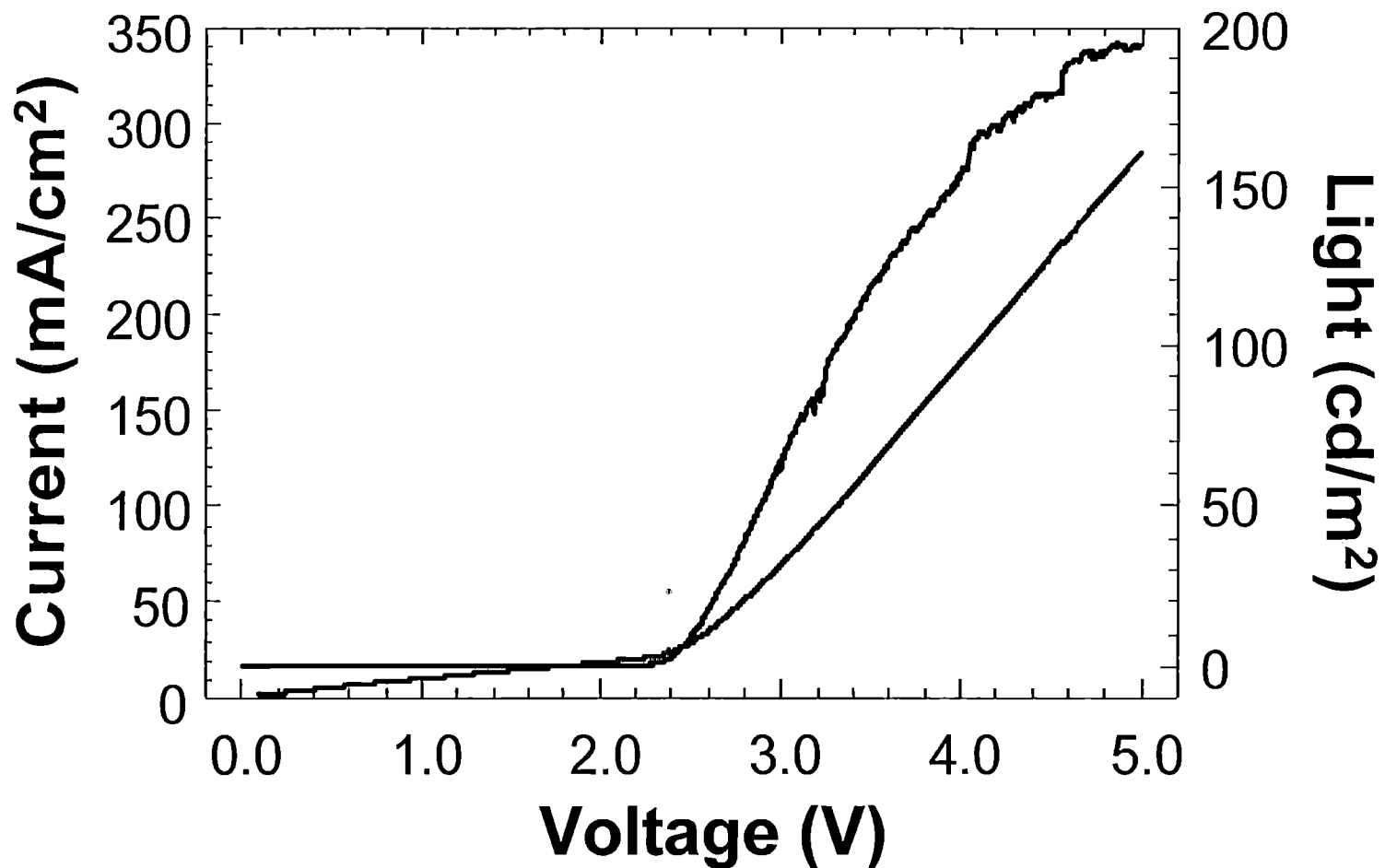
Inset: UV-vis Absorption Spectrum Of The Film



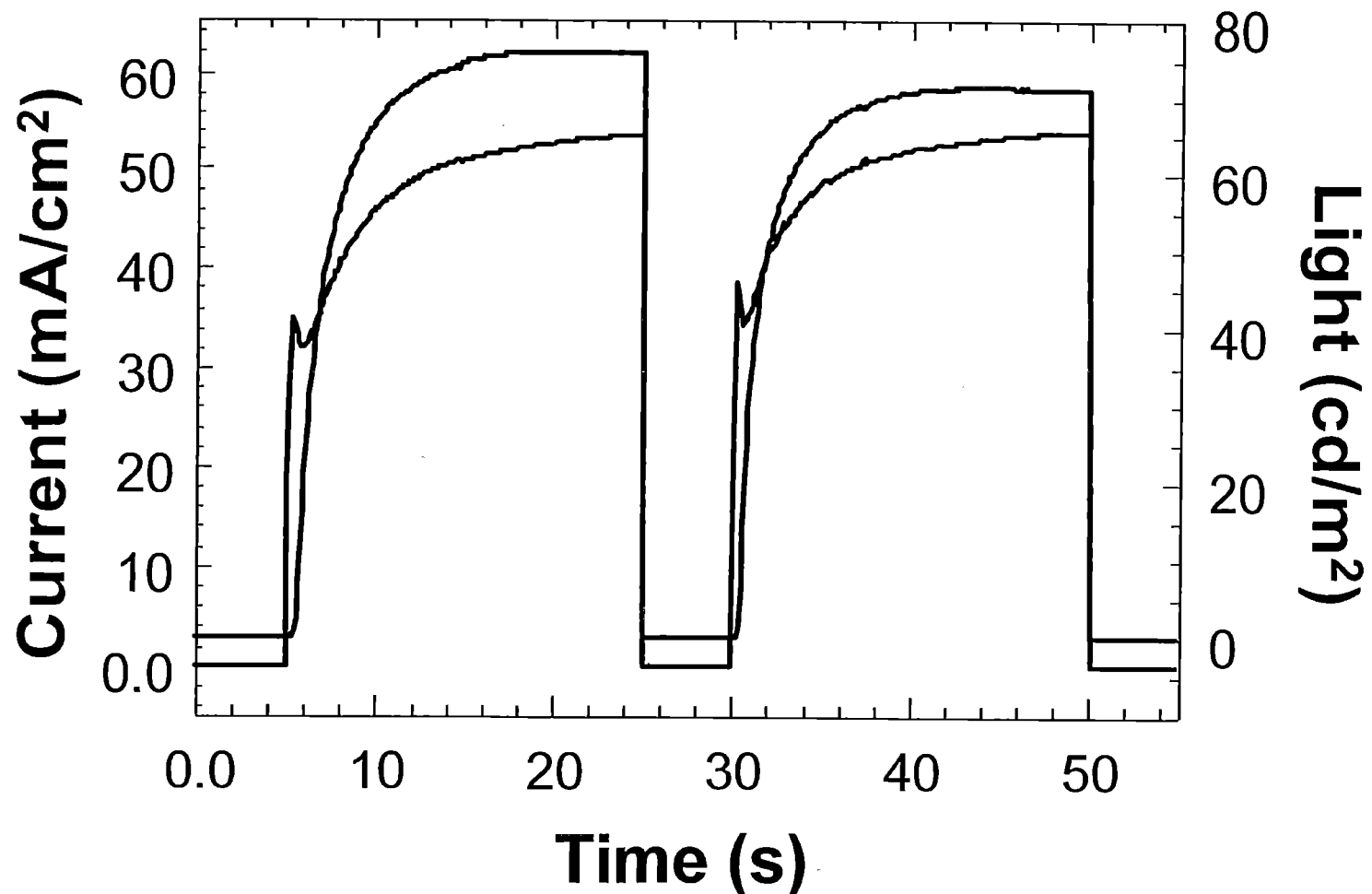
Light-Voltage (red) And Current-Voltage (blue) Plots For An OLED



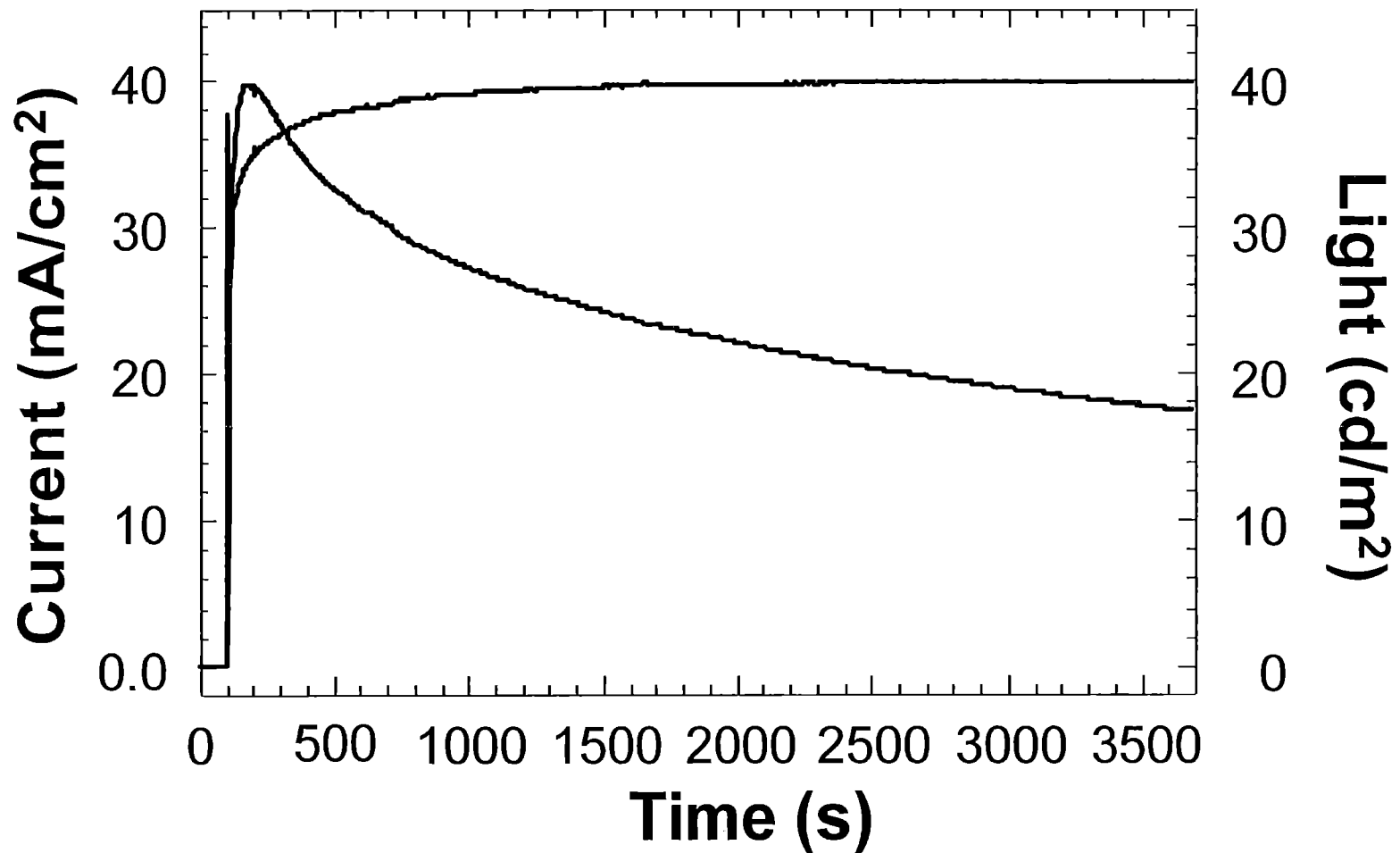
Light Emission Intensity Of 200 cd/m² At 5 V Was Realized For An OLED



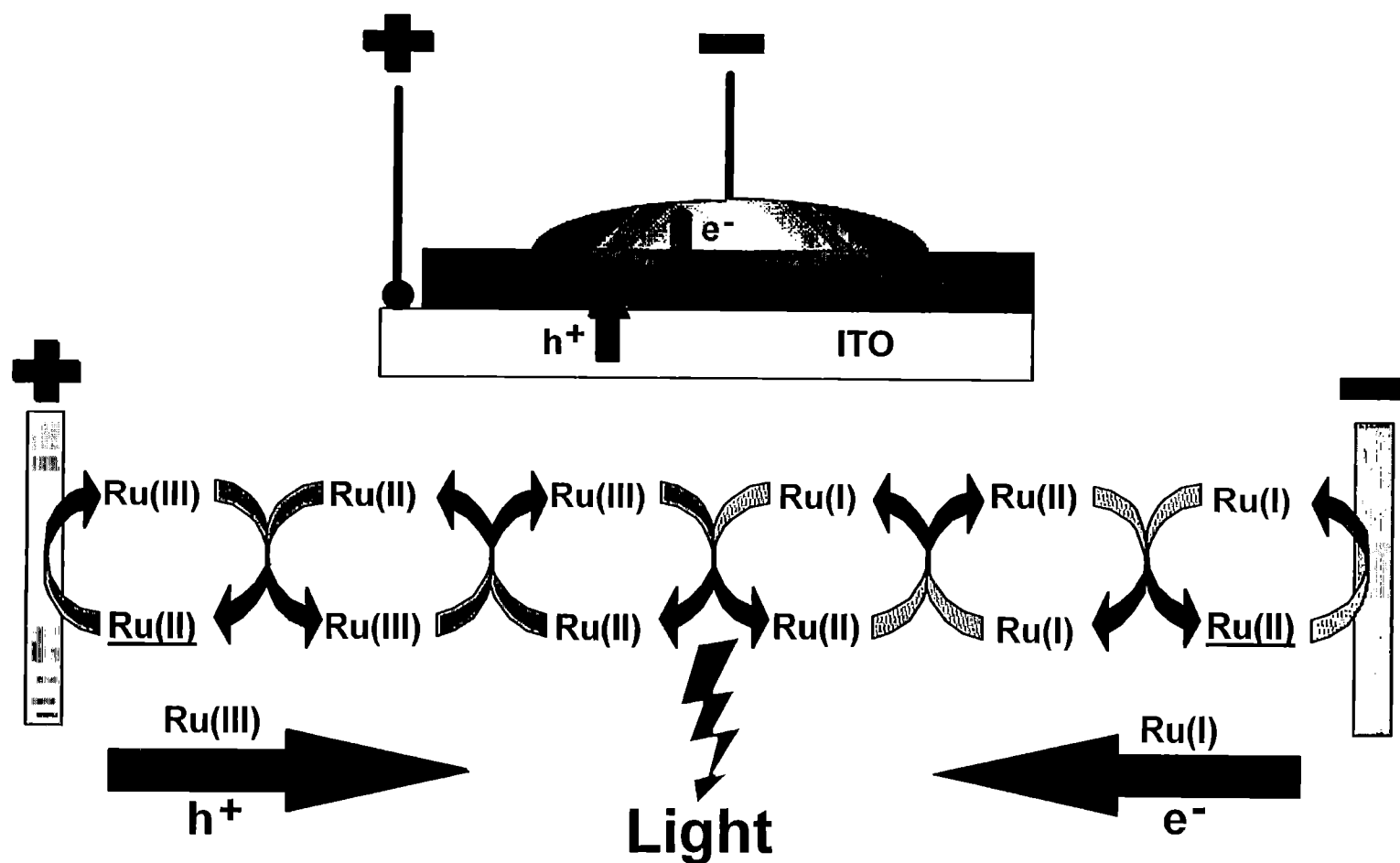
Light And Current As A Function Of Time Upon 0 - 3 V Voltage Steps



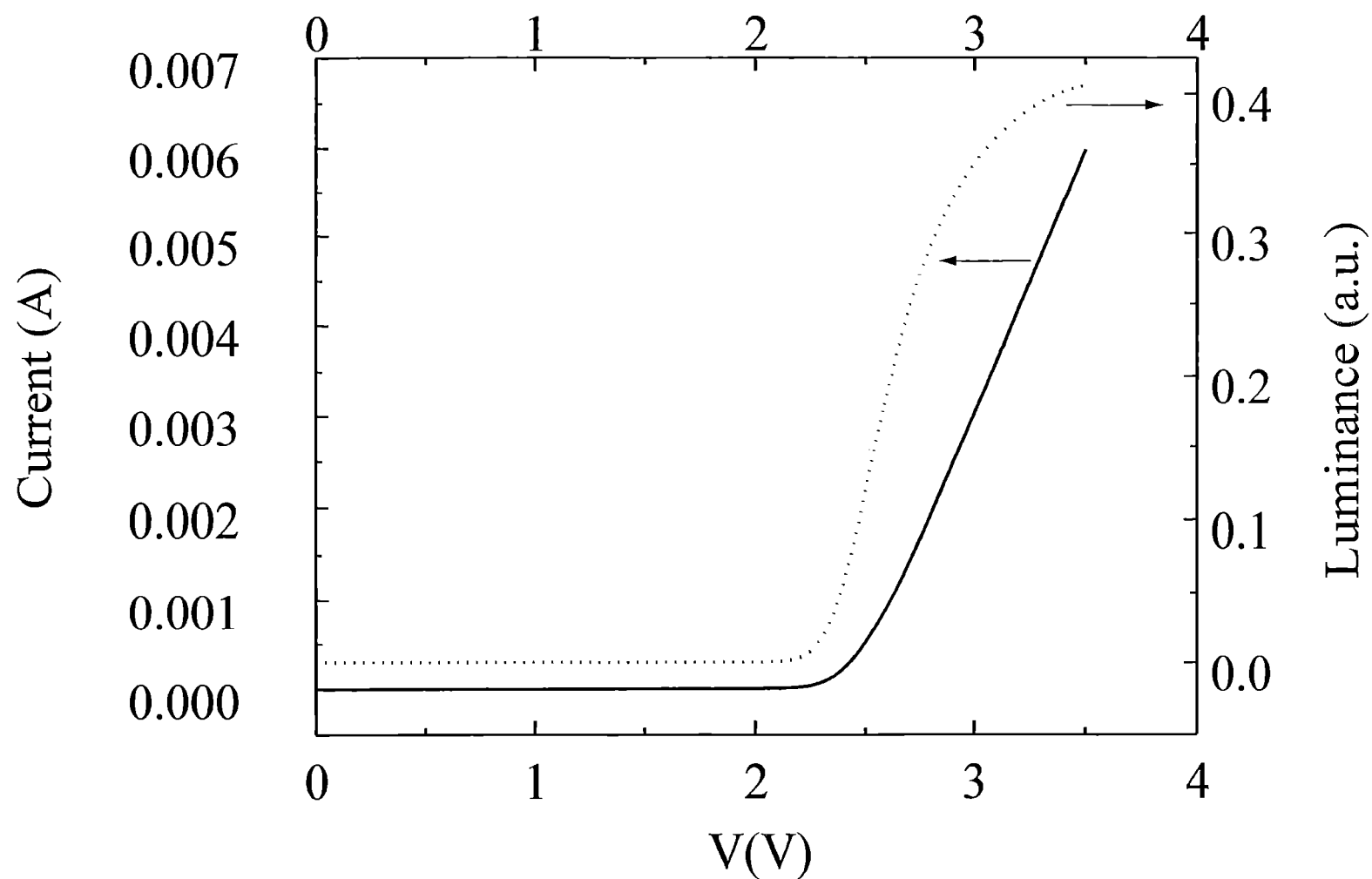
Light Output As A Function Of Time (2.8 V hold)



Cartoon Of The Bimolecular Hopping Transport Of Electrons Between Ru(II) And Ru(III) Sites And Ru(I) And Ru(II) Sites

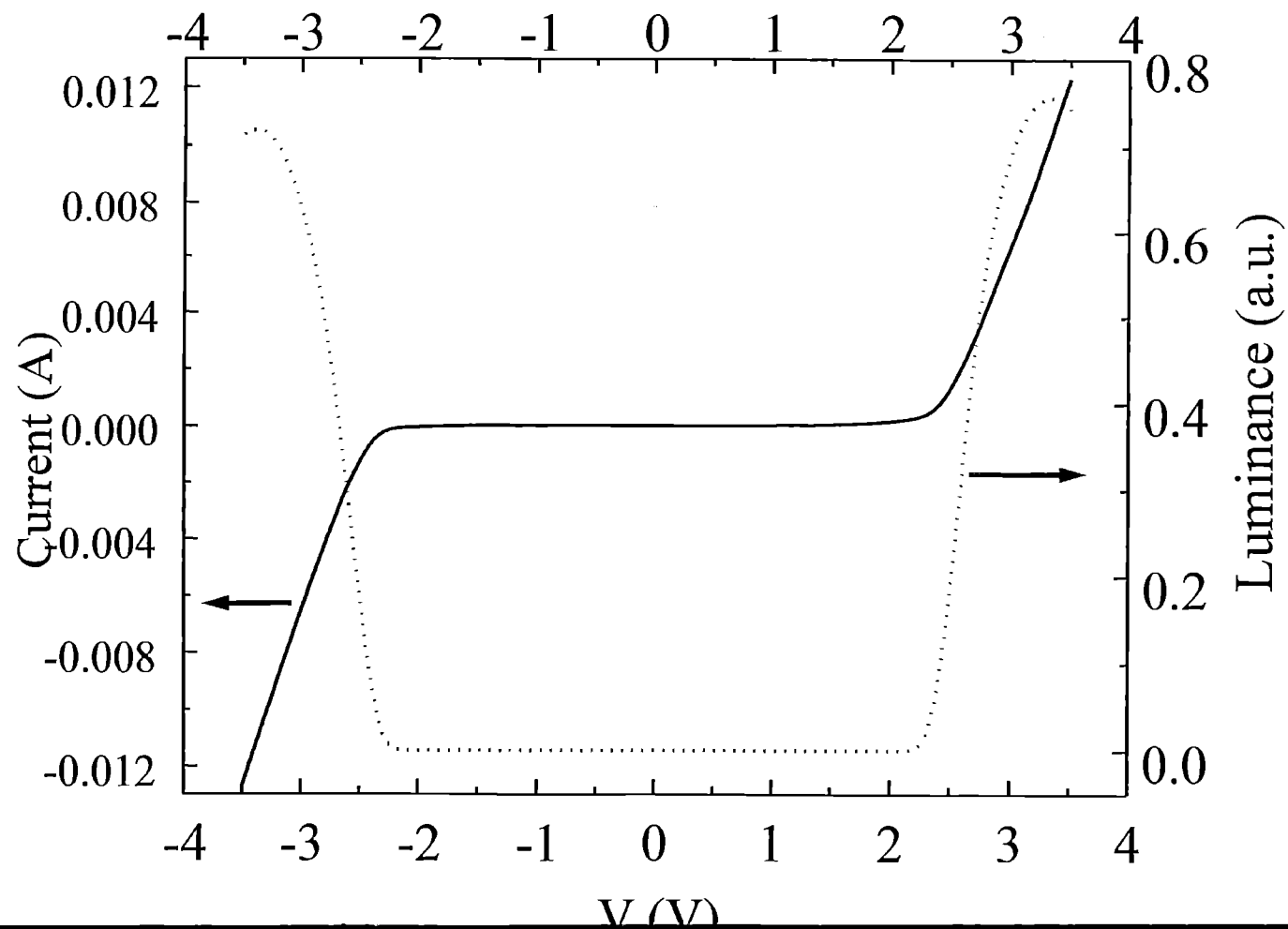


Current-voltage and luminance-voltage characteristics (50 mV/s)
ITO/Ru(bpy)₃(ClO₄)₂ (~150 nm)/Ga:Sn;

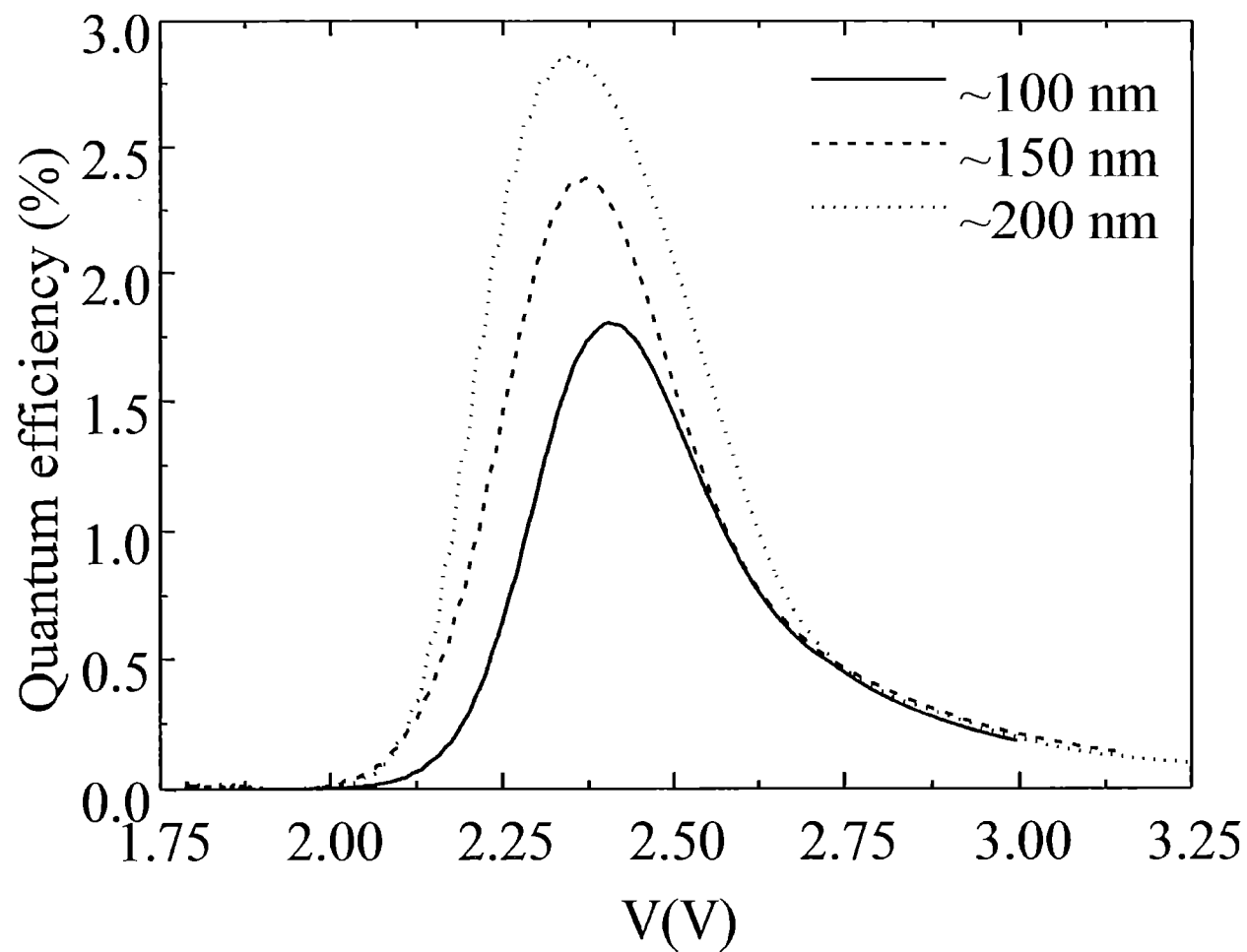


Current-voltage and luminance-voltage characteristics (50
mV/s)

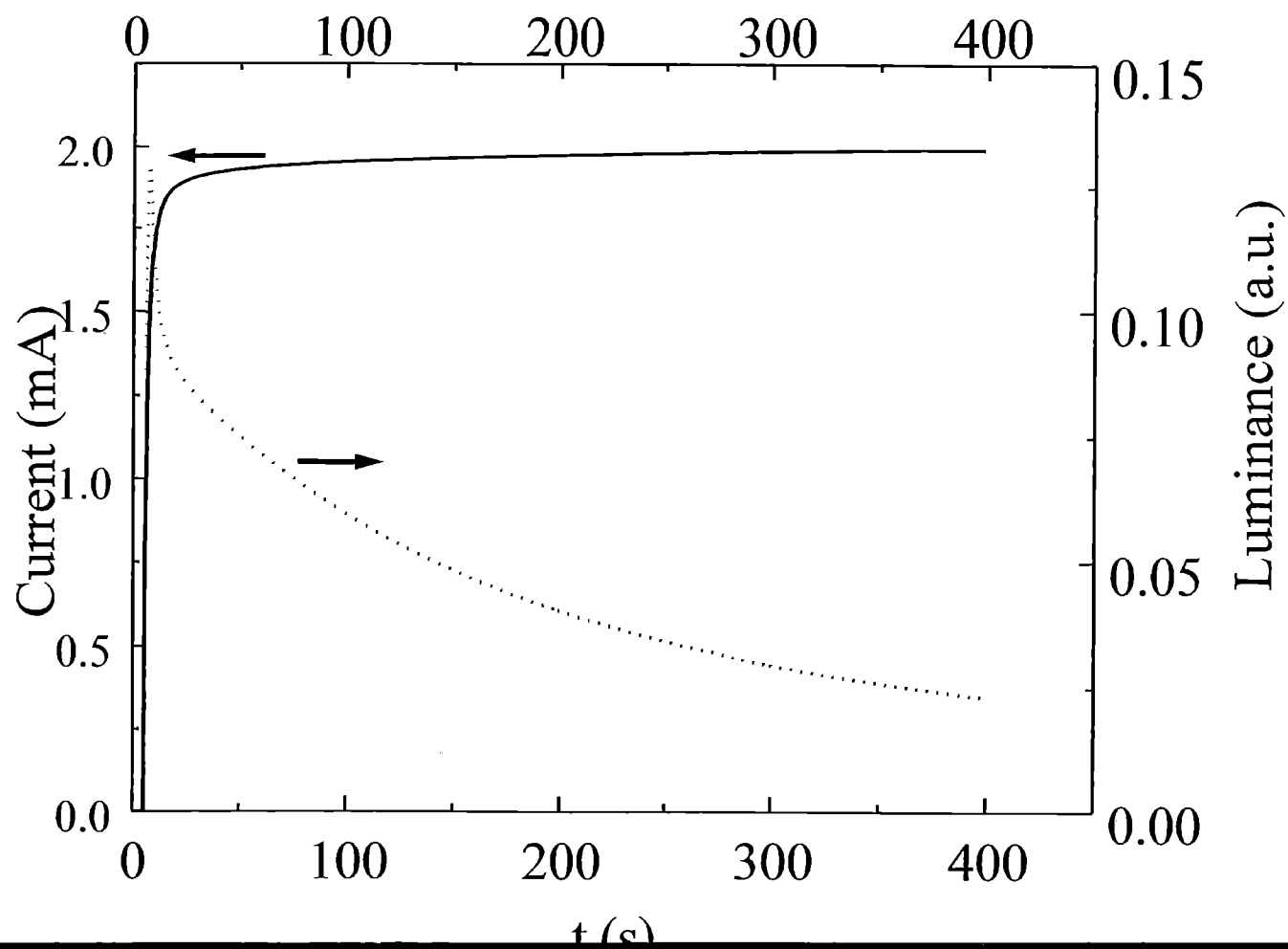
ITO/Ru(bpy)₃(ClO₄)₂(~100 nm)/Au;



Quantum efficiencies (50 mV/s)
ITO/Ru(bpy)₃(ClO₄)₂/Ga:Sn



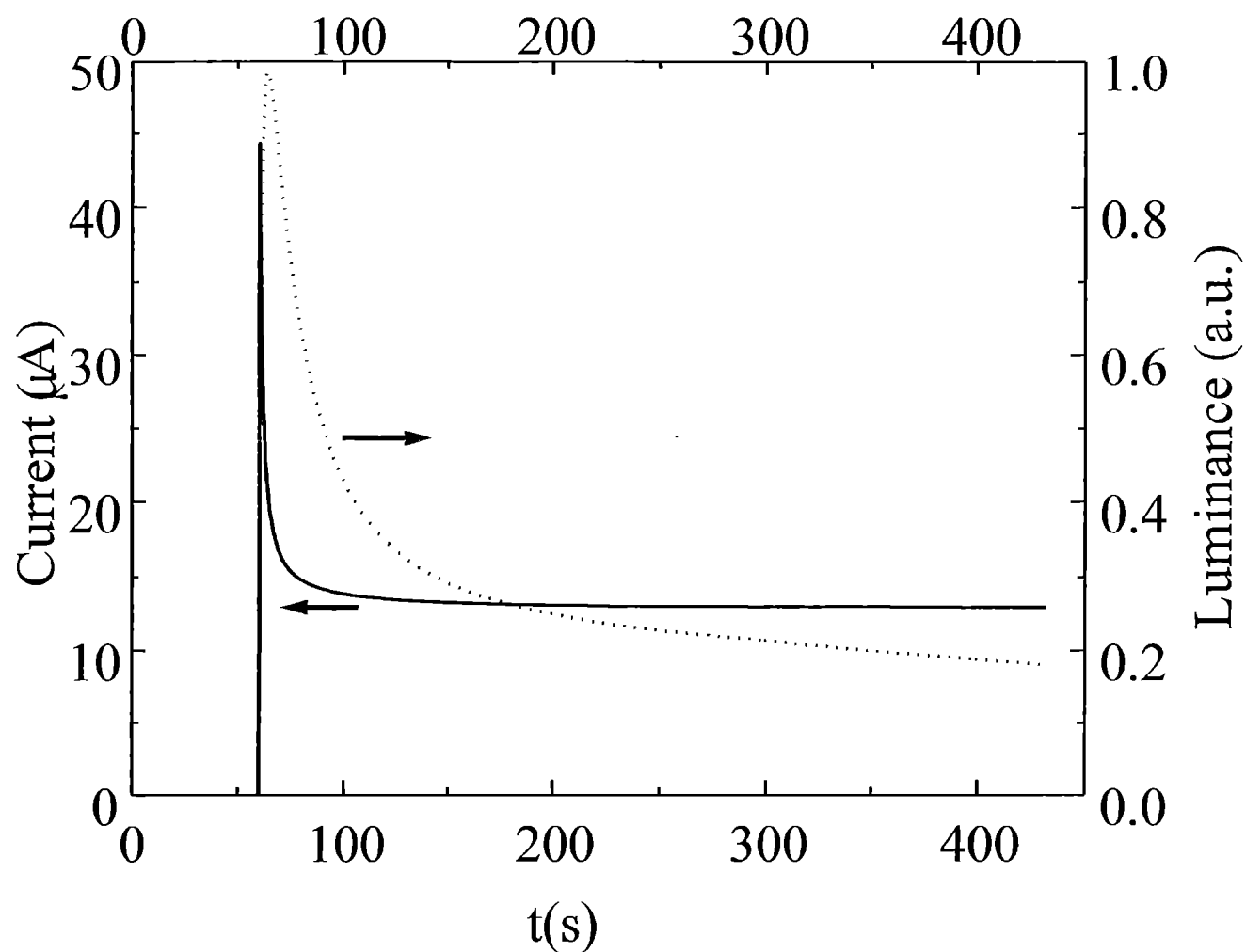
Current-time and luminance transients
2.75 V hold
ITO/Ru(bpy)₃(ClO₄)₂ (~150 nm)/Ga:Sn



Current-time and luminance transients

2.25 V hold

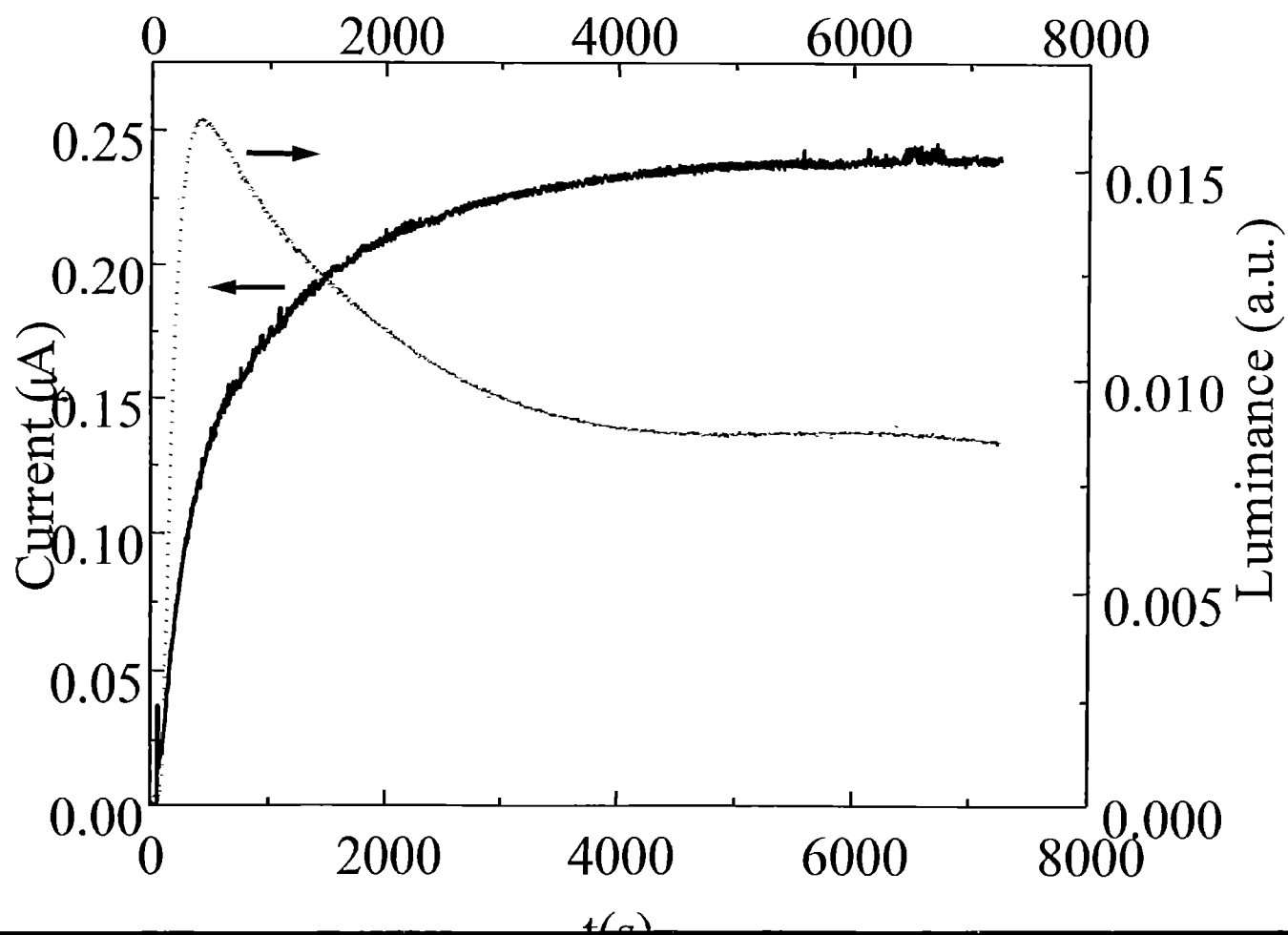
ITO/Ru(bpy)₃(BF₄)₂ (~150 nm)/Ga:Sn



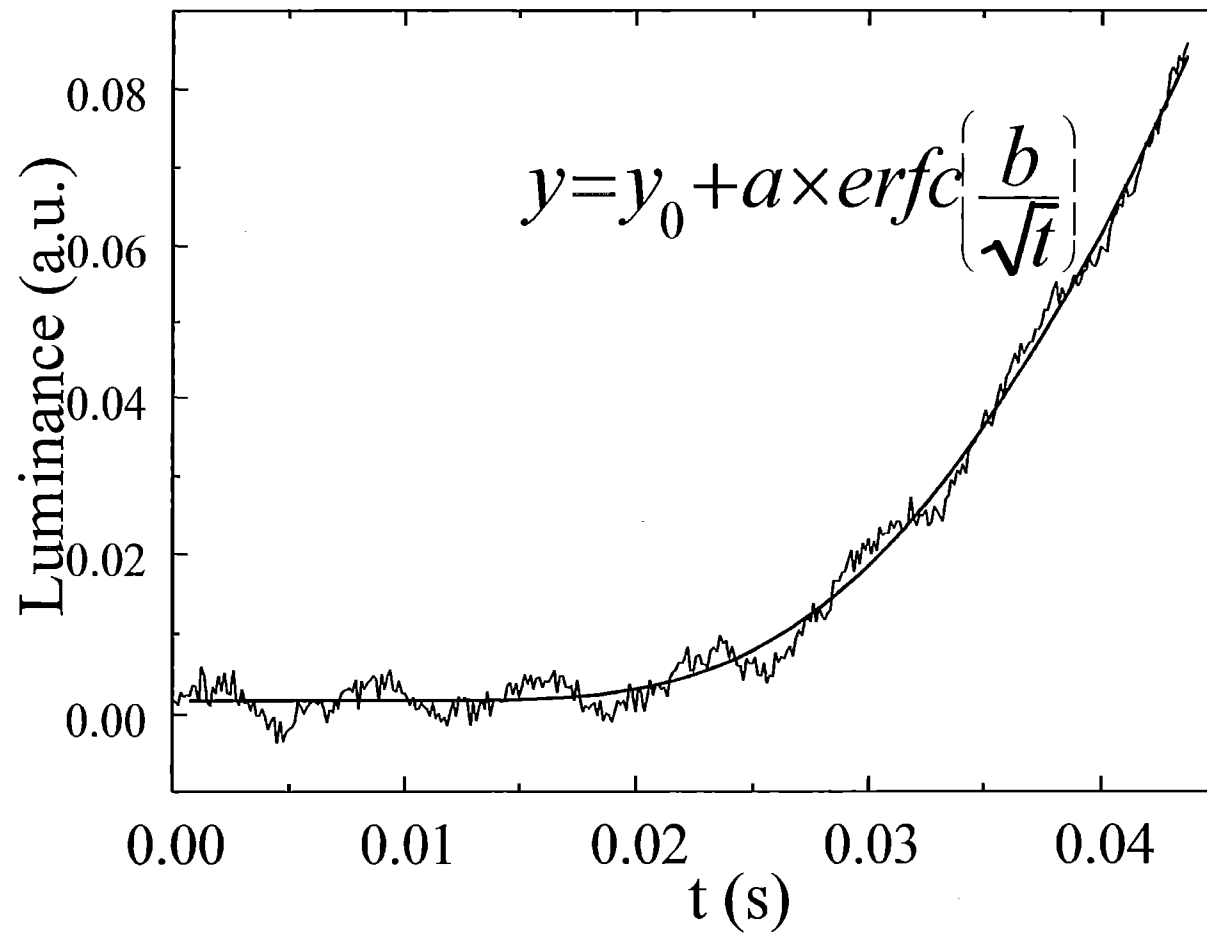
Current-time and luminance transients

2.5 V hold

ITO/Ru(bpy)₃(PF₆)₂ (~200 nm)/Ga:Sn

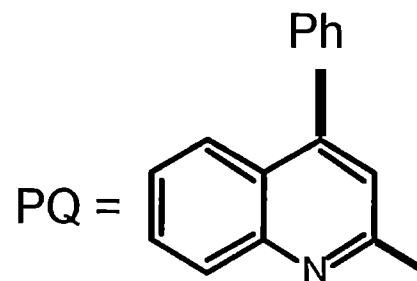
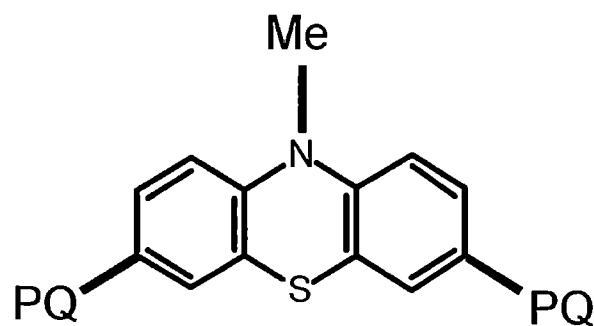
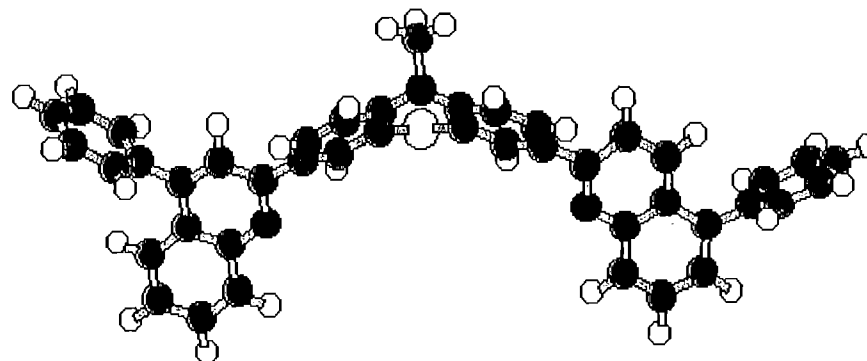


Transient luminance at short times:
ITO/Ru(bpy)₃(ClO₄)₂(~100 nm)/Ga;Sn

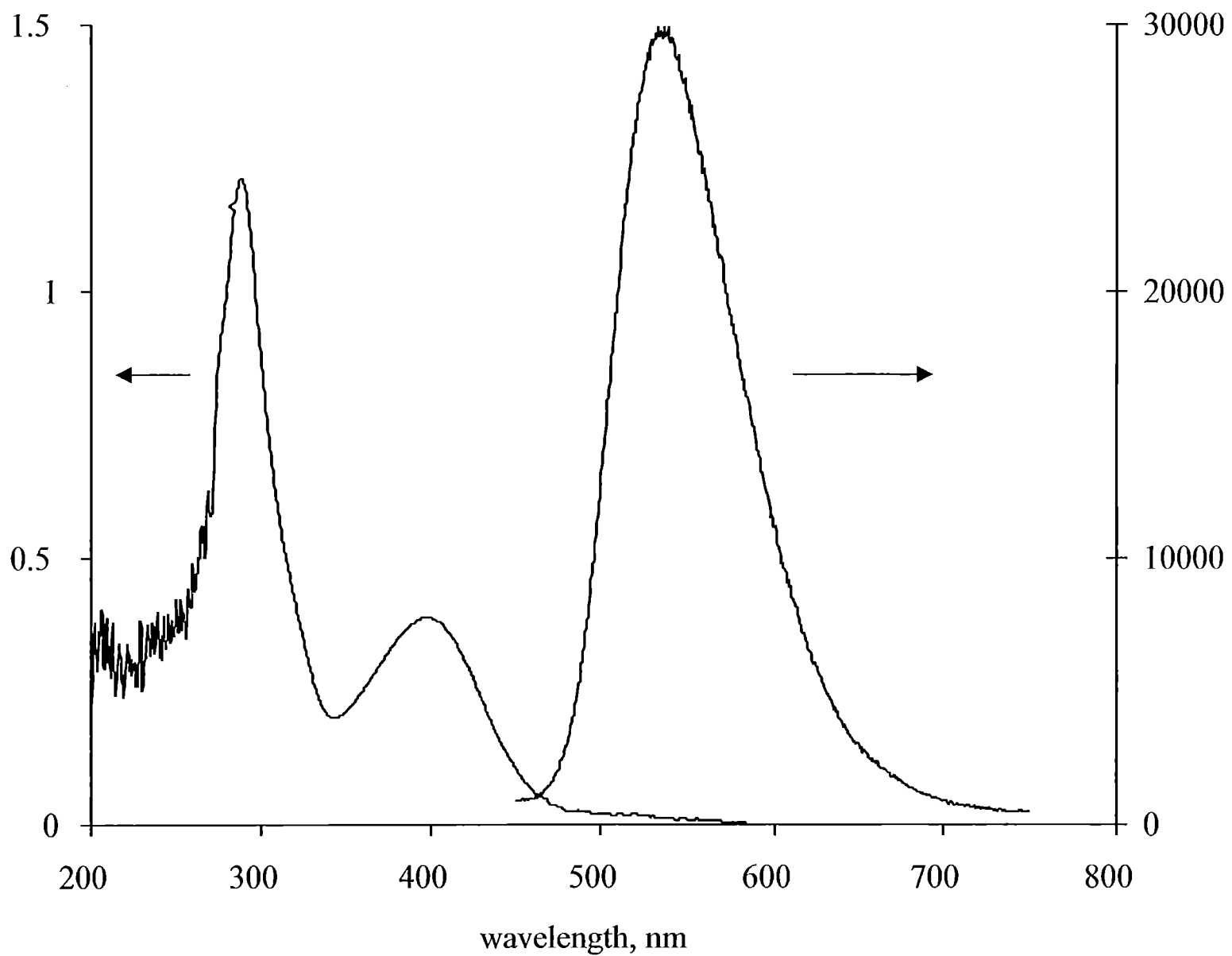


Anion	D _{app} (cm ² /s)
BF ₄ ⁻	~ 10 ⁻⁹
ClO ₄ ⁻	~ 10 ⁻¹⁰
PF ₆ ⁻	~ 10 ⁻¹³
AsF ₆ ⁻	~ 10 ⁻¹⁴

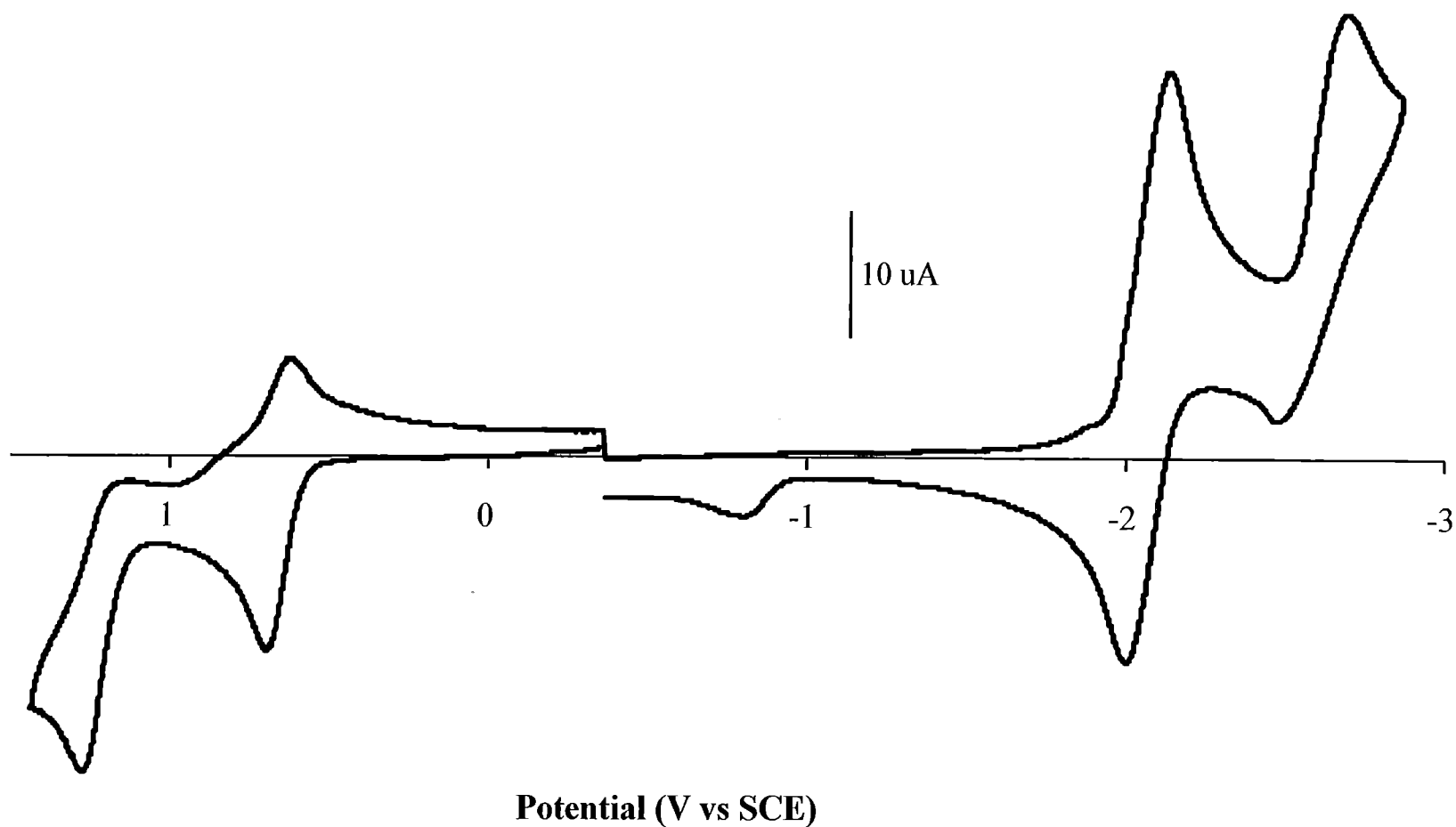
Electrochemistry and ECL of Bis(4-phenylquinoline)-10-Methylphenothiazine (BPQ-PTZ)



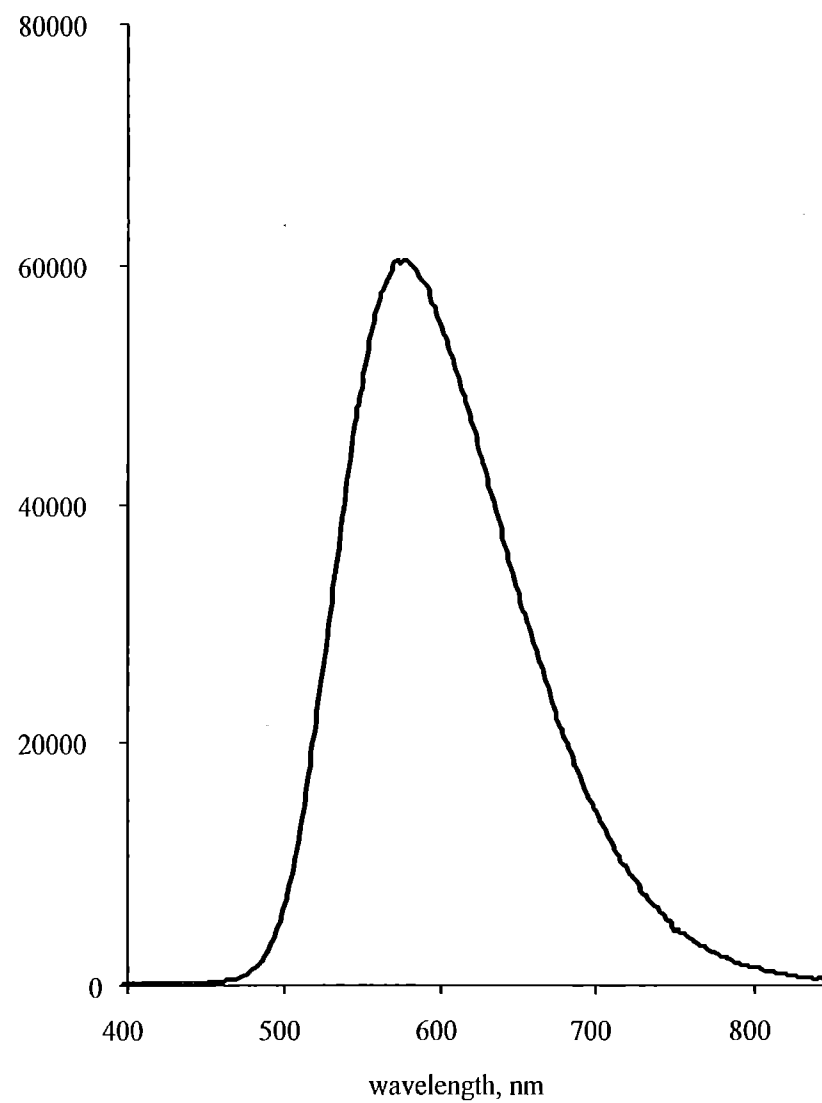
Absorption and Photoemission of BPQ-PTZ in Benzene/MeCN



Cyclic Voltammogram of BPQ-PTZ (0.67 mM) in 0.1 M TBAP in Benzene/MeCN at Pt Electrode at 250 mV/s

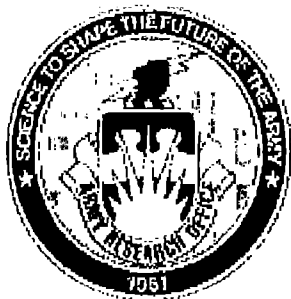


ECL of BPQ-PTZ in Benzene/MeCN

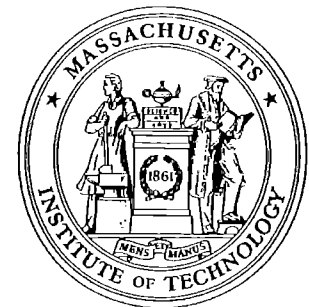


Thin Film Electrochromic Devices

ARO TOPS MURI



Dean M. DeLongchamp
Professor Paula T. Hammond



Electrochromism

Bleached



Colored

reduction or
oxidation

- Color by Reduction - *Cathodic electrochrome*

$+ \rightarrow 0$ or $0 \rightarrow -$

- Color by Oxidation - *Anodic electrochrome*

$- \rightarrow 0$ or $0 \rightarrow +$

Transition: IR $\rightarrow$ Vis or UV $\rightarrow$ Vis



Current Shortcomings of ECDs

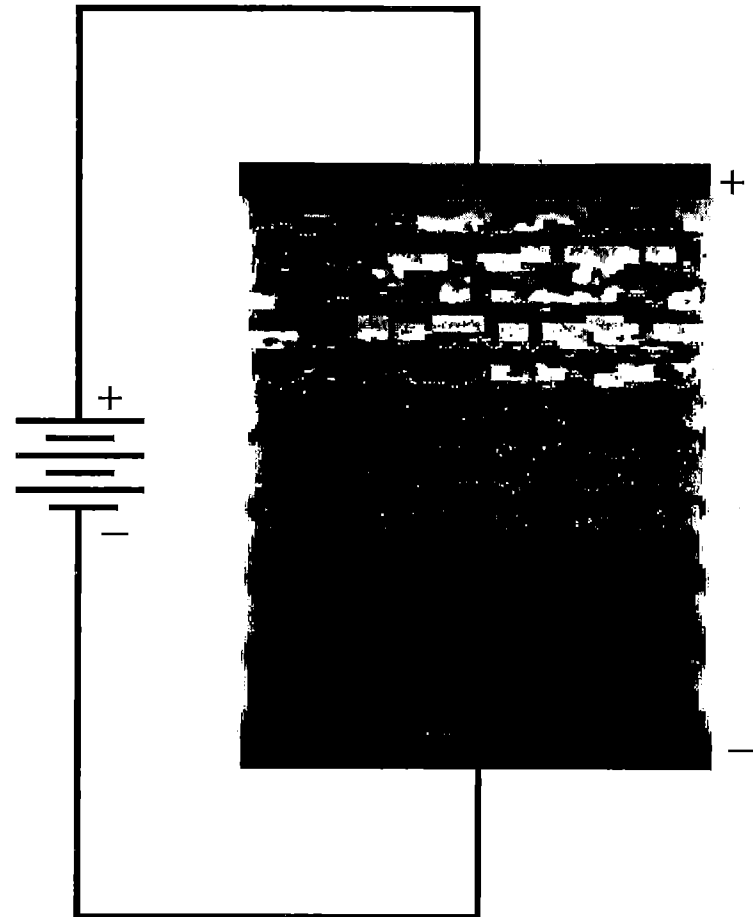
- Switching speed of electrochromic devices (ECDs) is too slow for advanced applications.
 - Smart Windows : seconds to minutes ☒
 - Displays: milliseconds ☒
 - Optical Switches: even faster ☒
- Cycle lifetime is too short for many products.
 - Smart Windows : 10^4 - 10^5 deep cycles ☒
 - Displays: 10^9 - 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

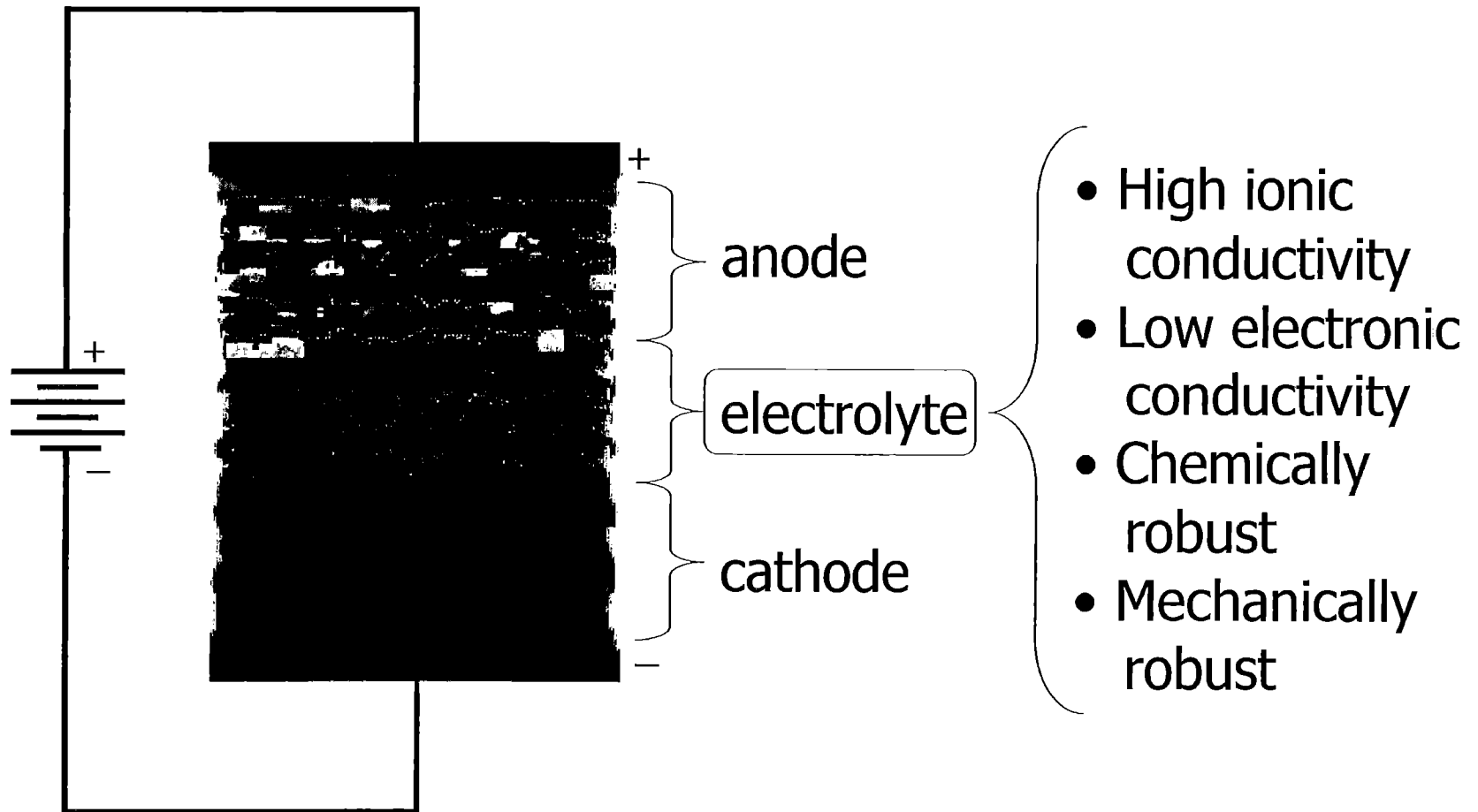


Dual Focus

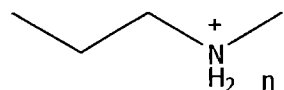
- Electrolyte
 - Evaluate the performance of ion-conducting multilayered systems
 - Determine the optimum system for ECDs
- Electrochromism
 - Characterize the electrochemistry of electrochromic multilayered systems
 - Study effects of material system and deposition conditions



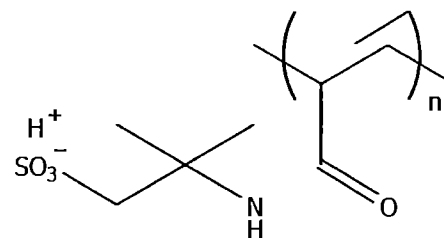
Focus: Electrolyte



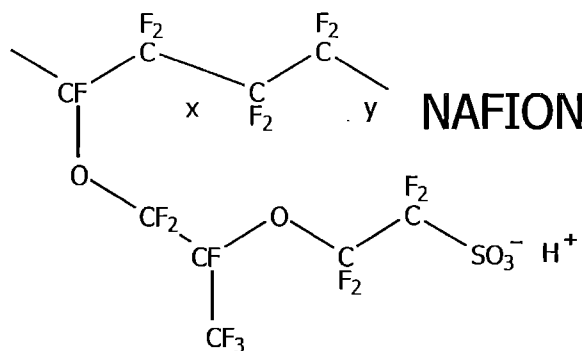
Ion-Conducting Polyelectrolytes



PEI
Poly(ethylene imine)



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



NAFION

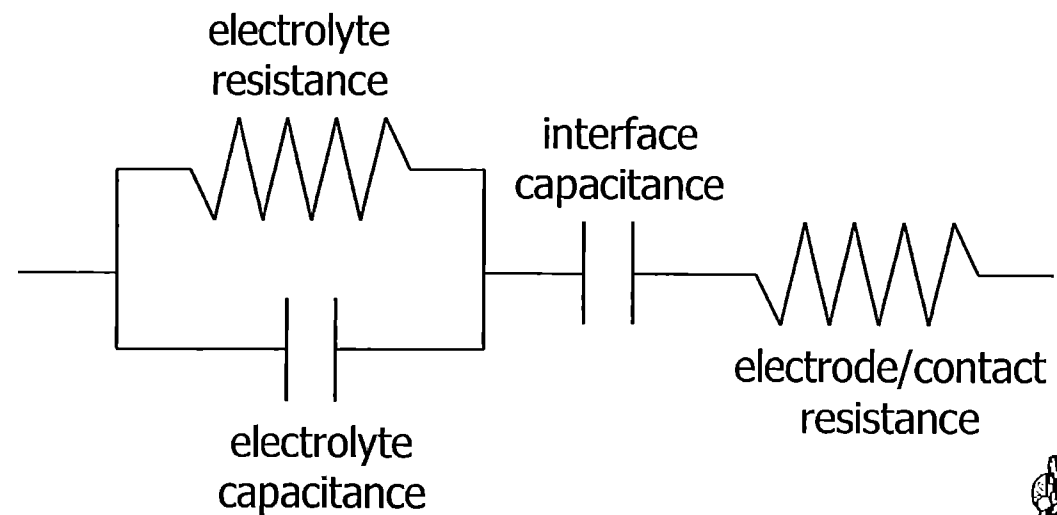


Impedance Analysis

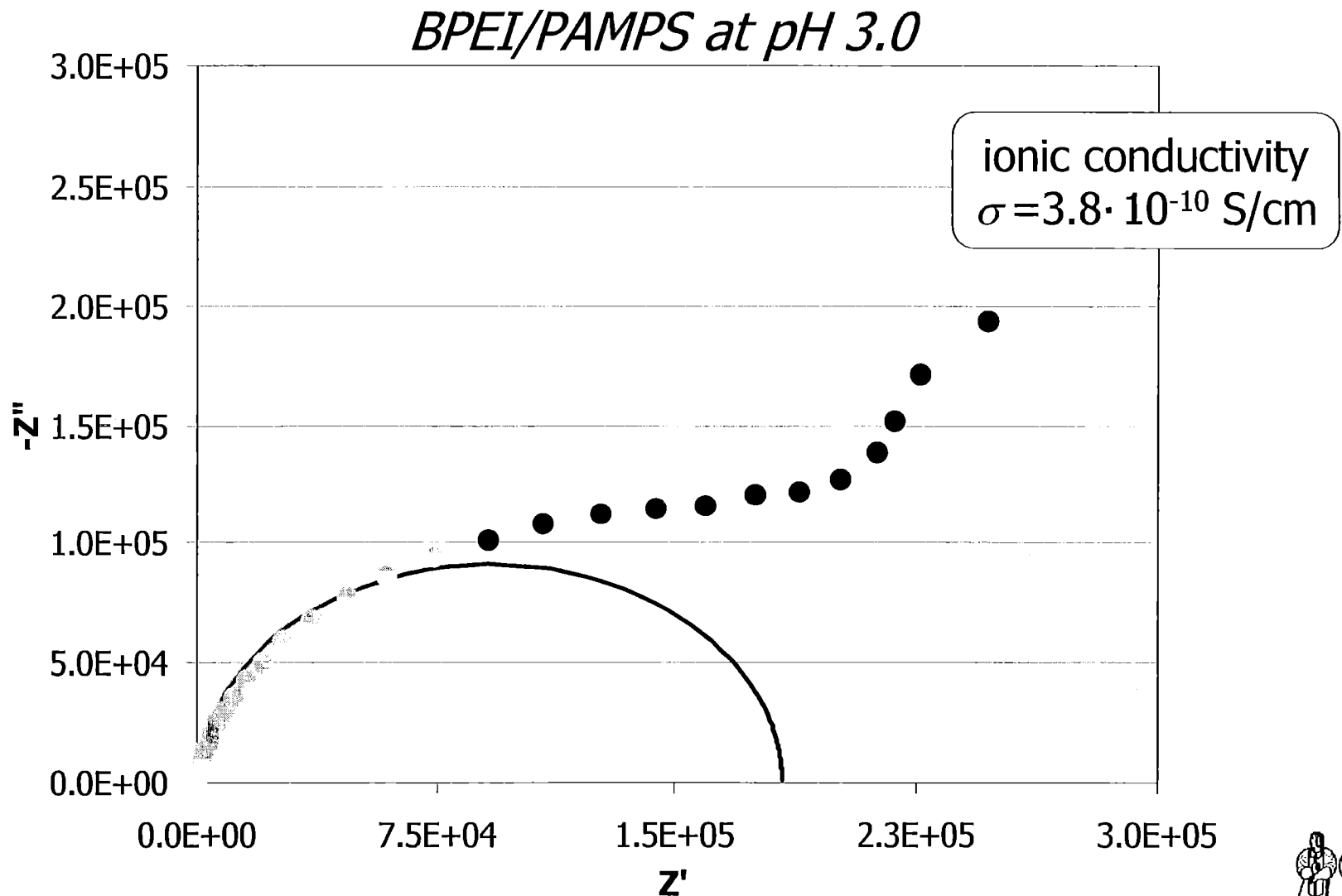
Impedance Analysis Experimental Setup



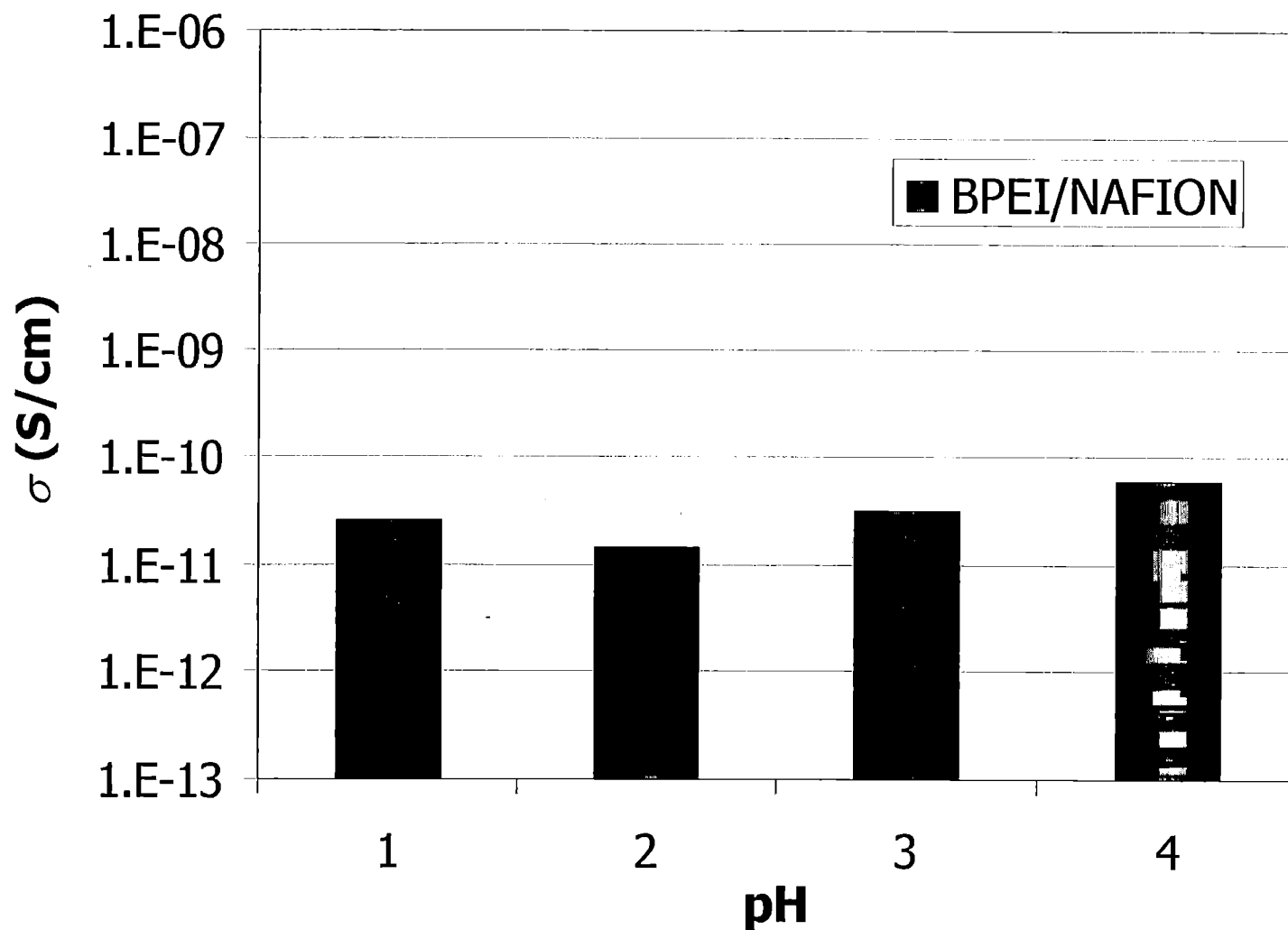
Equivalent Circuit



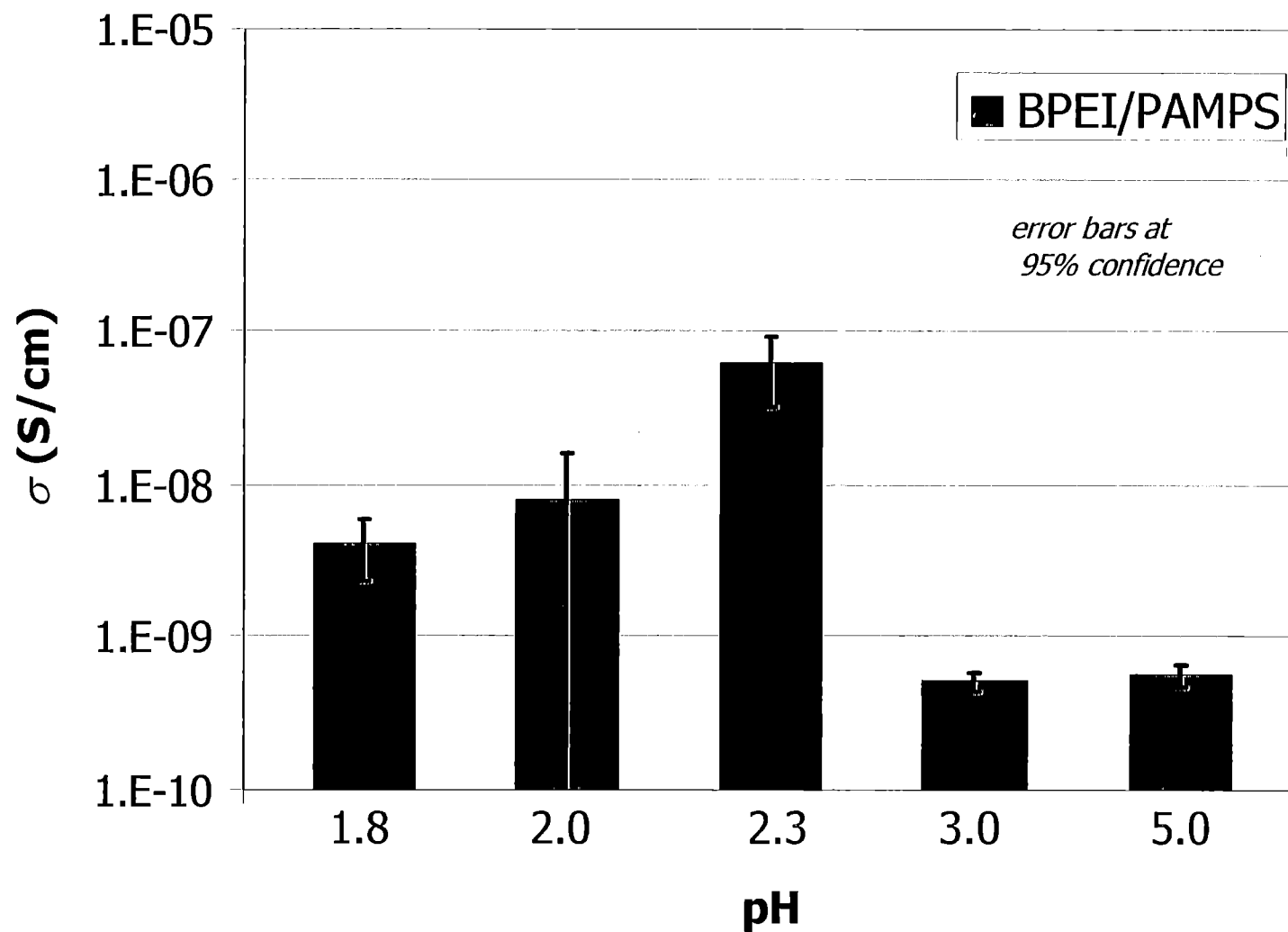
Typical Impedance Response



BPEI/NAFION Conductivity Trend



BPEI/PAMPS Conductivity Trend



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

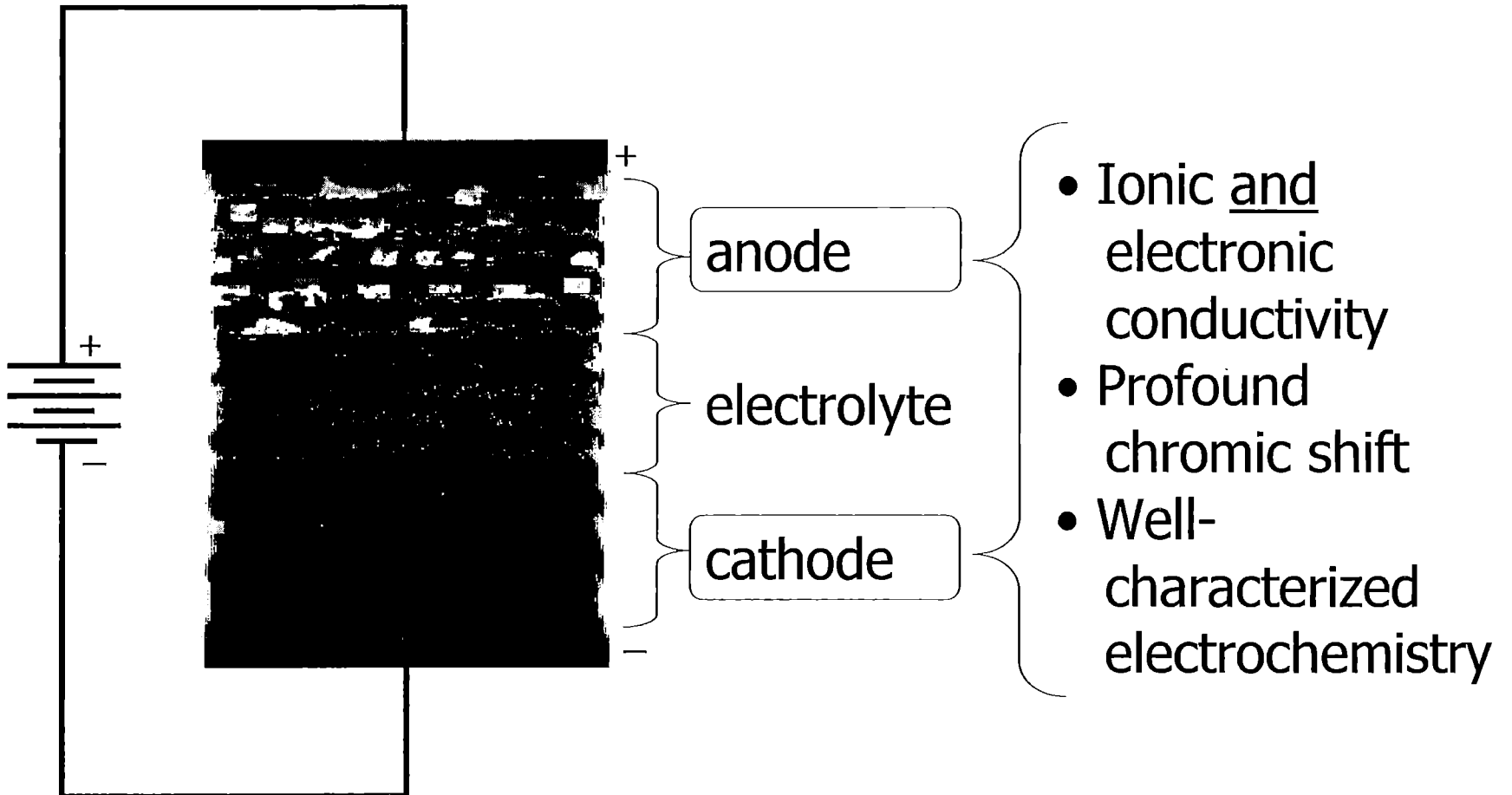
Conductivity is also greatest near acid pKa

Less charge density → More preserved charge
carriers (protons)

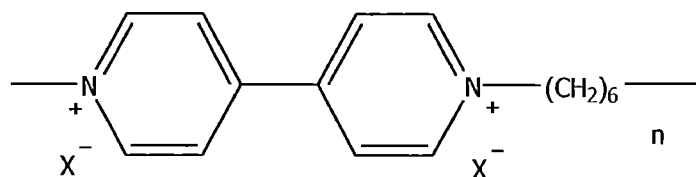
Conductivity 3-4 orders of magnitude higher than
NAFION/BPEI system



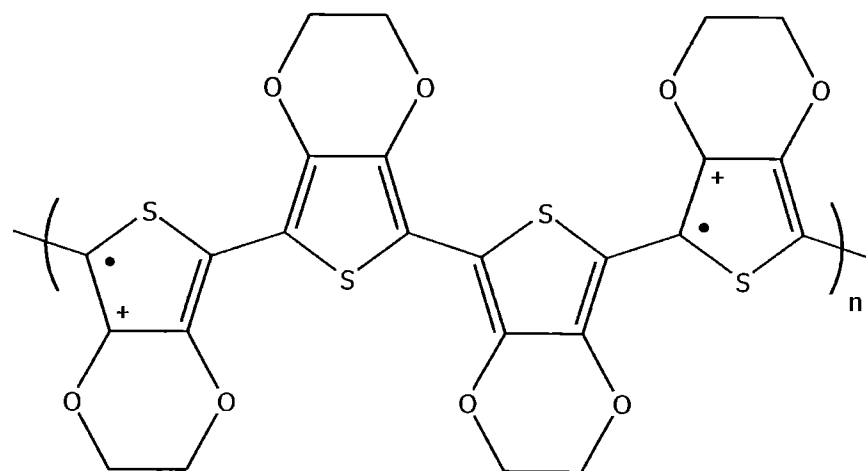
Focus: Electrochemistry



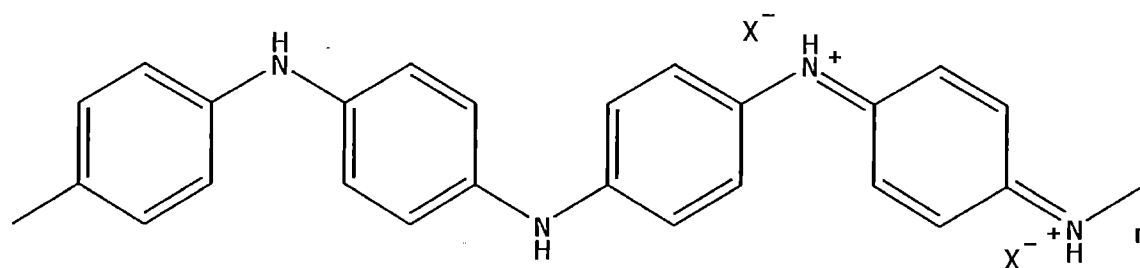
Polyelectrochromes



PXV
Polyhexylviologen



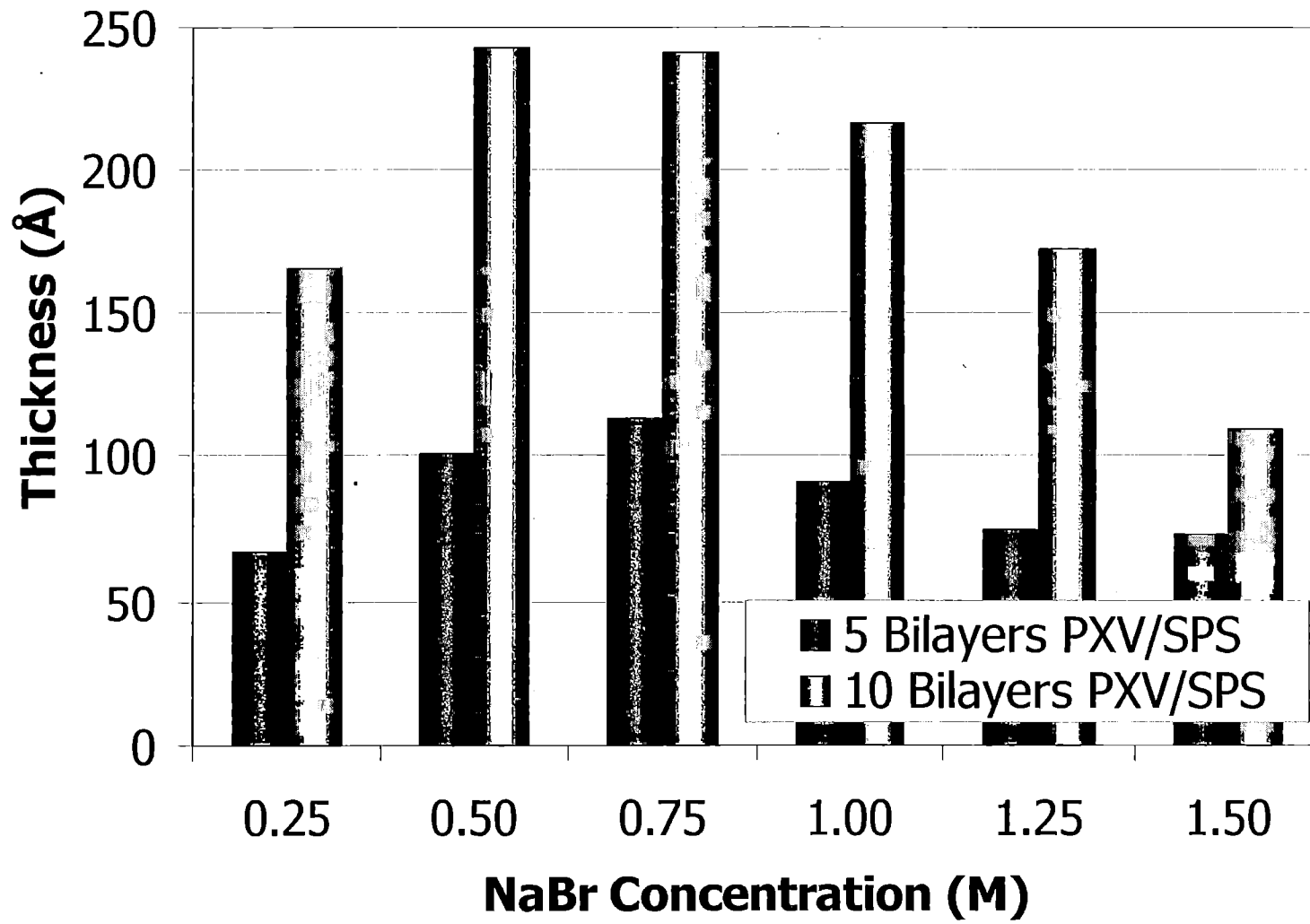
PEDOT
Poly(3,4-ethylenedioxythiophene)



PANi
Polyaniline)

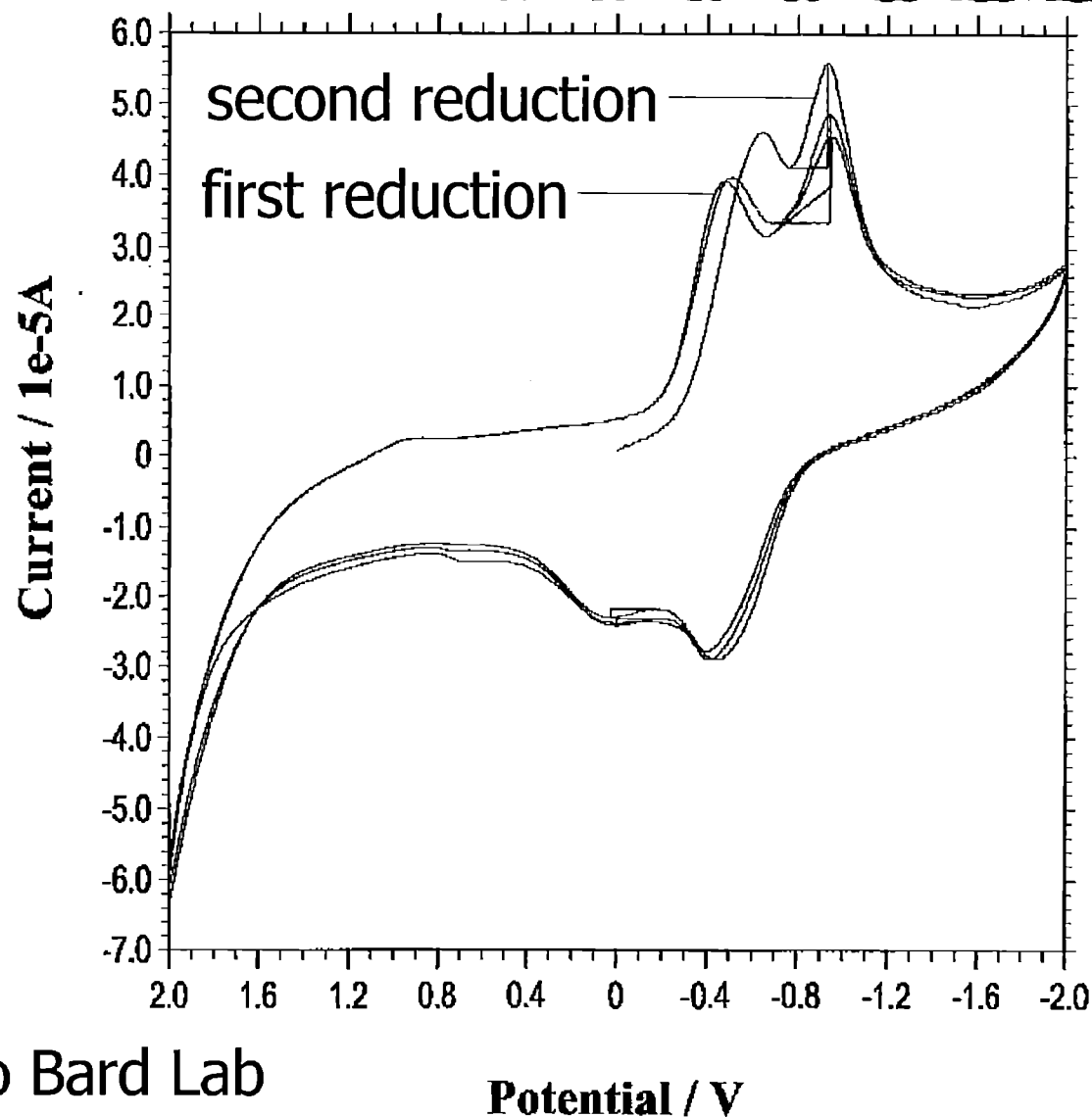


Thickness Dependence on Salt



Cyclic Voltammetry Results

PXV/SPS
System



* Thanks to Bard Lab



Electrochromism Summary

PXV/BPEI System:

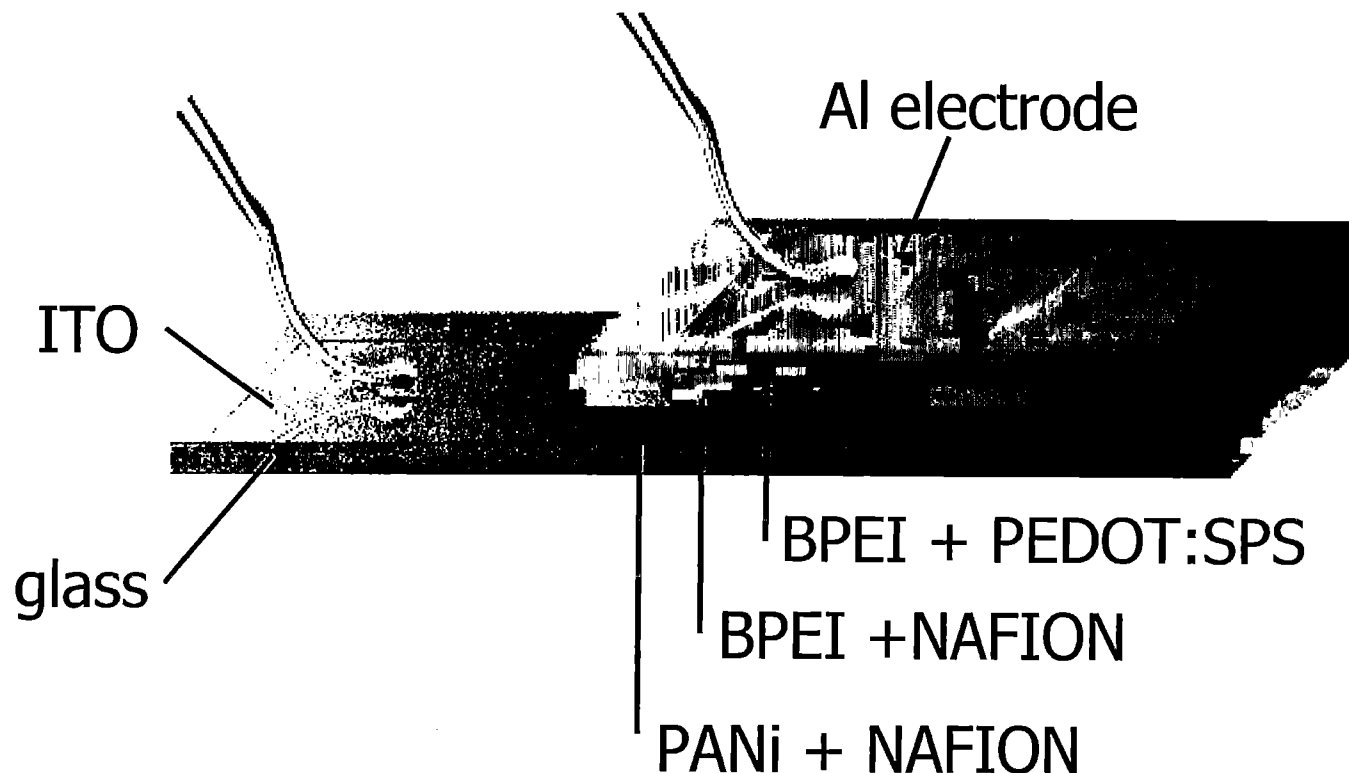
Thickness control achievable with salt or pH
Characterizable, reversible electrochromism

PEDOT/BPEI and PANi/BPEI Systems:

Typical film growth via multilayering
CV results pending



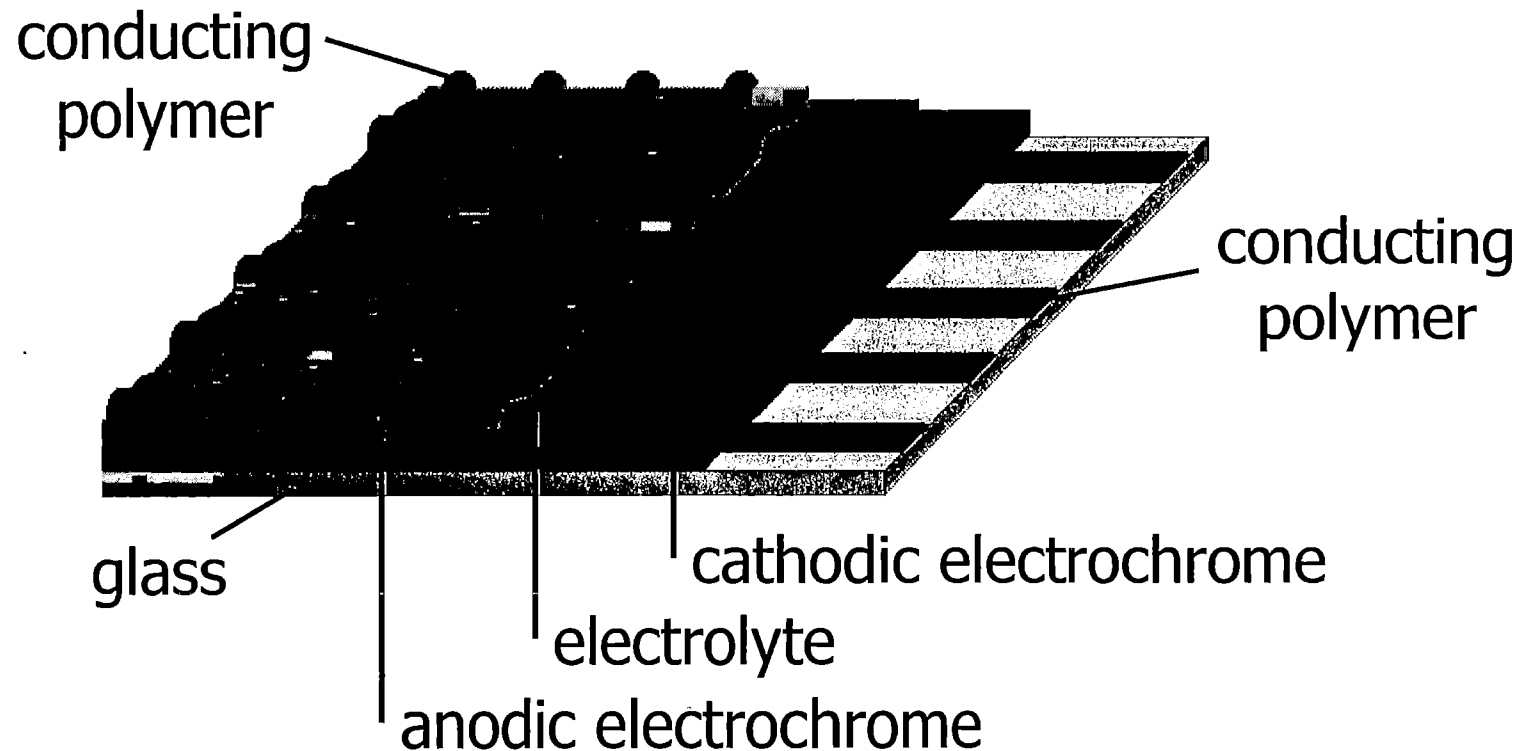
Single Film Device



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

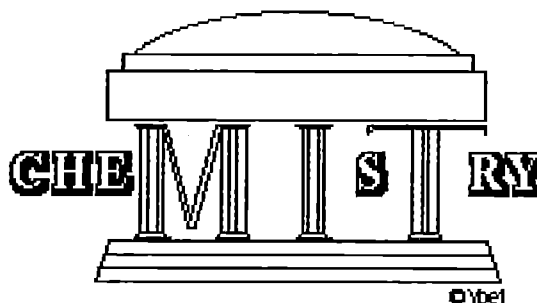
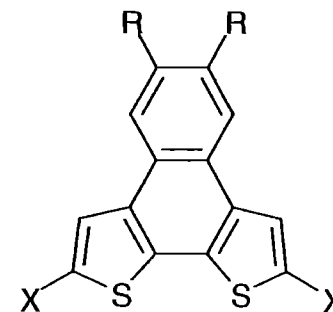
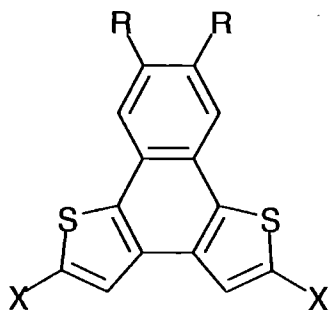
- Army Research Office (ARO TOPS MURI)
- Bard Lab
- Rubner Lab
- Hammond Lab
- Department of Defense NDSEG Fellowship



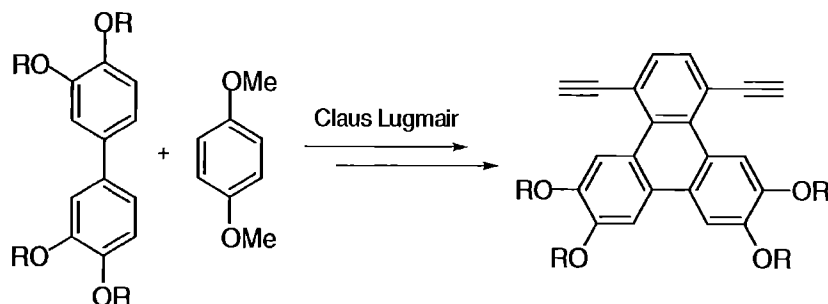
Naphthodithiophenes: A new class of electroactive materials

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Current interest in planar fused thiophenes

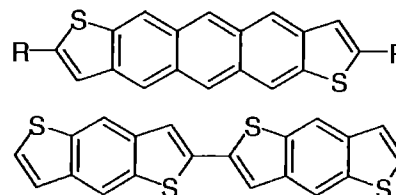


Challenging synthetic approach ... could thiophenes allow for easier functionalization?

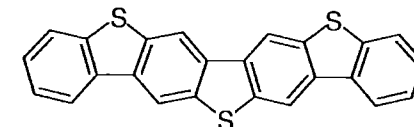
- Halogenation to provide monomers
- Fine-tuning of molecular properties
- Incorporation into LC or sensory polymers

High mobility organic FET materials

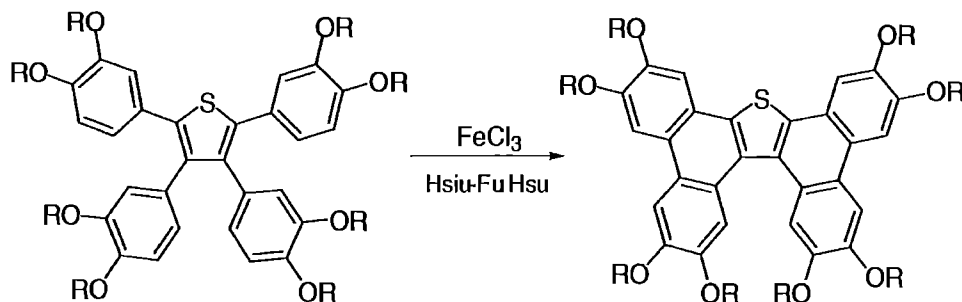
- polycyclic aromatics
- well-defined oligomers



H. E. Katz *et al.* *Adv. Mater.* **1997**, 9, 36;
J. Am. Chem. Soc. **1998**, 120, 664-672.

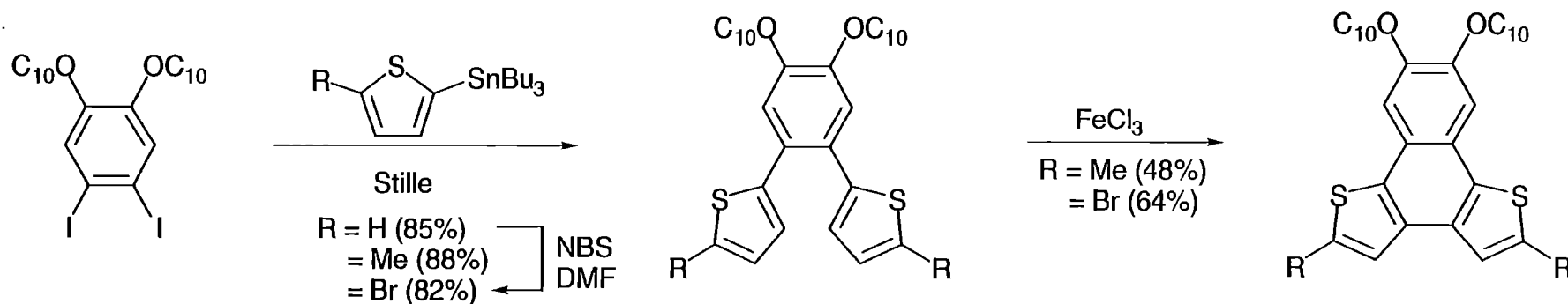


Sirringhaus, Friend, Müllen *et al.*
J. Mater. Chem. **1999**, 9, 2095-2101.

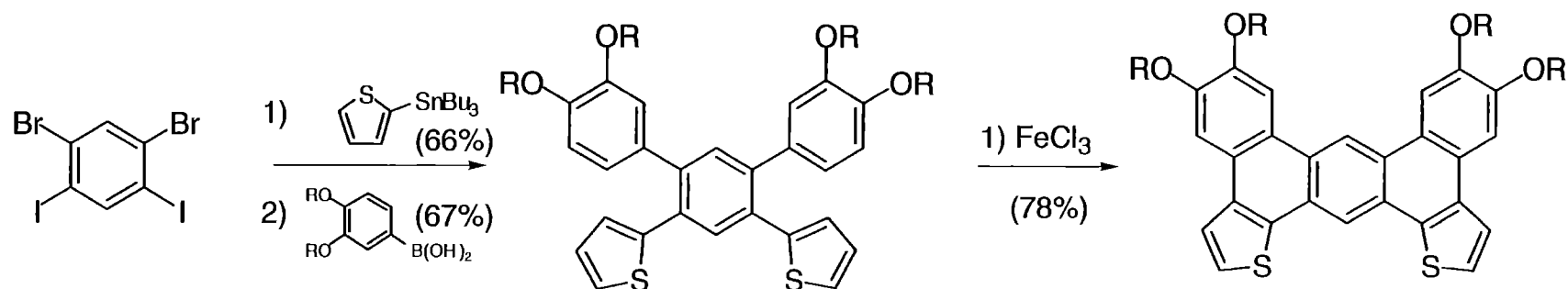


Structural similarity to triphenylene:
New discotic core mesogens?

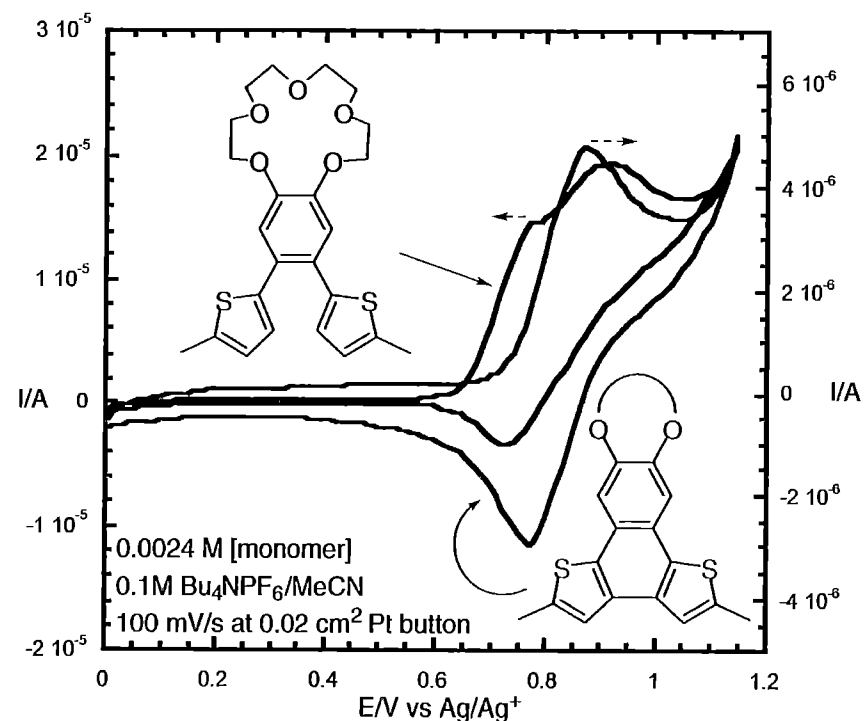
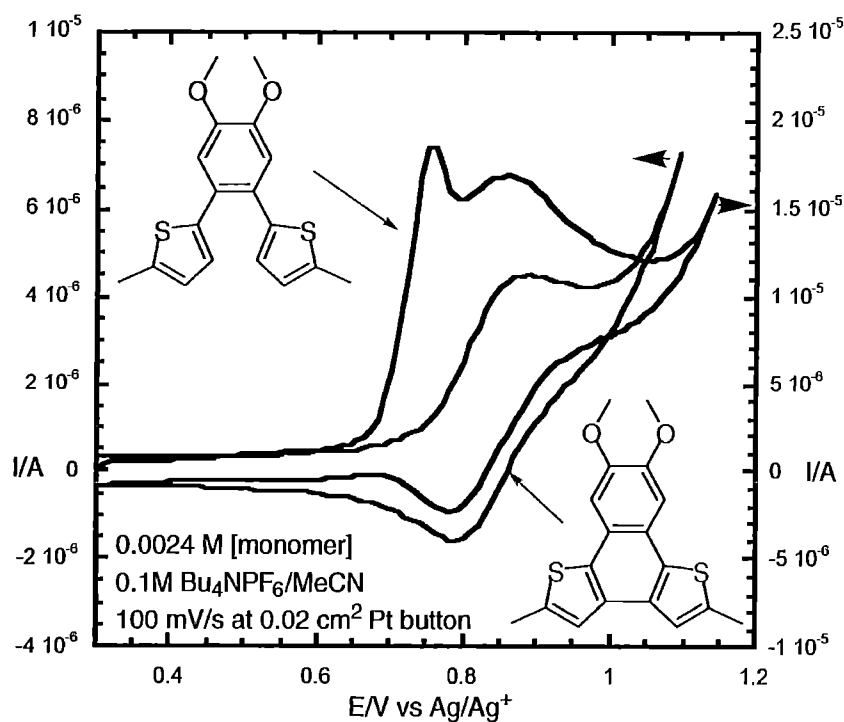
Synthesis of α -thienyl systems



This strategy also applies to extended aromatic systems:

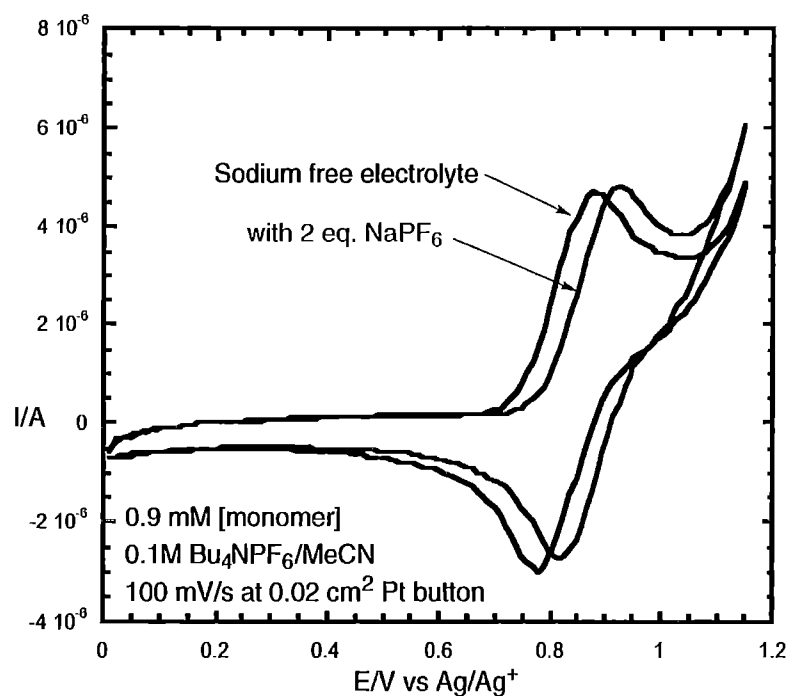


Cyclization-redox activity: α -blocked models

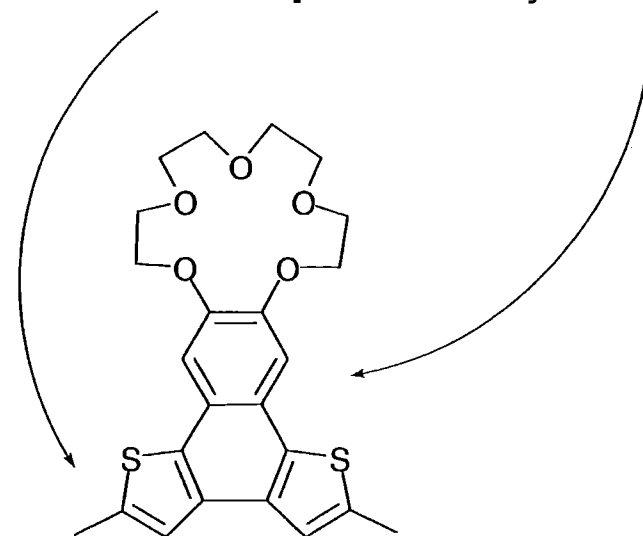


Both display a loss of irreversible oxidation after chemical cyclization

Sodium binding with a 15-crown-5 monomer

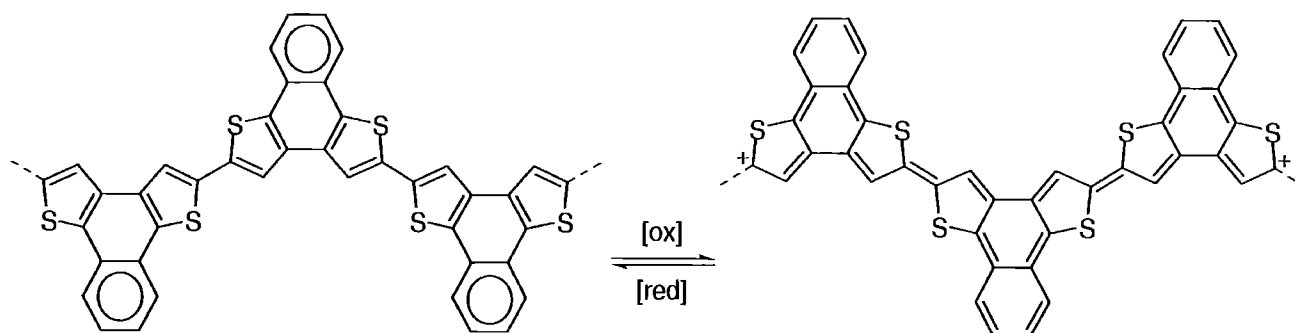


The shift to higher potential suggests communication between the **benzeno** bridge and the fused **bithiophene** moiety



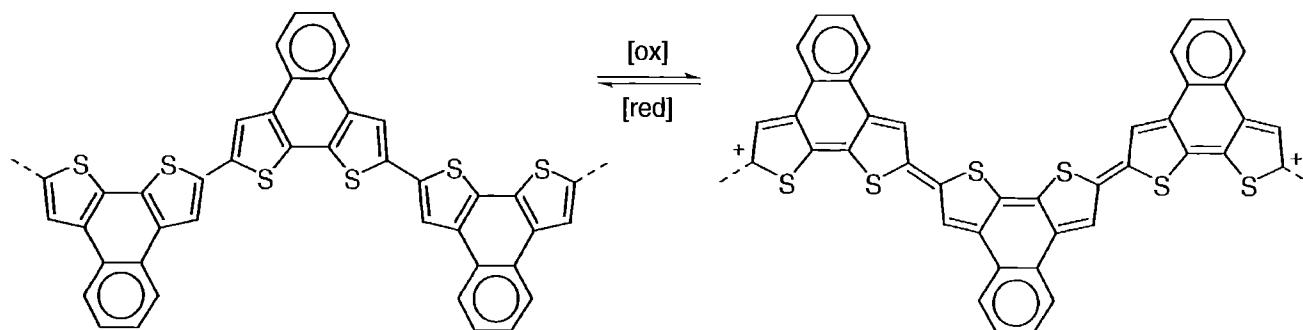
Could this be exploited in a polymer?

Moving on to β -thiophenes



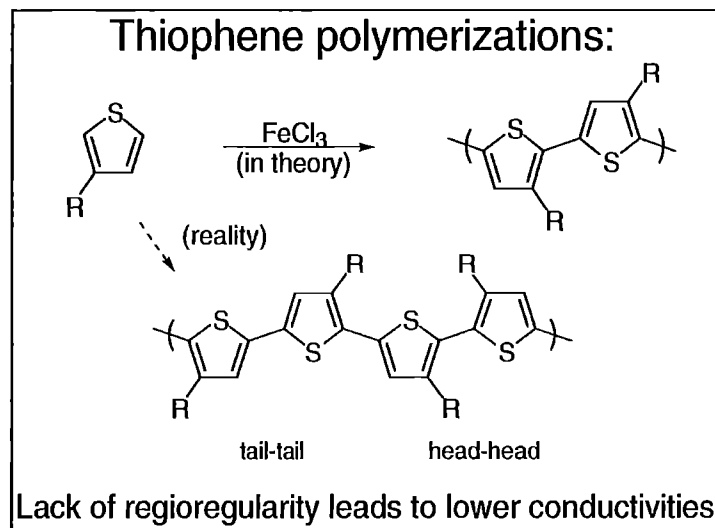
Here, quinoid resonances must
disrupt pendant ring aromaticity ...

... while here, conjugation
mainly through the planar
poly(bithiophene) backbone

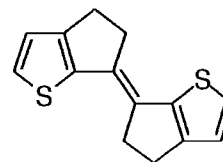


Planar thiophene polymerizations:

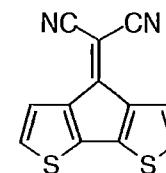
Chemical and electrochemical methods



Planarized monomers

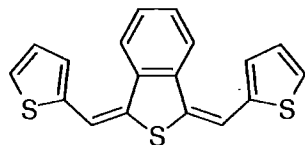


Roncali, *J. Chem. Soc. Chem. Commun.* **1994**, 2249-2250



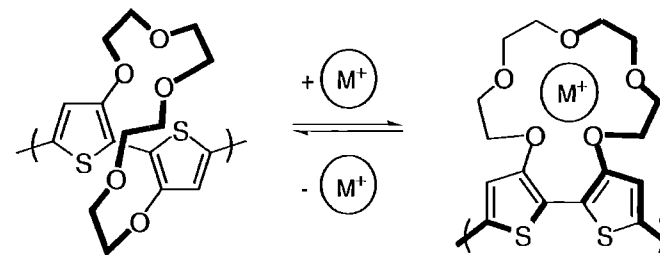
Ferraris, *ibid.* **1991**, 1268-1270

Quinoidal monomers



Hanack, *Synth. Met.* **1993**, 55-57, 827-832

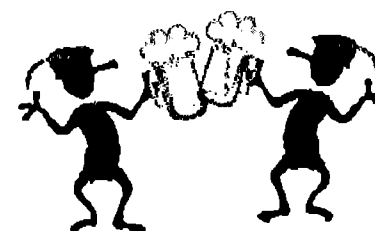
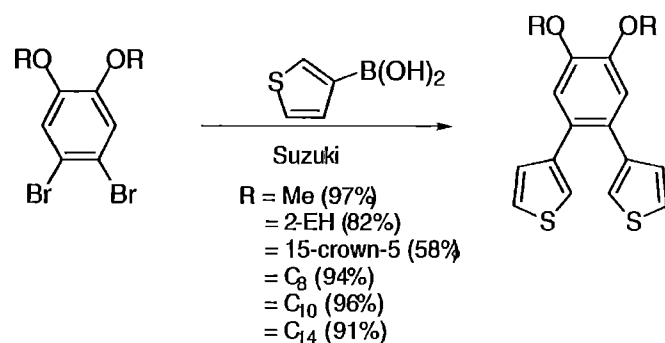
Disruption of planarity



Swager, *J. Am. Chem. Soc.* **1993**, 115, 12214-12215

Synthesis of β -thienyl monomers

Preliminary CV studies



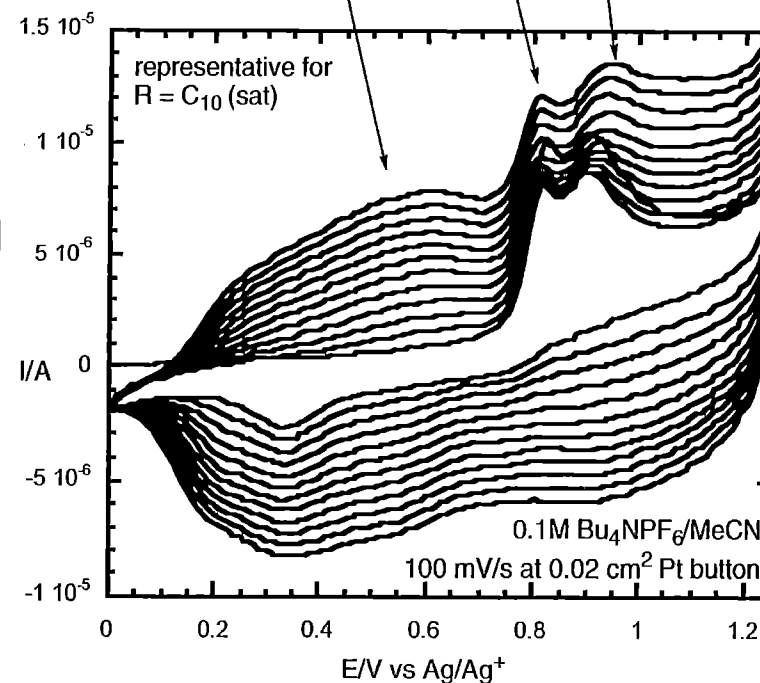
Polymer redox
after growth

Leads to
cyclization?

Oxidation of
aromatic monomer?

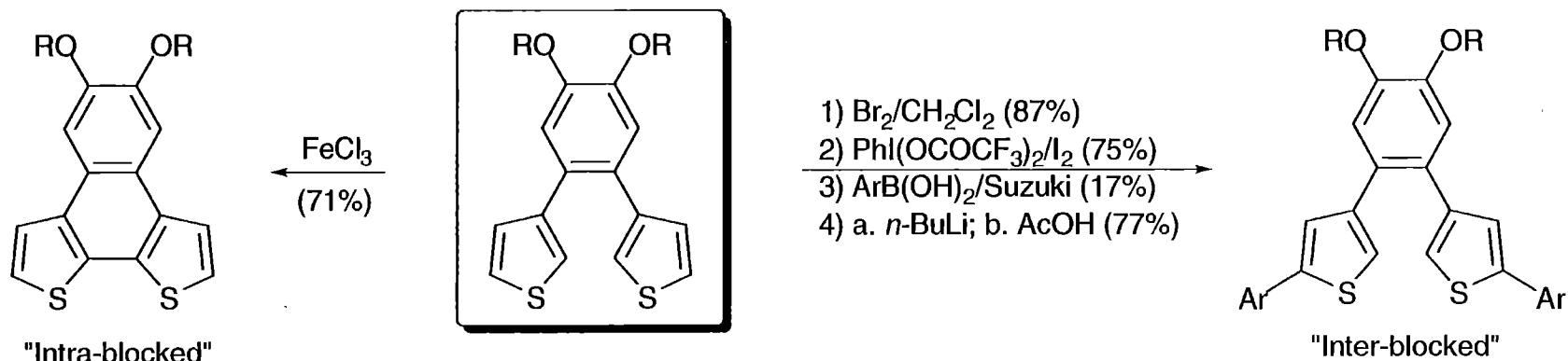
Lack of reduction activity implies discrete chemical reactions ...

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

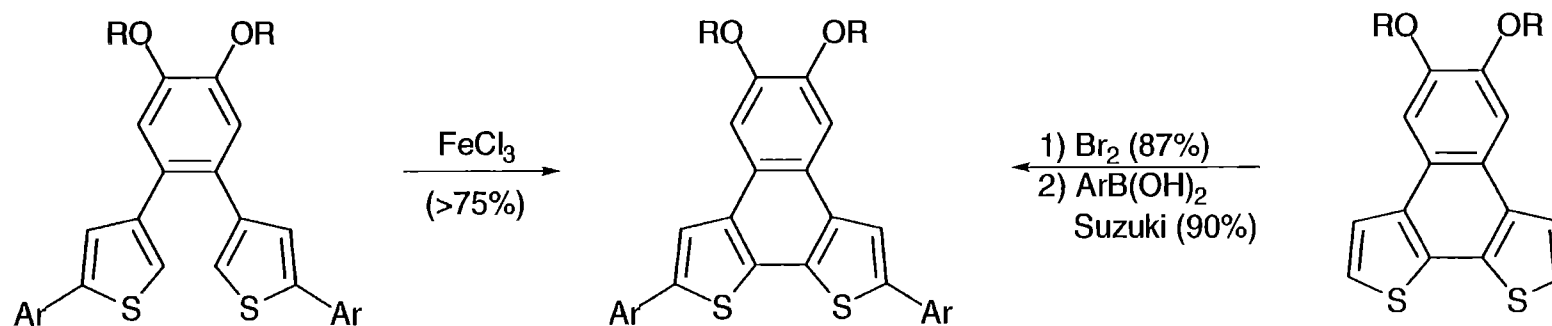


Deconvoluting the electrochemistry:

Synthesis of model compounds ...



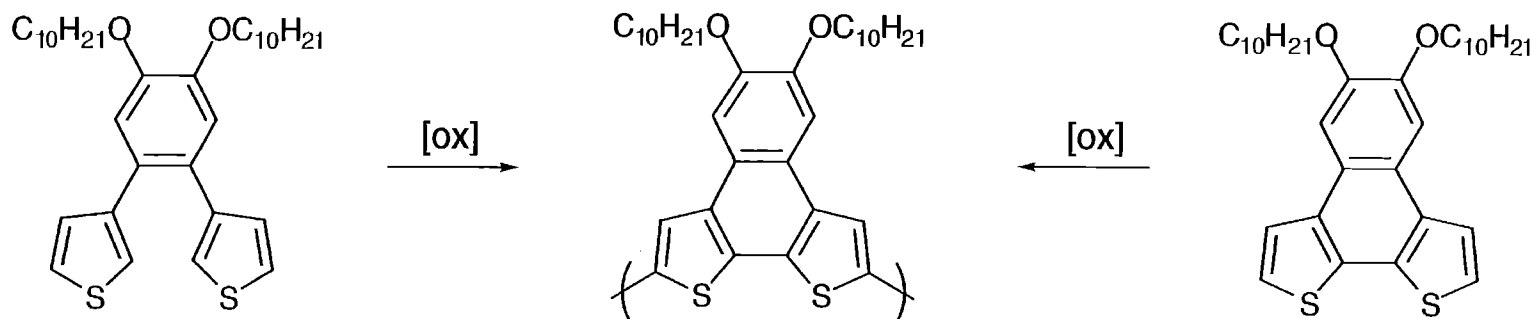
... and verification of the connectivity through independent syntheses



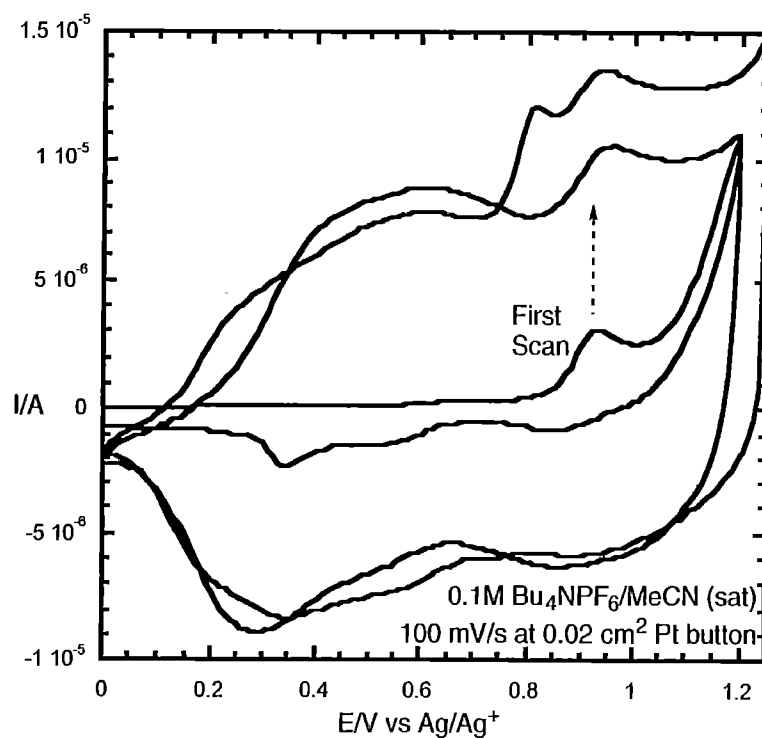
No evidence for β -coupling

Selective α -bromination

CV studies: Tandem cyclization-polymerization

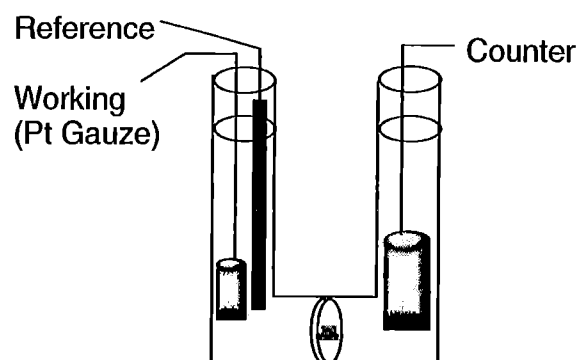
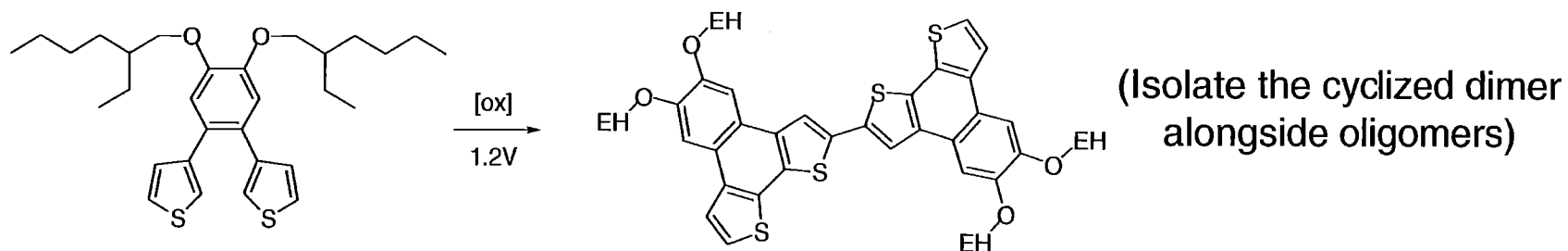


Two distinct
monomer
oxidations



Only one
monomer
oxidation!

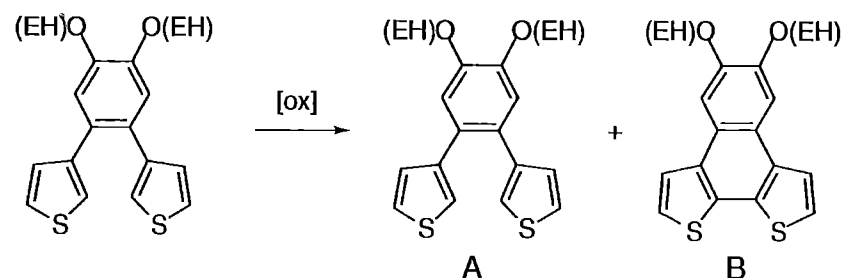
Assessing the regioregularity: bulk electrolysis



Ethylhexyl for solubility:

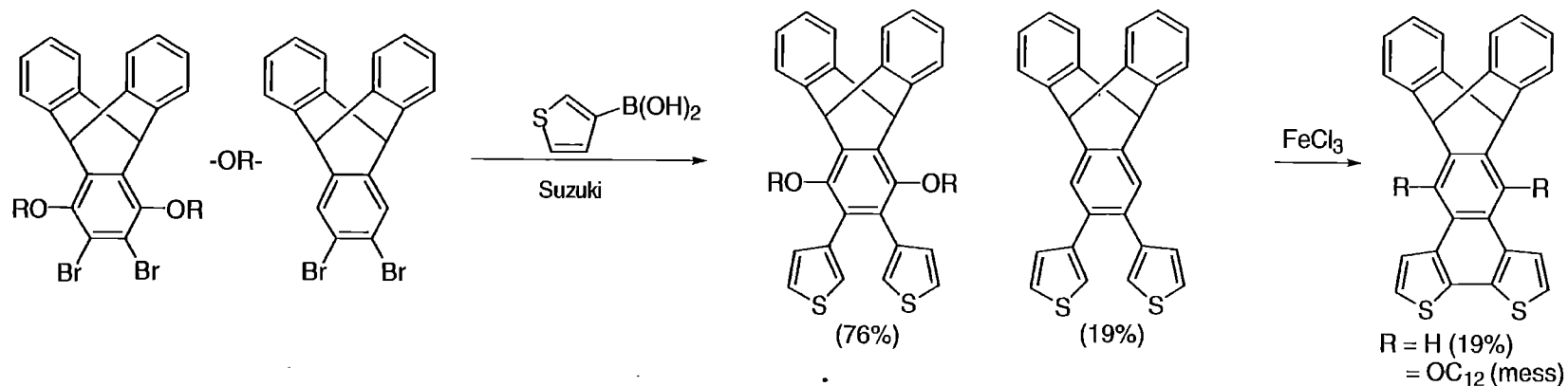
- GPC shows oligomers

Constant potential electrolyses:

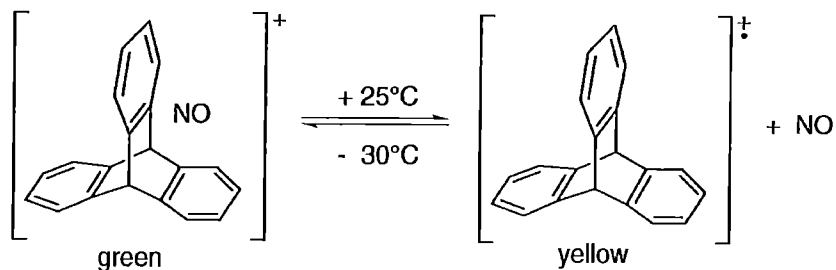


Potential/V	e-/mol	A	B	
0.75		0.96	0.04	
0.85	1.09	0.49	0.51	
0.85	2.02	0.03	0.97	(74% isolated)

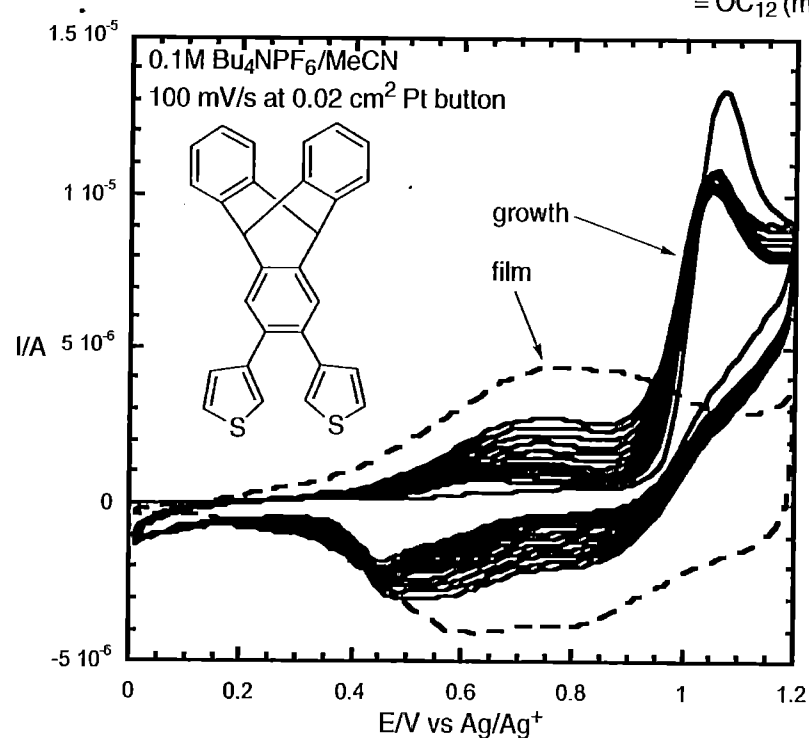
Attempts toward more diverse systems



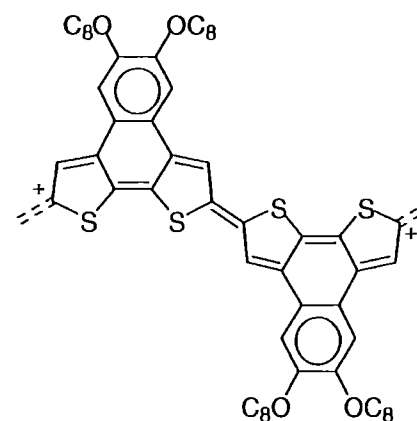
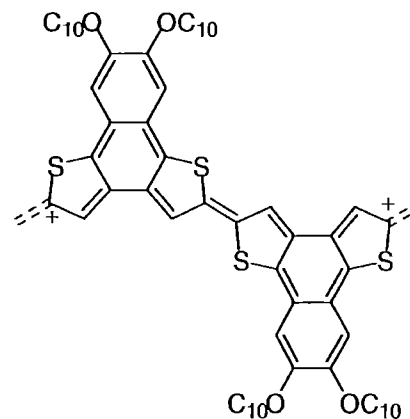
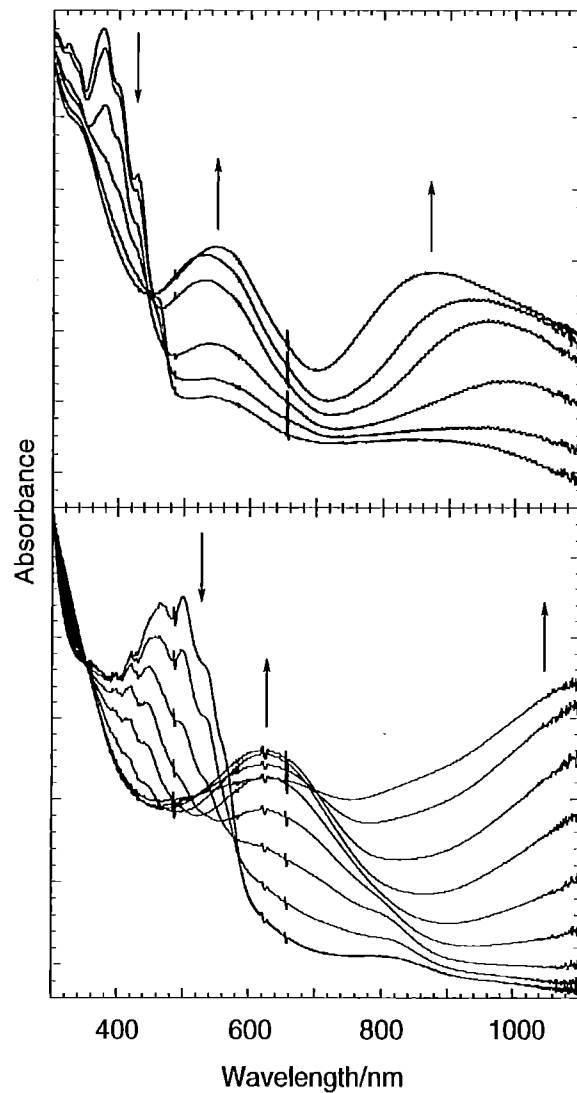
For redox-active NO sensors?



Kochi, *J. Org. Chem.* **1998**, 63, 8630-8631



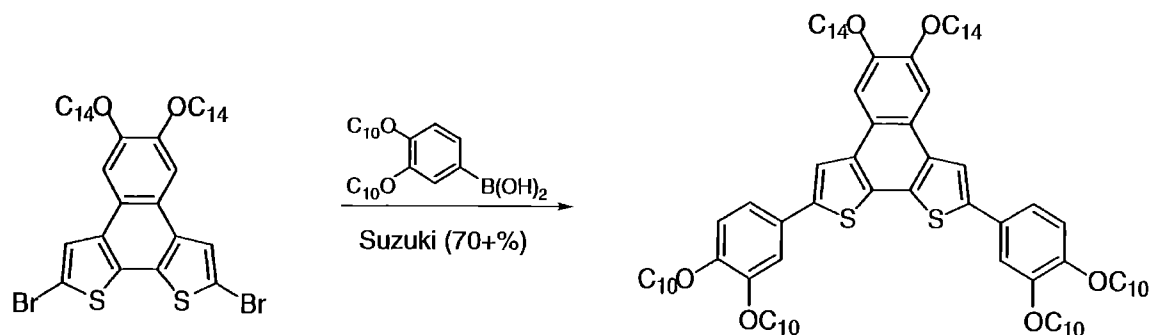
Spectroelectrochemical studies: assessing the electrochromicity



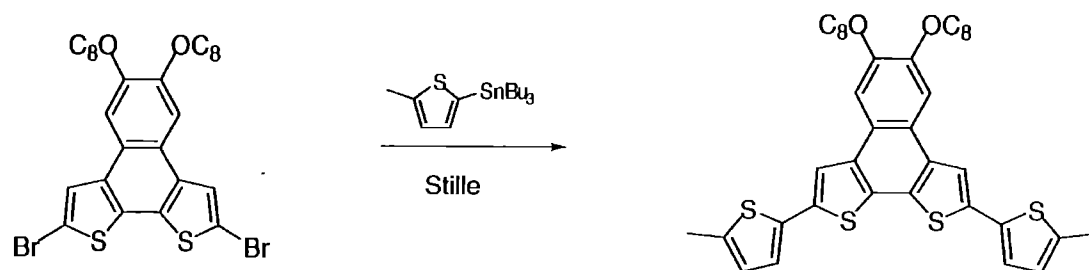
Substitution on the pendant phenyl moieties should allow for tuning of
optical absorption/ conductivity

Demonstrations of facile functionalization

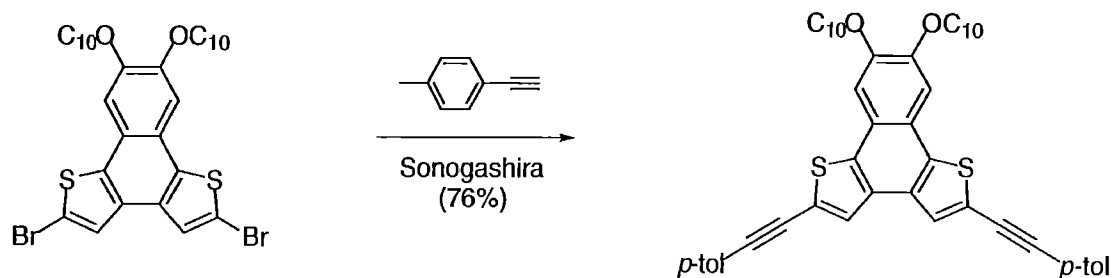
future directions



Liquid crystals?



Tuneable electroactivity?



Incorporation into conducting polymers?

Acknowledgements

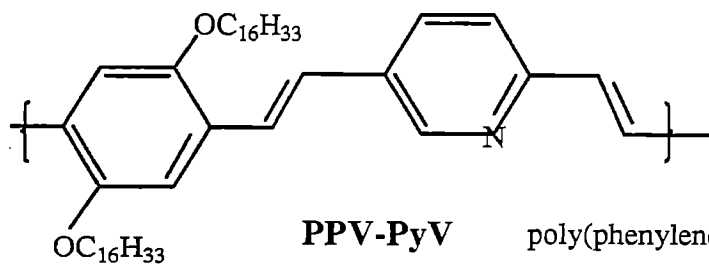
Prof. Timothy M. Swager

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

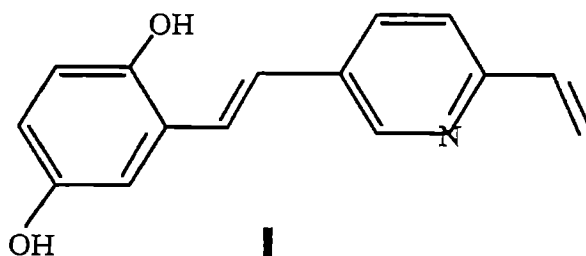
MODEL SYSTEMS



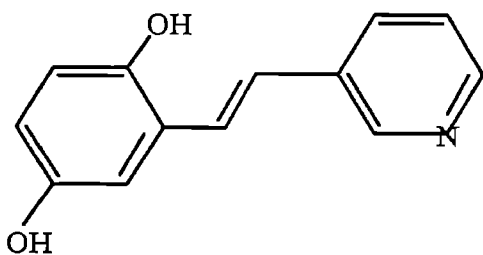
absorption shifted to red by
protonation

PPV-PyV

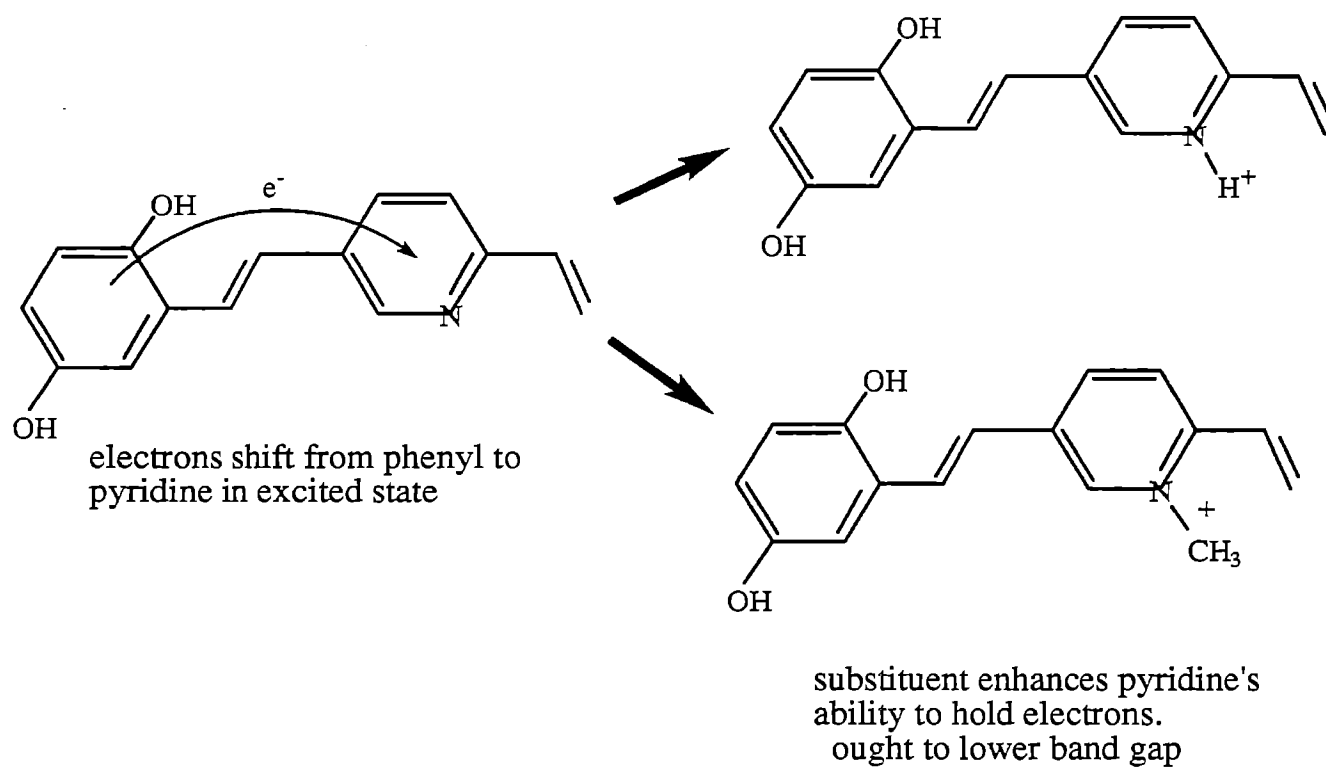
poly(phenylene vinylene pyridyl vinylene)

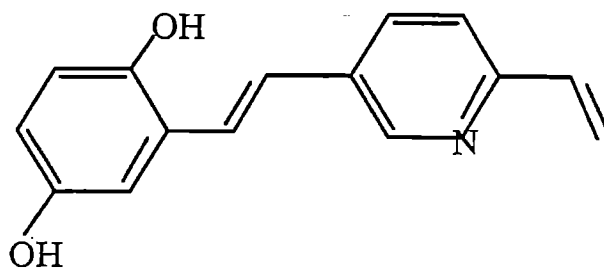


replace hydrocarbon chain by H



may not need terminal vinyl group





PROCEDURE

- Optimize geometry

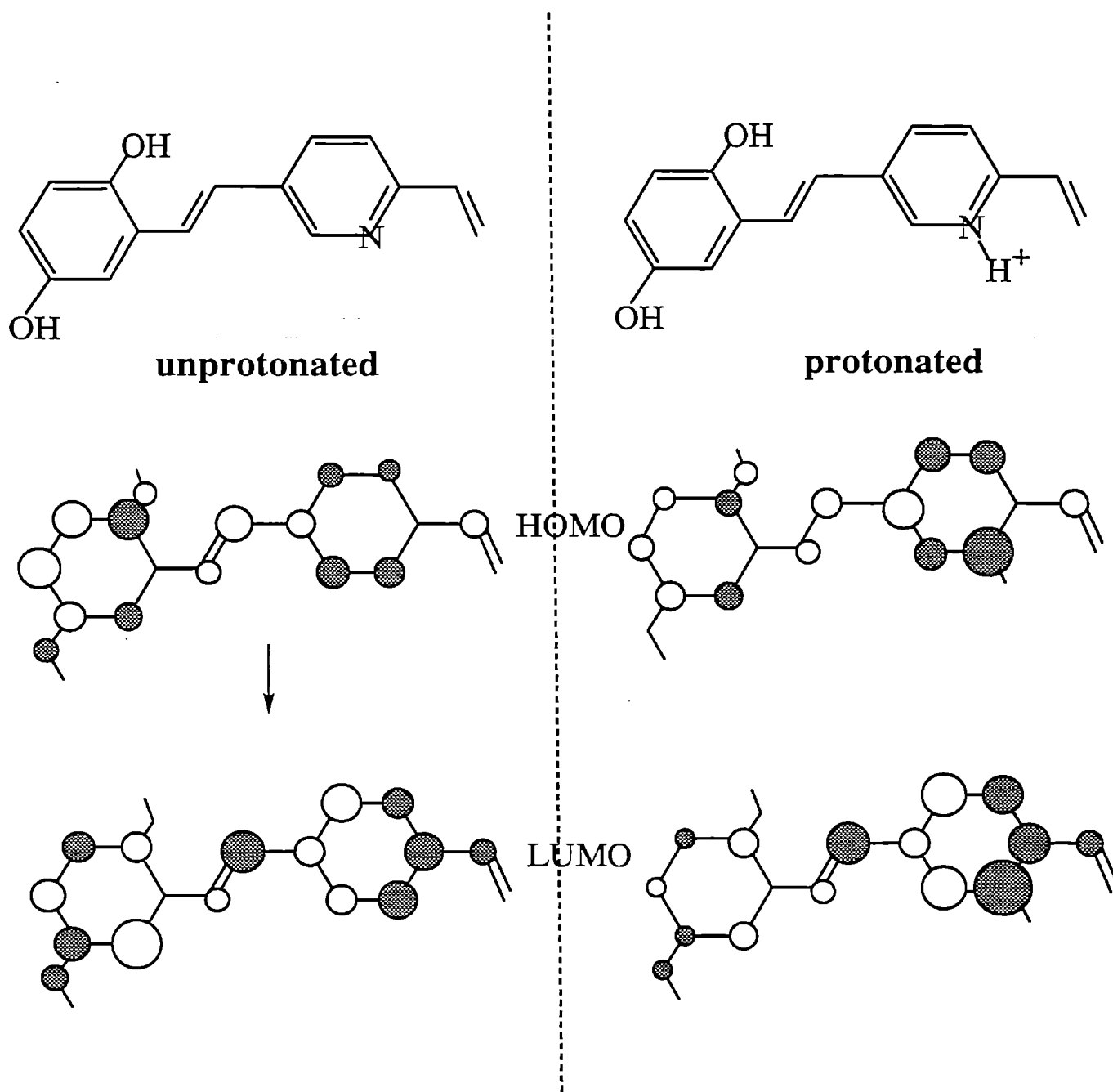
INDIVIDUAL MOs

- 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

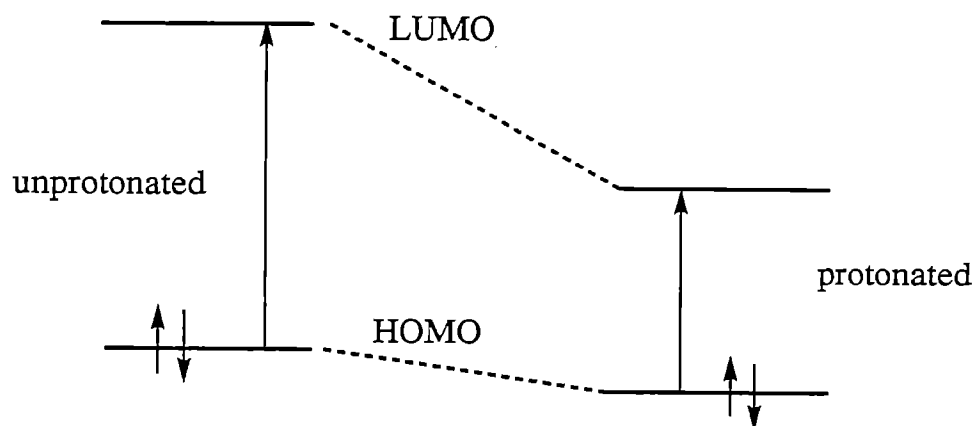
TOTAL ELECTRON DENSITY ρ

- Display ρ for ground state
- Display ρ 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



Energy Levels

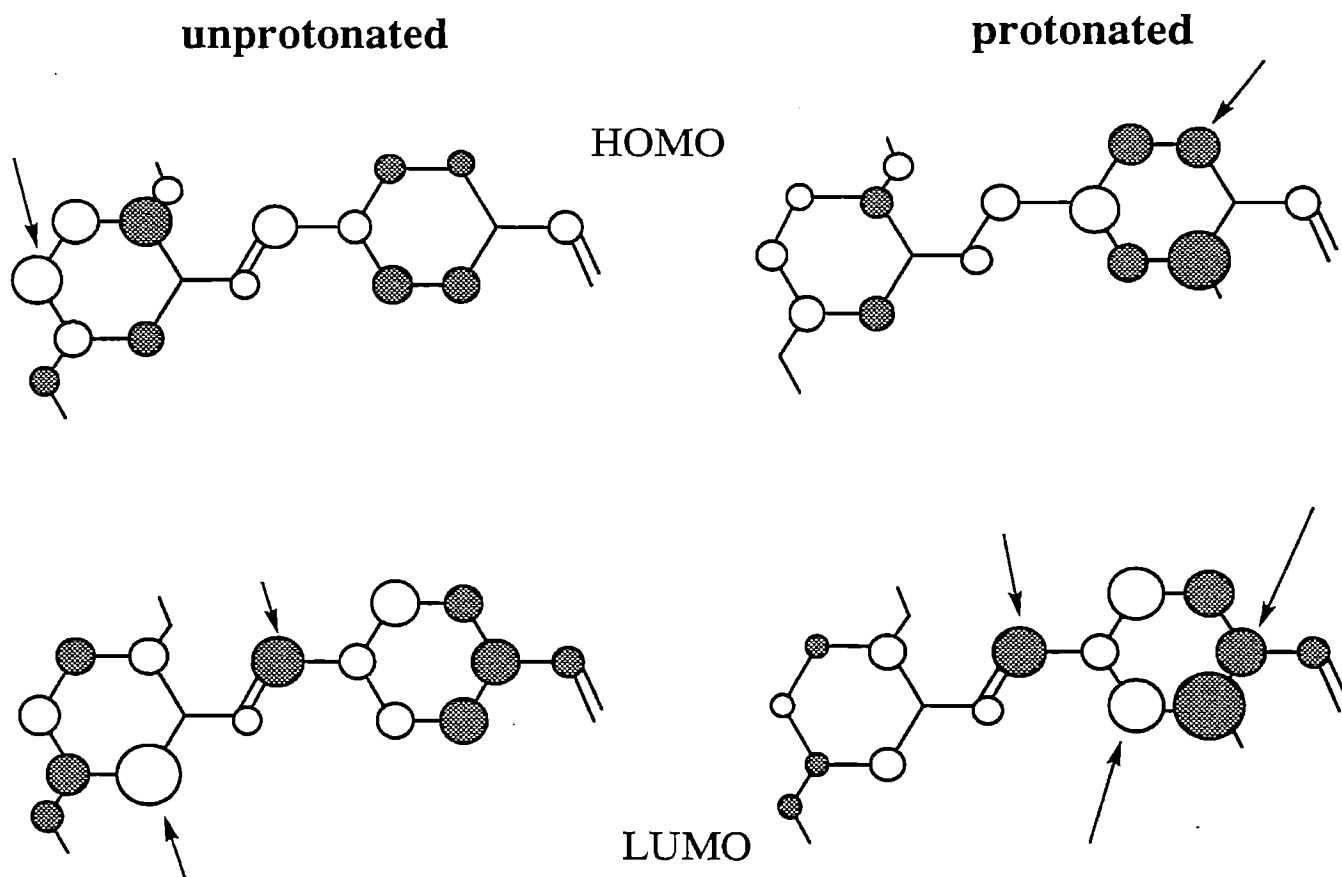


Steve Scheiner, SIU

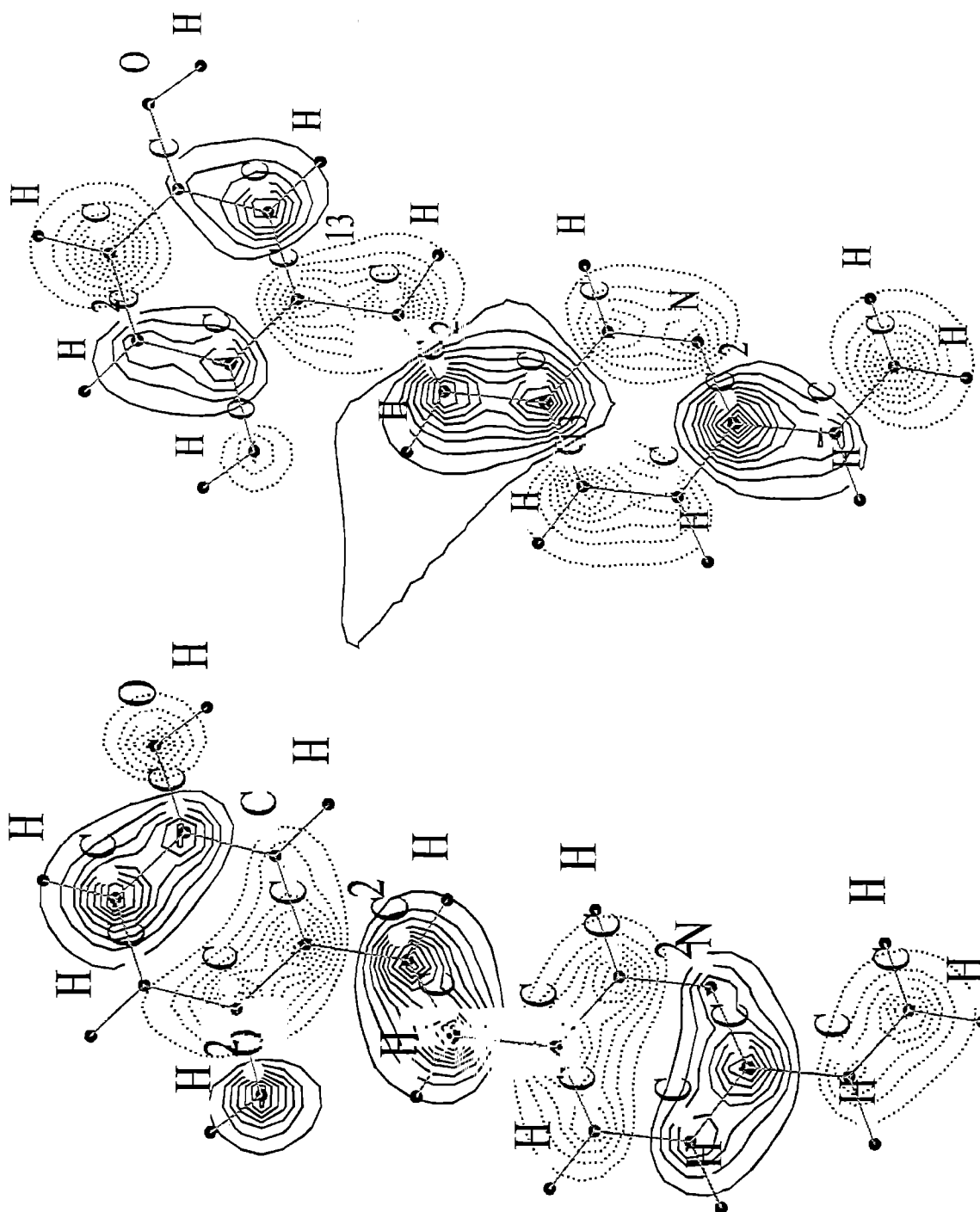
Tunable Absorption Systems

ARO MURI

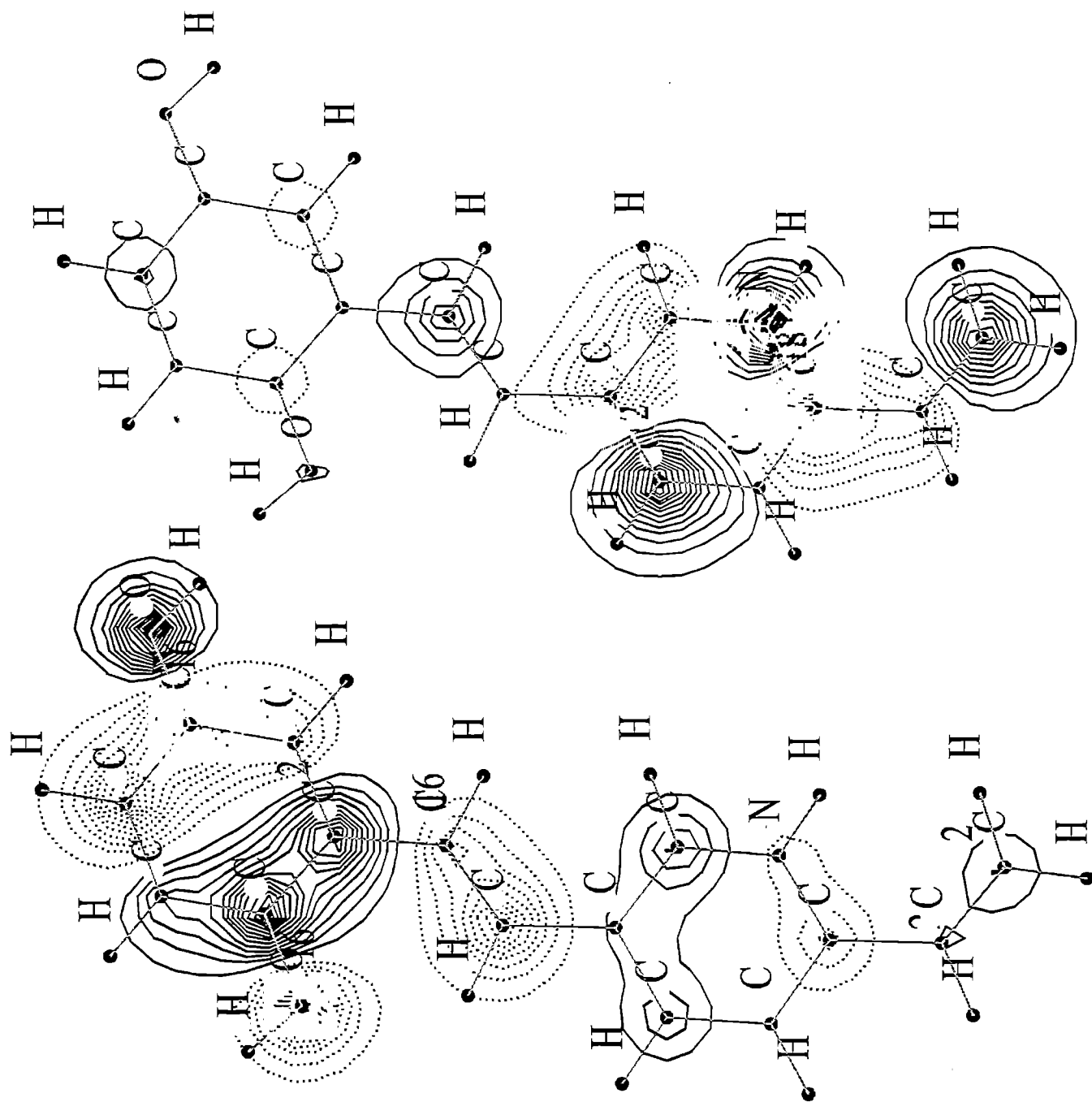
identification of "hot spots"



areas of potential substitution



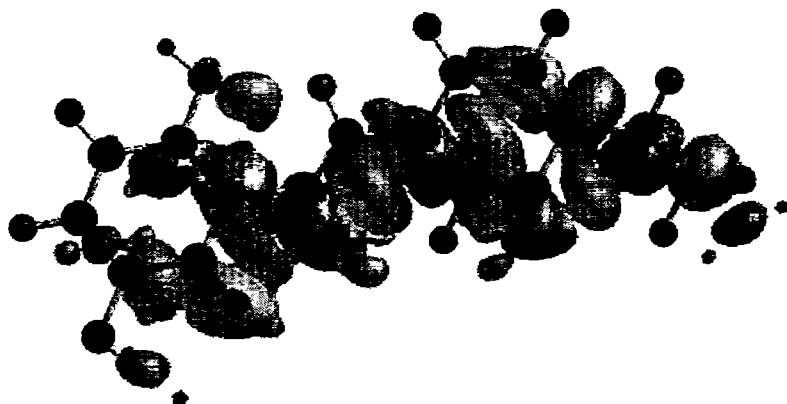
UNPROTONATED HOMO/LUMO



PROTONATED HOMO/LUMO

total electron density shifts caused by excitation

unprotonated (blue=gain; red=loss)



protonated



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

	unprotonated	
	ring 1	ring 2
S ₀ charge	-0.028	-0.063
$\pi\pi^*$ charge	-0.014	-0.073
change	+0.014	-0.010
	protonated	
S ₀ charge	0.053	0.751
$\pi\pi^*$ charge	0.297	0.483
change	+0.245	-0.268

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)

	unprotonated	protonated	difference
6-31G*	4.72	4.33	-0.39
3-21G	4.90	4.48	-0.42

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

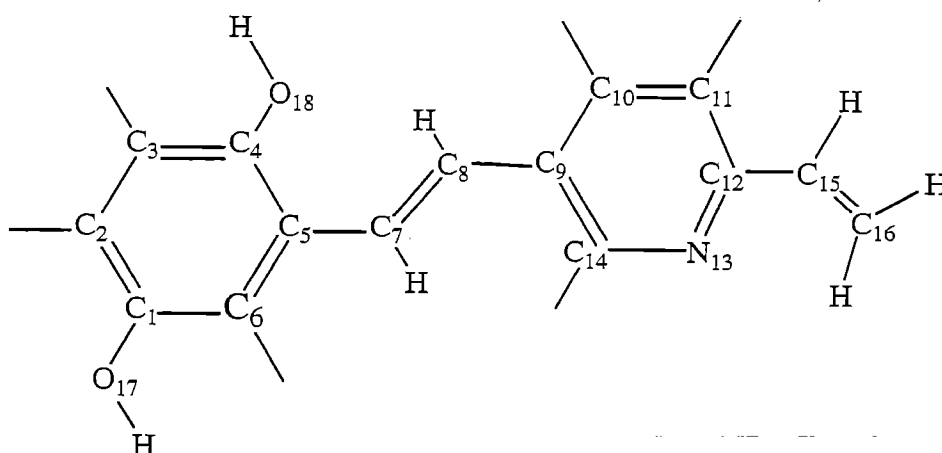
Where to make these replacements?
use MOs as a preliminary guide.

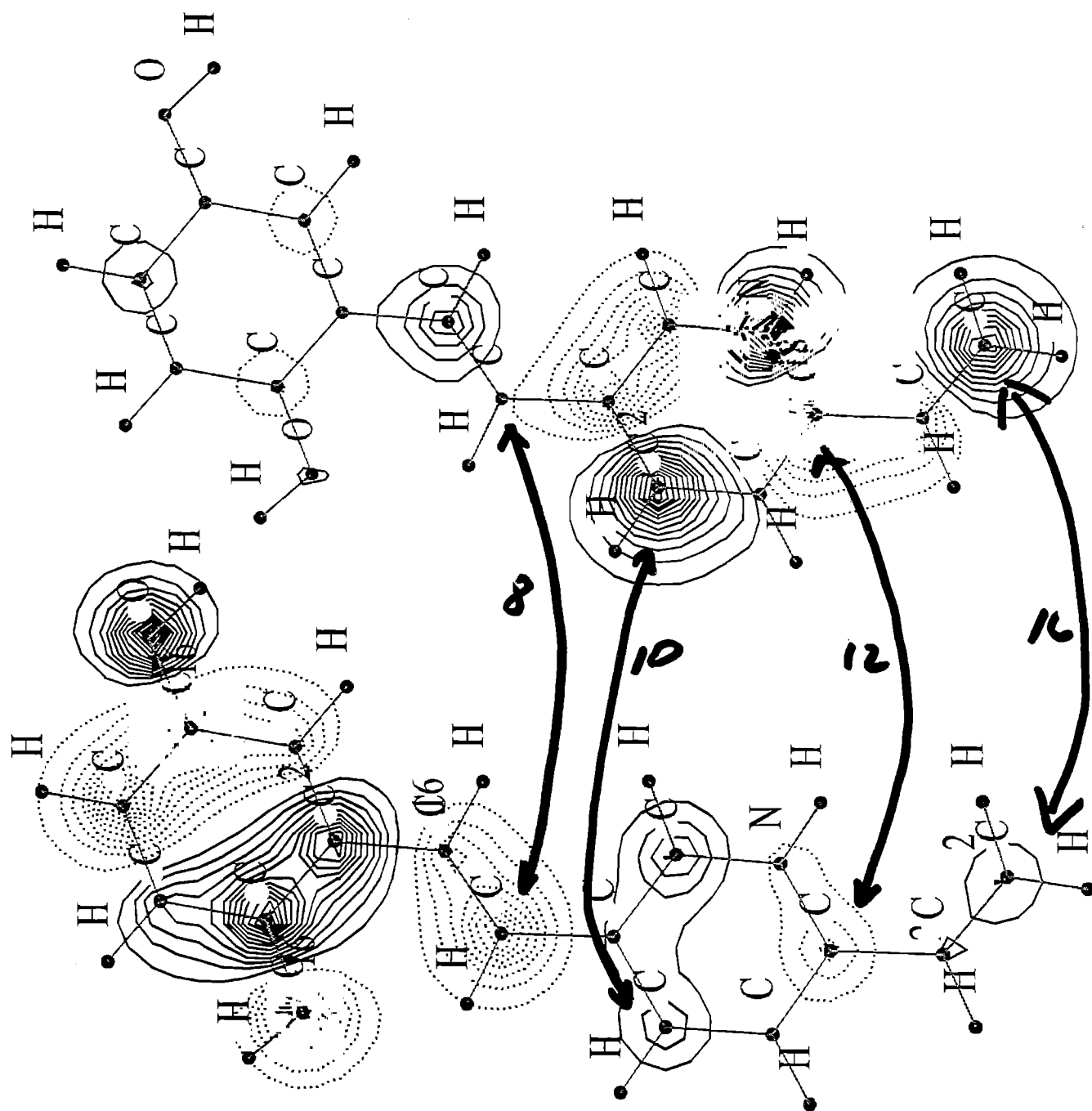
changes in individual atomic charges caused by excitation:

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

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

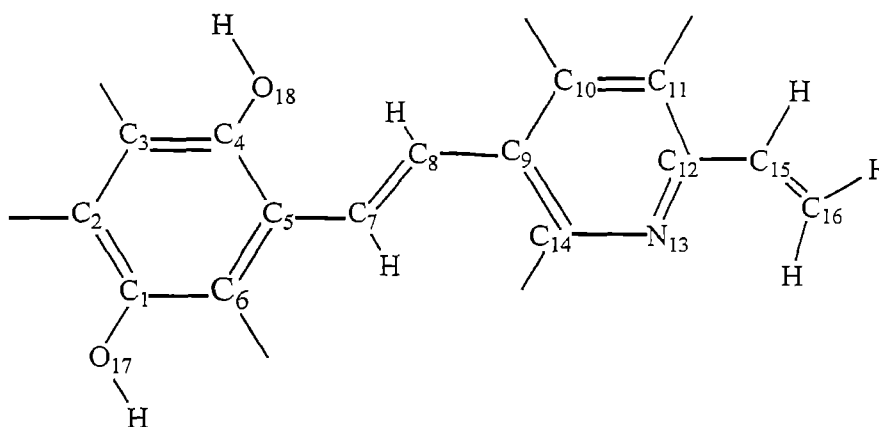
F-substitution	unprotonated	protonated	difference
none	4.72	4.33	-0.39
C2	4.76	4.35	-0.40
C6	4.75	4.45	-0.31
C8*	4.78	4.30	-0.48
C10*	4.75	4.36	-0.38
C14	4.73	4.19	-0.54

*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?)



calculations with smaller 3-21G basis set

F-substitution	unprotonated	protonated	difference
none	4.90	4.48	-0.42
C2	4.92	4.51	-0.41
C6	4.93	4.61	-0.32
C14	4.89	4.28	-0.61
C8*	4.95	4.44	-0.51
C10*	4.91	4.46	-0.45
C16*	4.91	4.44	-0.47

*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

	unprotonated	protonated	difference
none	4.90	4.48	-0.42
C8-F	4.95	4.44	-0.51
C8-NO ₂	4.50	4.51	0.01*
C10-F	4.91	4.46	-0.45
C10-NO ₂	4.49	4.14	-0.35

*strong repulsions make this planar structure not a minimum

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

removal of planarity constraint

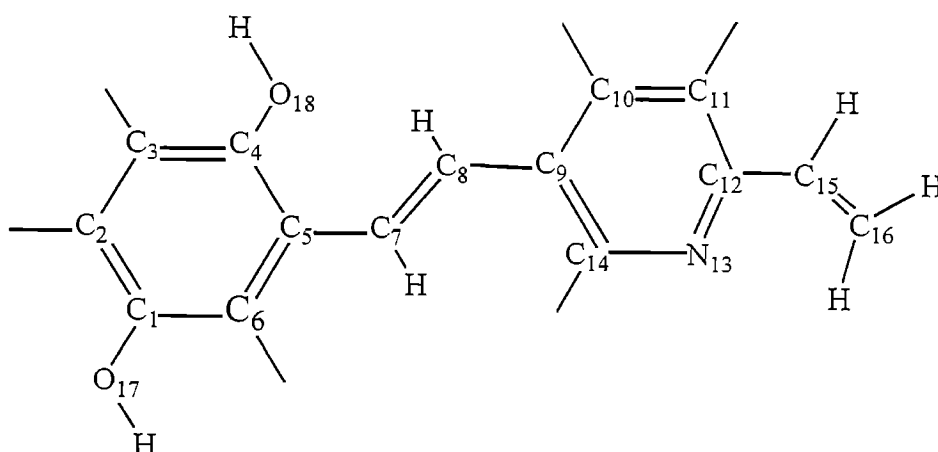
3-21G basis set

F-substitution	unprotonated	protonated	difference
none pl	4.72	4.33	-0.39
none npl	5.00	4.68	-0.32
			+0.07
C10-F pl	4.75	4.36	-0.38
C10-F npl	4.91	4.65	-0.26
			+0.12
C8-F pl	4.78	4.30	-0.48
C8-F npl	5.27	4.72	-0.54
C8-F npl (HB)	5.13	4.70	-0.43

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



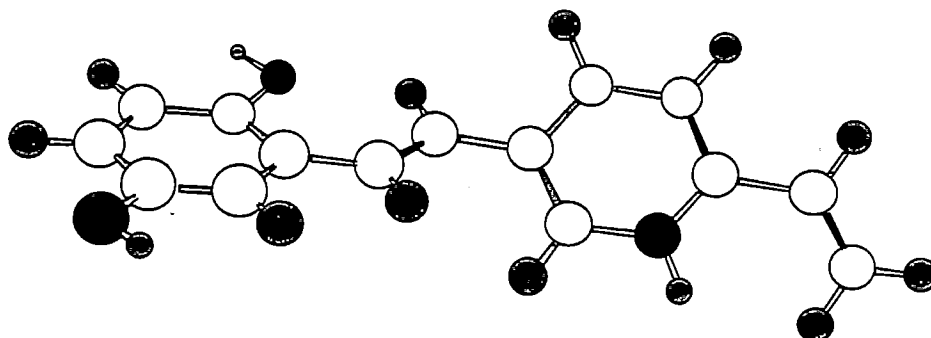
other substitutions - (all nonplanar)

none	5.00	4.68	-0.32
C10-F	4.91	4.65	-0.26
C10-CH ₃	5.15	4.78	-0.37
C10-NO ₂	4.33	3.75	-0.58
C10-NH ₂	5.96	5.65	-0.30
none	5.00	4.68	-0.32
C8-F	5.13	4.70	-0.43
C8-NO ₂	4.42	4.26	-0.16

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

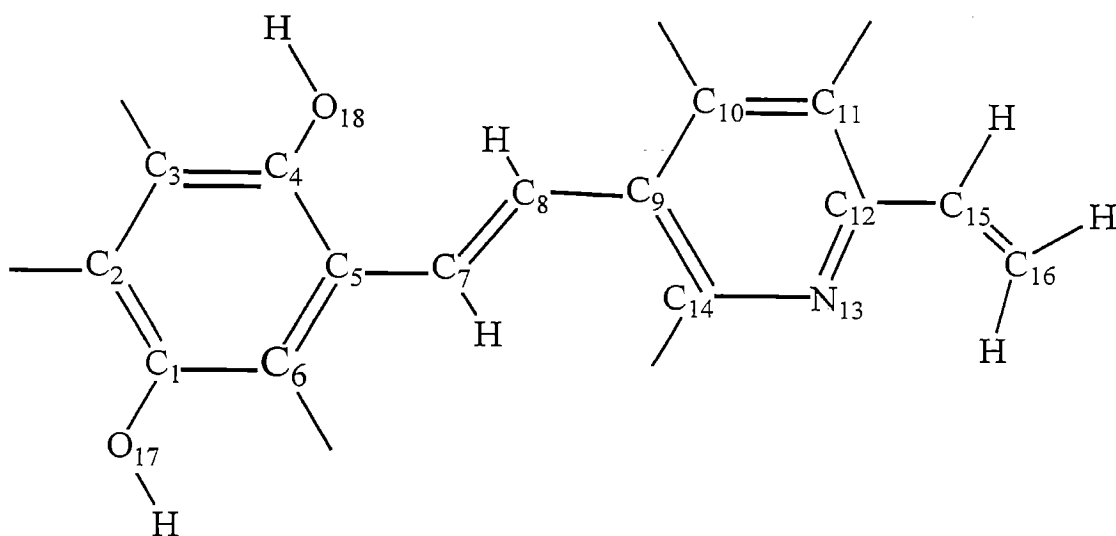
for C8, F raises drop, NO₂ decreases drop

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



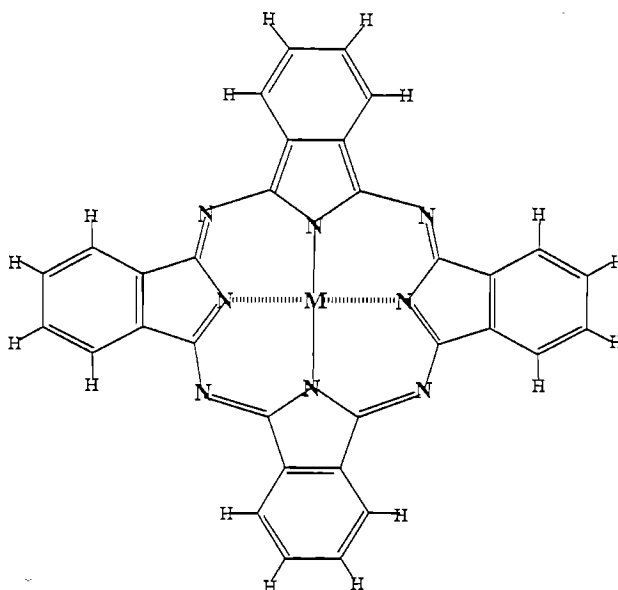
CONCLUSIONS

- calculations support 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



- 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

A 1996 paper (Toshima & Tominaga, Bull. Chem. Soc. Jpn. 1996, 69, 2111) had found interesting redox properties of complexes between several transition metals and phthalocyanine (pc) in thin films.



When $M = \text{Cu}, \text{Ni}$, reversible electrochromism
 $\text{Zn}, \text{Co}, \text{Fe}$ 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.

M	Electronegativity	reversible?
Fe	1.7	no
Co	1.7	no
Ni	1.8	yes
Cu	1.8	yes
Zn	1.6	no

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

ADF	less standard DFT, does not use “basis sets” as such
-----	--

Binding Energies of Metals to Pc^a, eV

	FePc	CoPc	NiPc	CuPc	ZnPc	MgPc
B3LYP (A) ^o	-4.39	-9.38	-7.81	-6.03	-5.12	
HF (A)	1.67		-6.11	-3.16		
MP2 (A)			-8.35			
B3LYP (B) ^c	-7.87	-8.44	-10.21	-10.06	-7.56	-8.07
HF (B)	-6.74	-4.79	-9.04	-5.51	-5.66	
MP2 (B)	-11.25	-10.95	-13.43	-8.87	-9.57	
ADF	-9.81	-10.49	-9.90	-6.96	-5.66	-8.14

^anegative quantity indicates favorable binding

^bLanL2DZ ^c6-31G*

HF probably useless; correlation very important

MP2: Ni > Fe > Co > Zn > Cu

B3LYP: Ni ~ Cu > Co > Fe ~ Zn

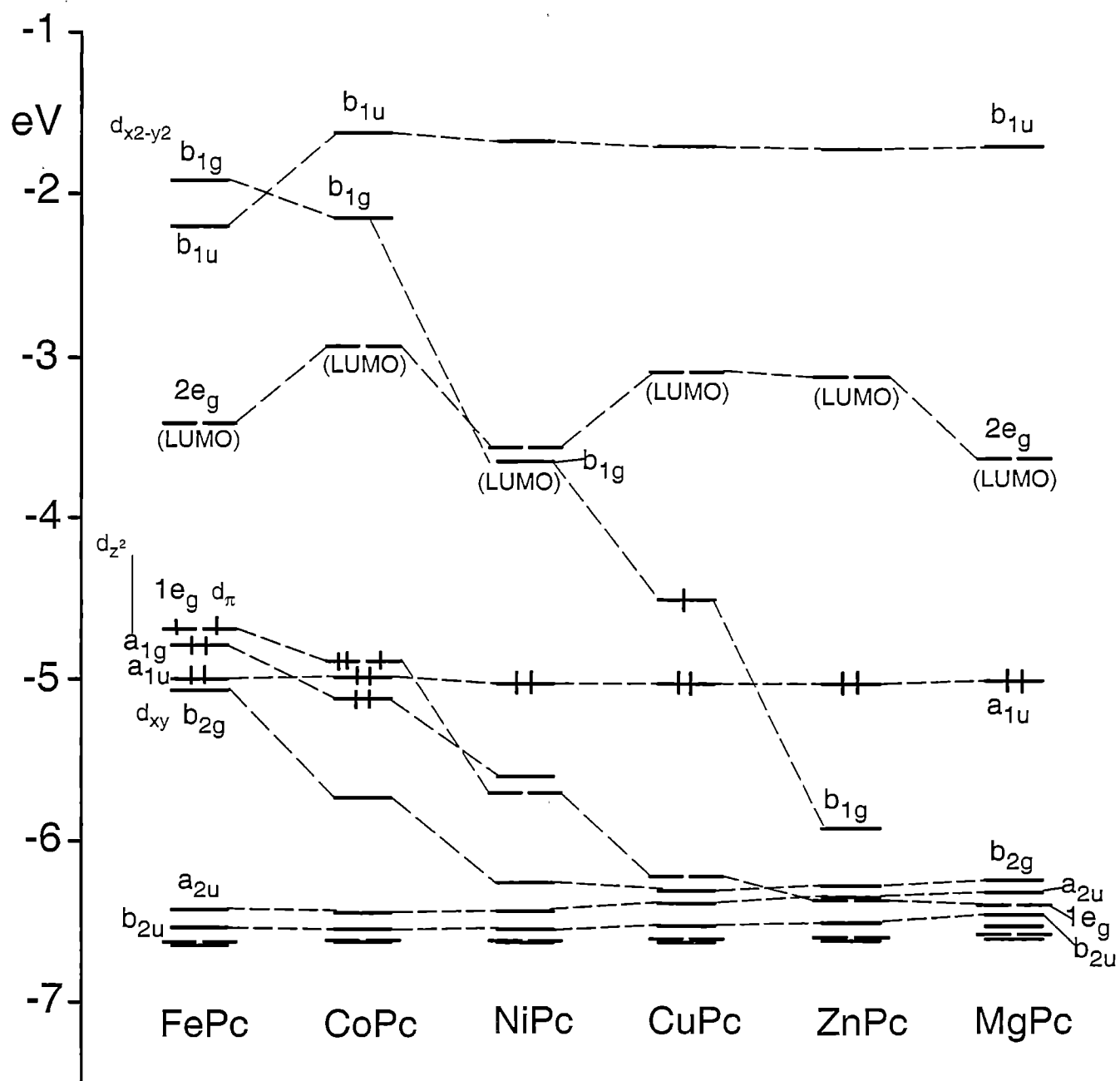
B3LYP makes Cu a better binder

ADF: Co > Ni ~ Fe > Cu > Zn

Co,Ni,Fe > Cu,Zn

binding energies are in the 5 – 10 eV range

MO DIAGRAM



IONIZATION POTENTIALS, eV

	Pc	FePc	CoPc	NiPc	CuPc	ZnPc	MgPc
B3LYP (A)		3.83	7.58	6.08	7.65	6.00	
HF (A)				4.54			
MP2 (A)				7.31			
B3LYP (B)	6.93	6.02	6.24	6.08	7.30	6.06	5.97
HF (B)		4.50	4.72	4.54	4.66	4.54	
MP2 (B)							
ADF	7.02	6.46	6.47	6.56	6.51	6.56	6.52
ADF (T)	6.98	6.49	6.47	6.51	6.51	6.52	6.48

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

Fe	Co	Ni	Cu	Zn	Mg
1.38	1.96	1.47	1.42	1.91	1.38
$1e_g \rightarrow 2e_g$	$1e_g \rightarrow 2e_g$	$a_{1u} \rightarrow b_{1g}$	$b_{1g} \rightarrow 2e_g$	$a_{1u} \rightarrow 2e_g$	$a_{1u} \rightarrow 2e_g$

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 IPs.

Charge assigned to metal atom

	FePc	CoPc	NiPc	CuPc	ZnPc	MgPc
B3LYP (A)	0.27	0.60	0.55	0.73	1.15	
HF (A)	0.45	0.57	1.02			
MP2 (A)			0.63			
B3LYP (B)	1.20	0.71	0.80	0.88	0.94	1.07
HF (B)	1.46	0.75	1.28	0.83	1.34	
MP2 (B)	1.23	0.66	0.90	0.74	1.04	
ADF	0.71	0.59	0.50	0.65	0.64	0.77

B3LYP: $Zn > Cu > Co \sim Ni$
 but Fe very sensitive to basis set

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

ADF: $Zn \sim Cu > Co > Ni$

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

ELECTRON AFFINITIES, EV

	Fe	Co	Ni	Cu	Zn	Mg
MPc	-2.92	-3.19	-2.14	-1.74	-2.23	-2.16

electrons are drawn to each species (negative values)

Cu and Ni the weakest, with $\text{Cu} < \text{Ni}$

among others, $\text{Zn} < \text{Fe} < \text{Co}$

this pattern generally consistent with electronegativities:

$\text{Zn} < \text{Fe} \sim \text{Co} < \text{Cu} \sim \text{Ni}$

in that Ni and Cu have weakest pull for an electron,

but Zn out of place here.

MORE DETAIL OF METAL CHARGE

orbital	Fe	Co	Ni	Cu	Zn	Mg
3d	6.59	7.63	8.61	9.50	10.0	0.42 (3d)
4s	0.42	0.41	0.42	0.39	0.55	0.36 (3s)
4p	0.29	0.37	0.48	0.46	0.81	0.45 (3p)
Q_M	0.71	0.59	0.50	0.65	0.64	0.77

total (positive) charge: $Ni < Co < Zn \sim Cu < Fe$

orbital populations (invert charge)

3d shell: $Zn < Cu < Ni < Co < Fe$

4s shell: $Zn < Fe \sim Co \sim Ni < Cu$

4p shell: $Zn < Ni \sim Cu < Co < Fe$

none of these show expt behavior

ATOMIC CHARGES AROUND THE PC SYSTEM

	M = Fe	M = Co	M = Ni	M = Cu	M = Zn	M = Mg
Q_M	0.71	0.59	0.50	0.65	0.64	0.87
Q_{N1}	-0.53	-0.50	-0.48	-0.51	-0.49	-0.57
Q_{N2}	-0.33	-0.33	-0.33	-0.33	-0.33	-0.33
Q_{C1}	0.32	0.32	0.32	0.32	0.32	0.33
Q_{C2}	0.09	0.09	0.09	0.09	0.08	0.08
Q_{C3}	0.14	0.14	0.14	0.14	0.14	0.13
Q_{C4}	0.17	0.17	0.17	0.17	0.17	0.17
Q_{H1}	-0.18	-0.18	-0.19	-0.18	-0.18	-0.18
Q_{H2}	-0.18	-0.18	-0.18	-0.18	-0.18	-0.18

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:

orbital	Fe	Co	Ni	Cu	Zn	Mg
3d	6.59	7.64	8.61	9.50	10.0	0.40
4s	0.40	0.36	0.40	0.37	0.54	0.31
4p	0.27	0.39	0.47	0.45	0.80	0.40
Q_M	0.74	0.62	0.52	0.68	0.65	0.90

total (positive) charge: $Ni < Co < Zn < Cu < Fe$

orbital populations (invert charge)

3d shell: $Zn < Cu < Ni < Co < Fe$

4s shell: $Zn < Fe \sim Ni < Co \sim Cu$

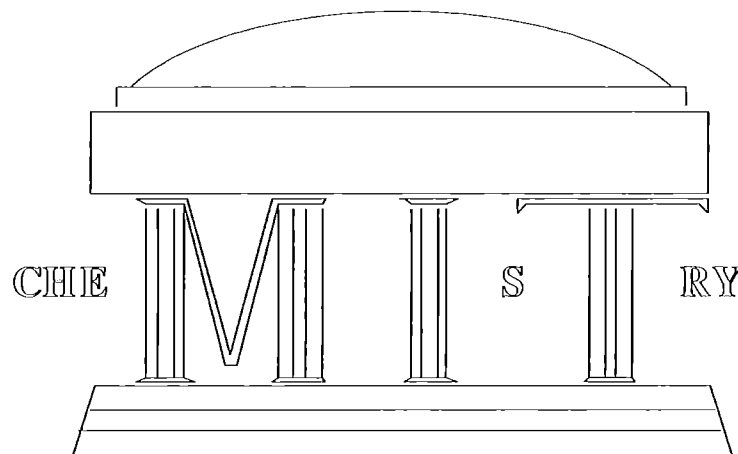
4p shell: $Zn < Ni \sim Cu < Co < Fe$

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

Timothy M. Swager



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)

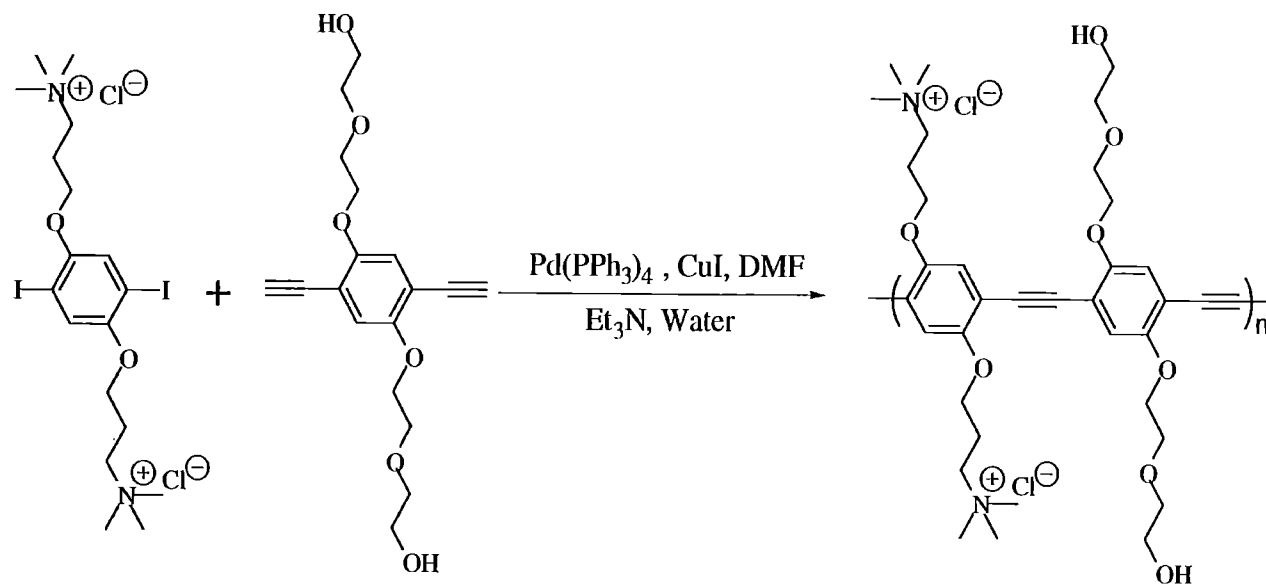
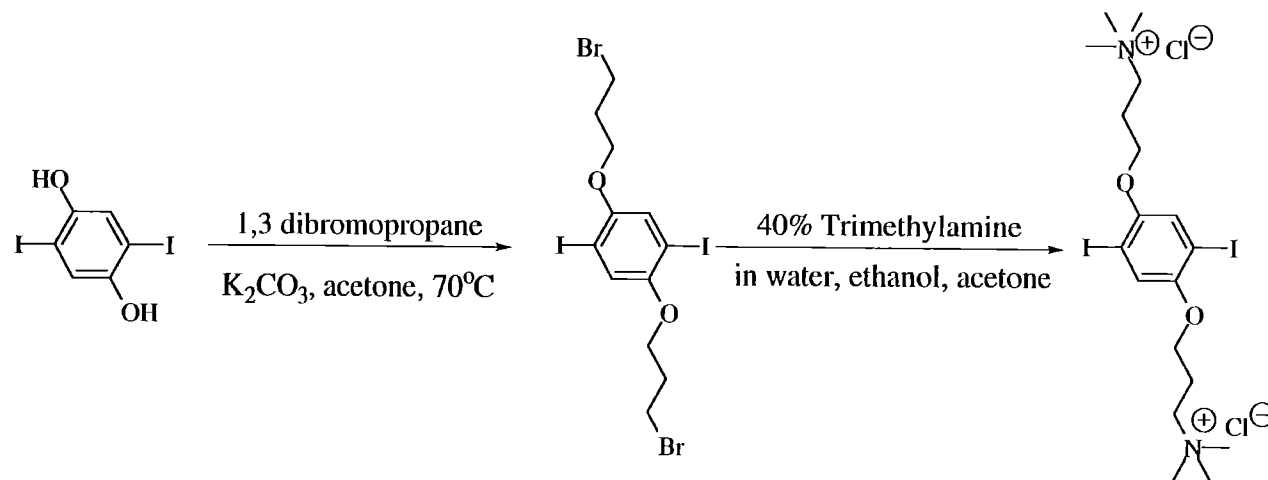
D. Tyler McQuade (NIH PD fellow)

Dr. Zhengguo Zhu (Funded by DARPA)

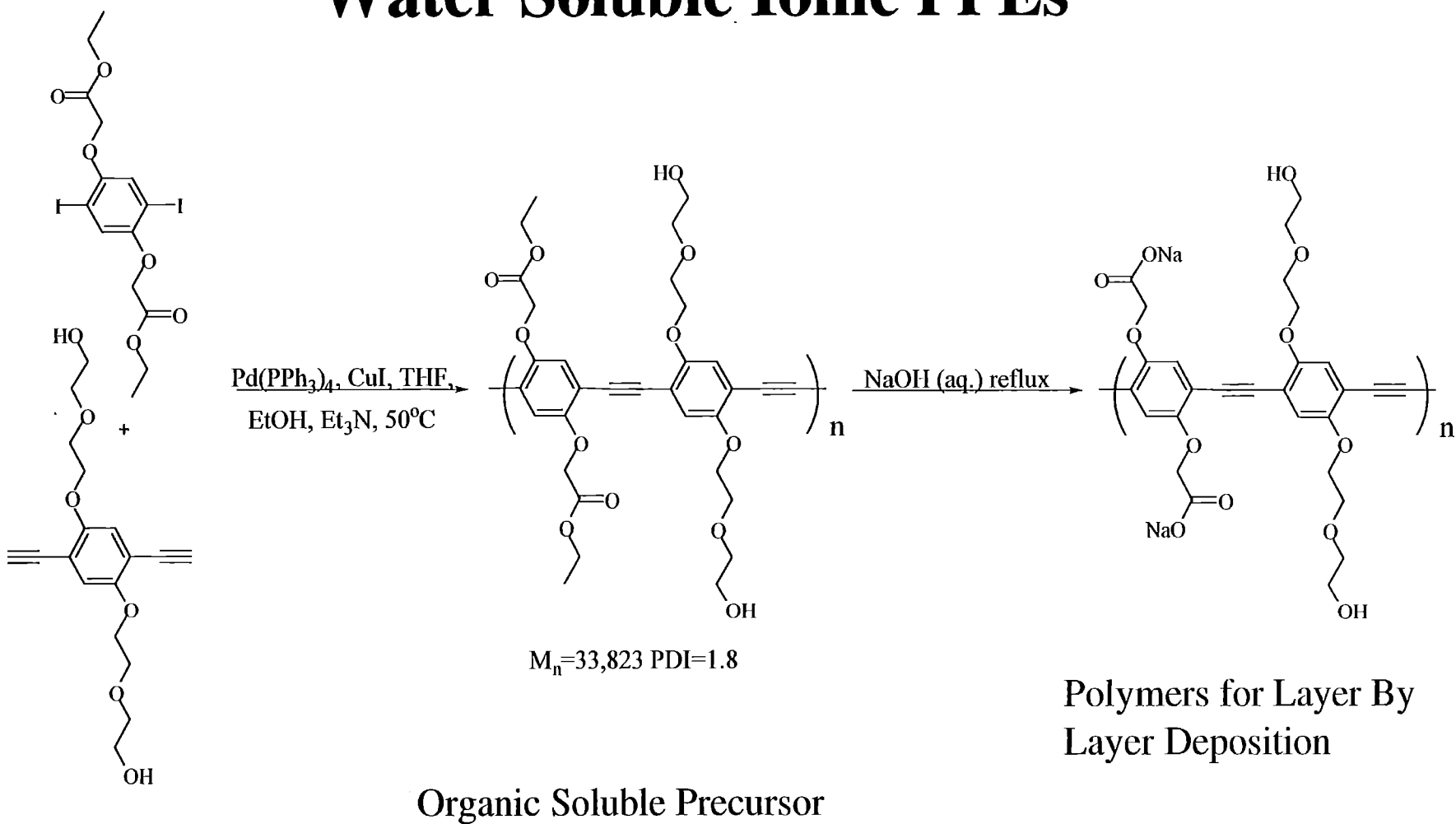
TOPS-MURI, T.M. Swager, MIT



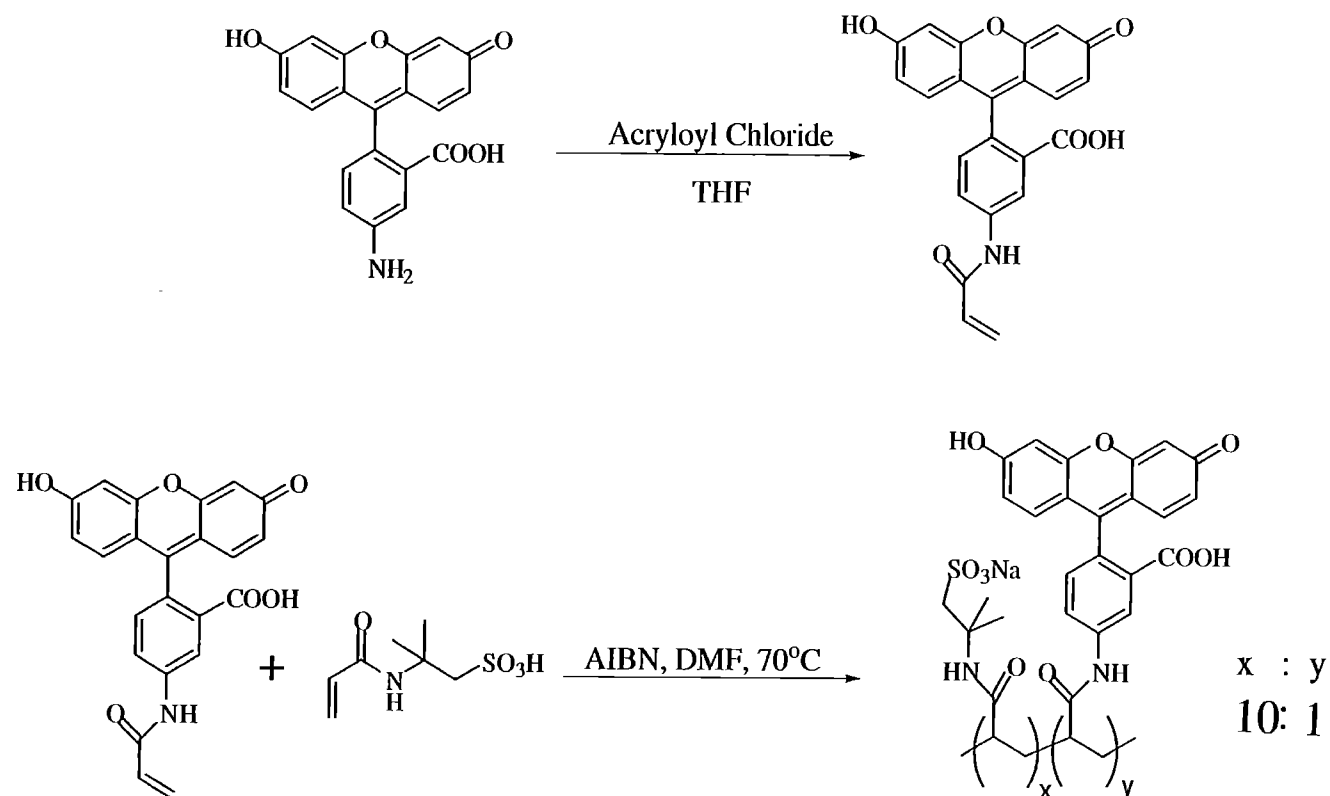
Cationic PPEs



Water Soluble Ionic PPEs



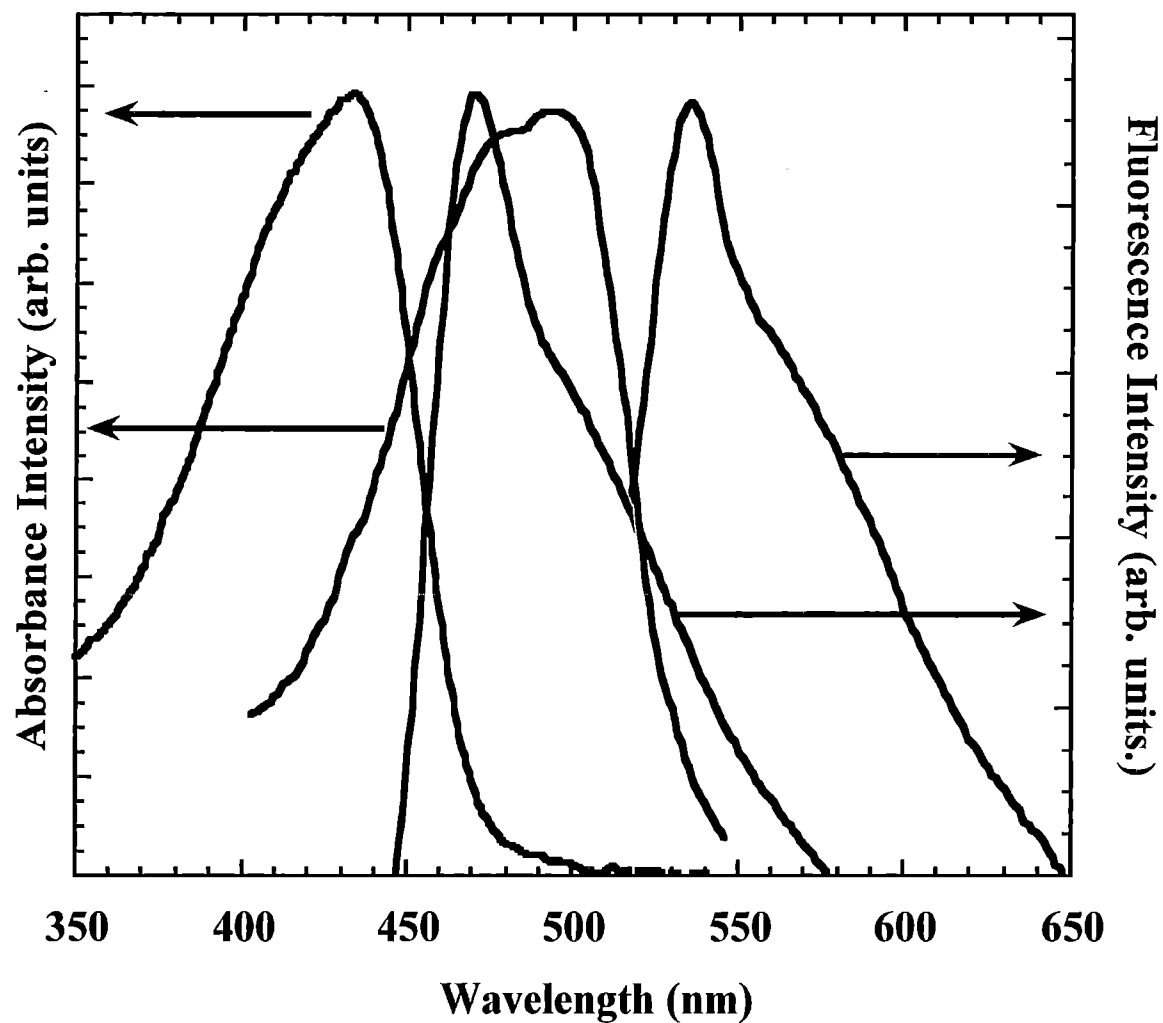
Formation of a pH Sensitive Polymeric Dye



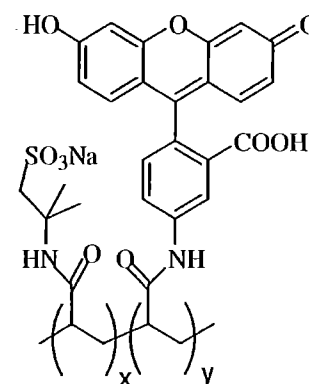
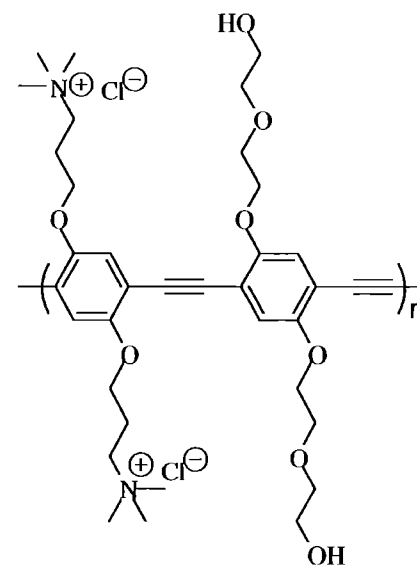
Fluoresceinamine
Emissive at High pH



Emission/Absorption of Donor and Acceptors

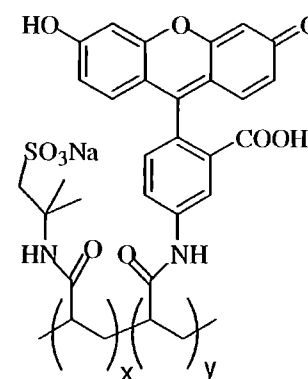
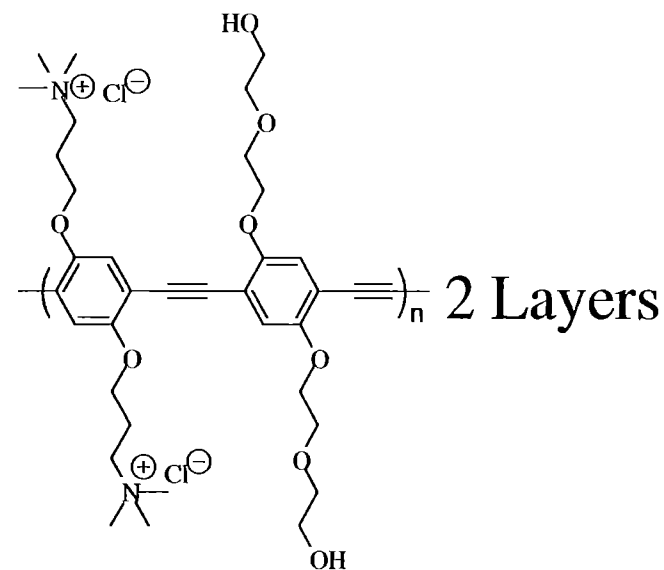
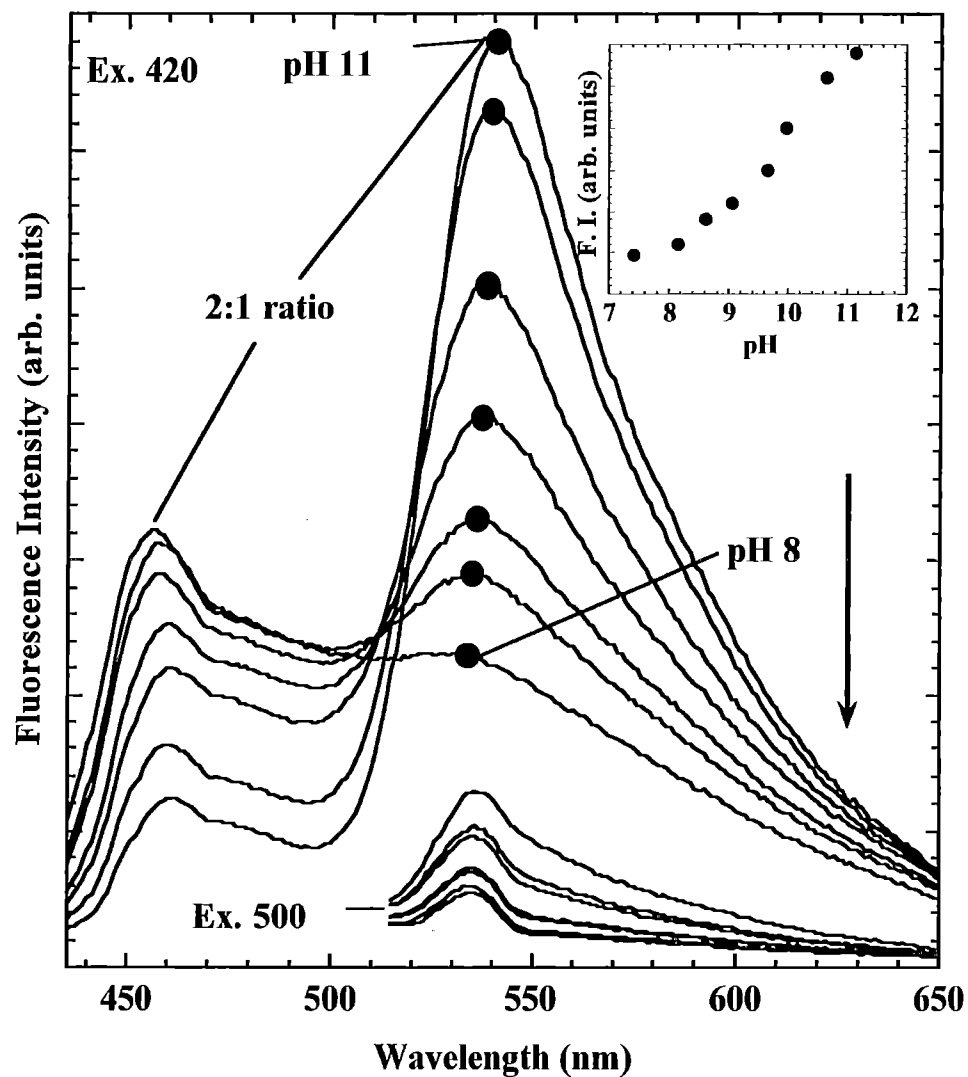


Fluorescence Intensity (arb. units.)



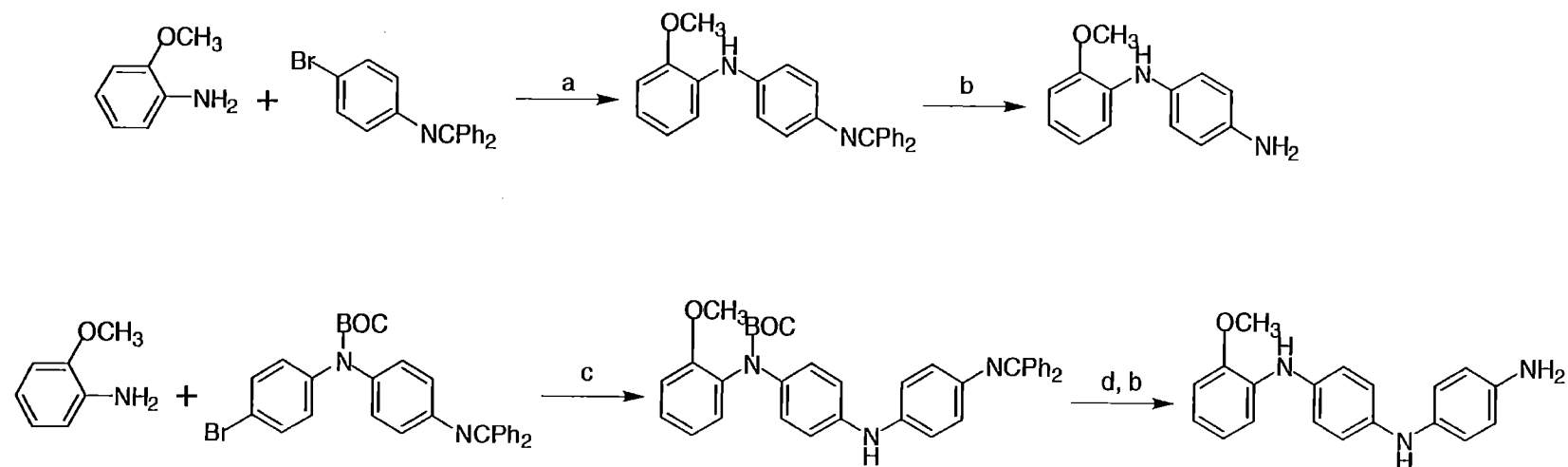
pH Response of Three-Layer Films

Get a Lower QY of the Polymer



Regiospecific Synthesis of Aniline Copolymers

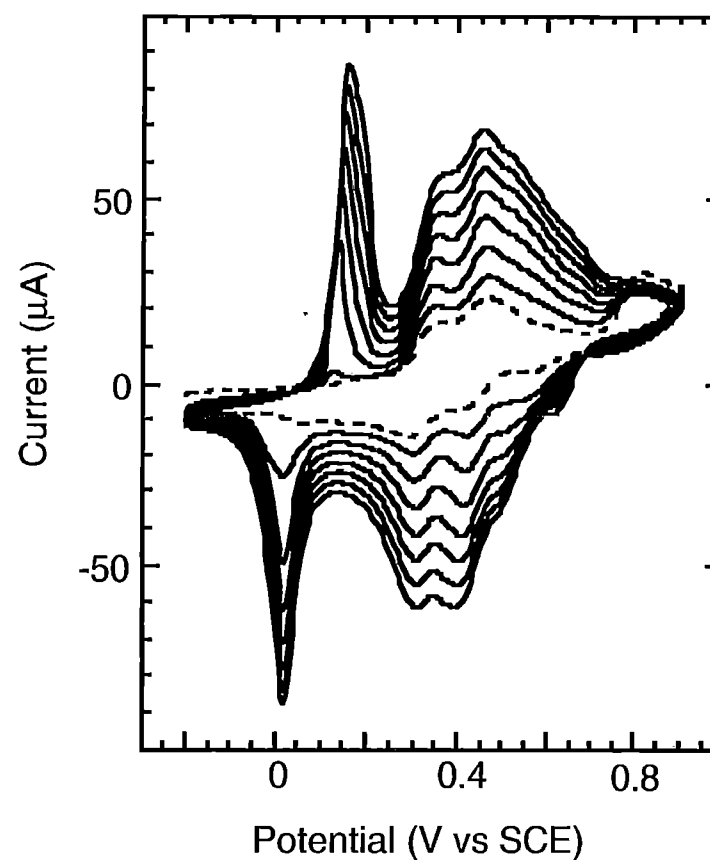
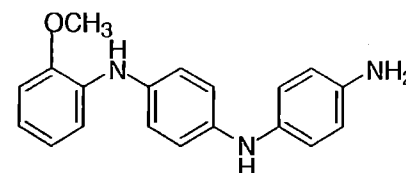
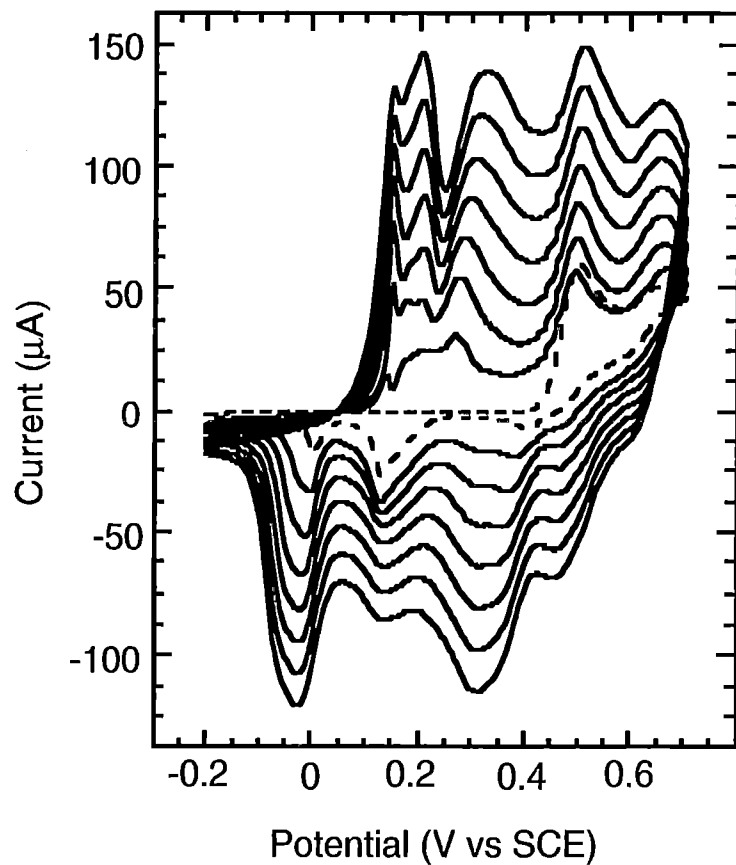
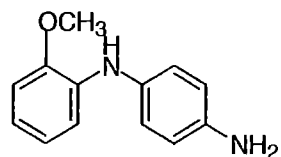
By Using Step-Wise Coupling
Precise More Structures can be Created



^a(a) Pd_2dba_3 , *rac*-BINAP, NaOtBu , THF, reflux; (b) 10% Pd/C, NH_4HCO_2 , THF, EtOH, 60°C ; (c) Pd_2dba_3 , *rac*-BINAP, NaOtBu , THF, reflux; (d) 160°C



Electro-deposition of Dimer and Trimers

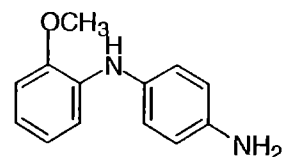
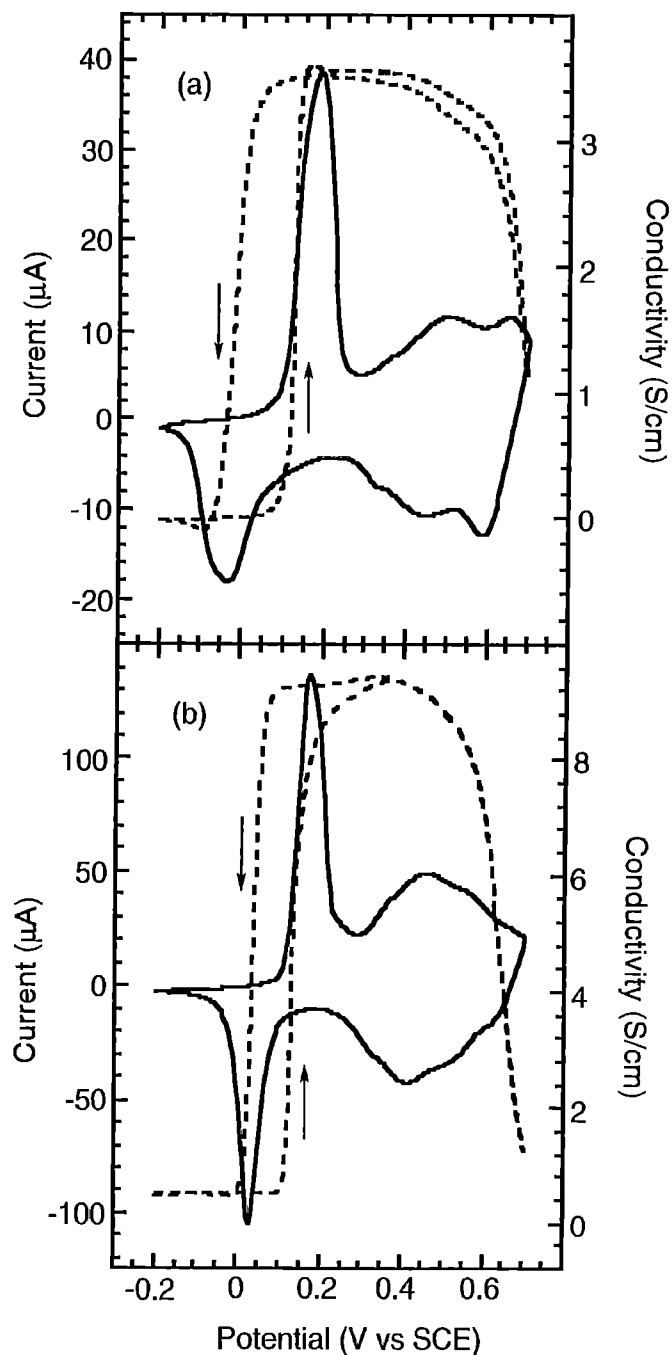


Dotted Line Indicates Initial Scan

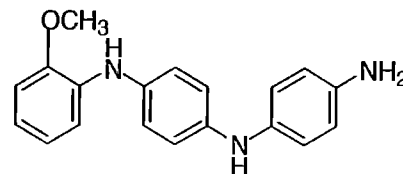
TOPS-MURI, T.M. Swager, MIT



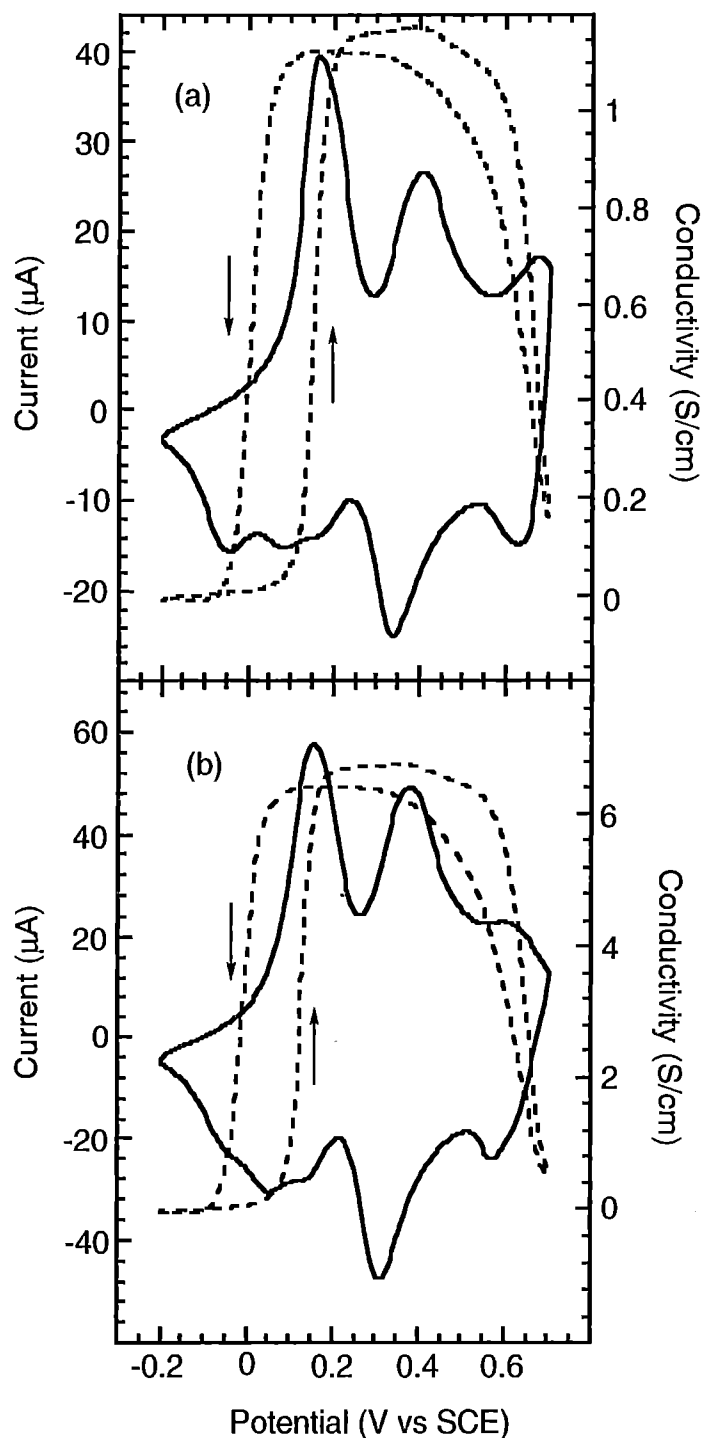
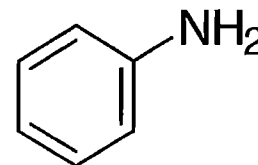
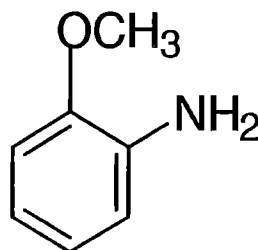
CV and Conductivity Profiles of Dimer and Trimer



Sharp CVs



Random Copolymers of Methoxy Aniline and Aniline

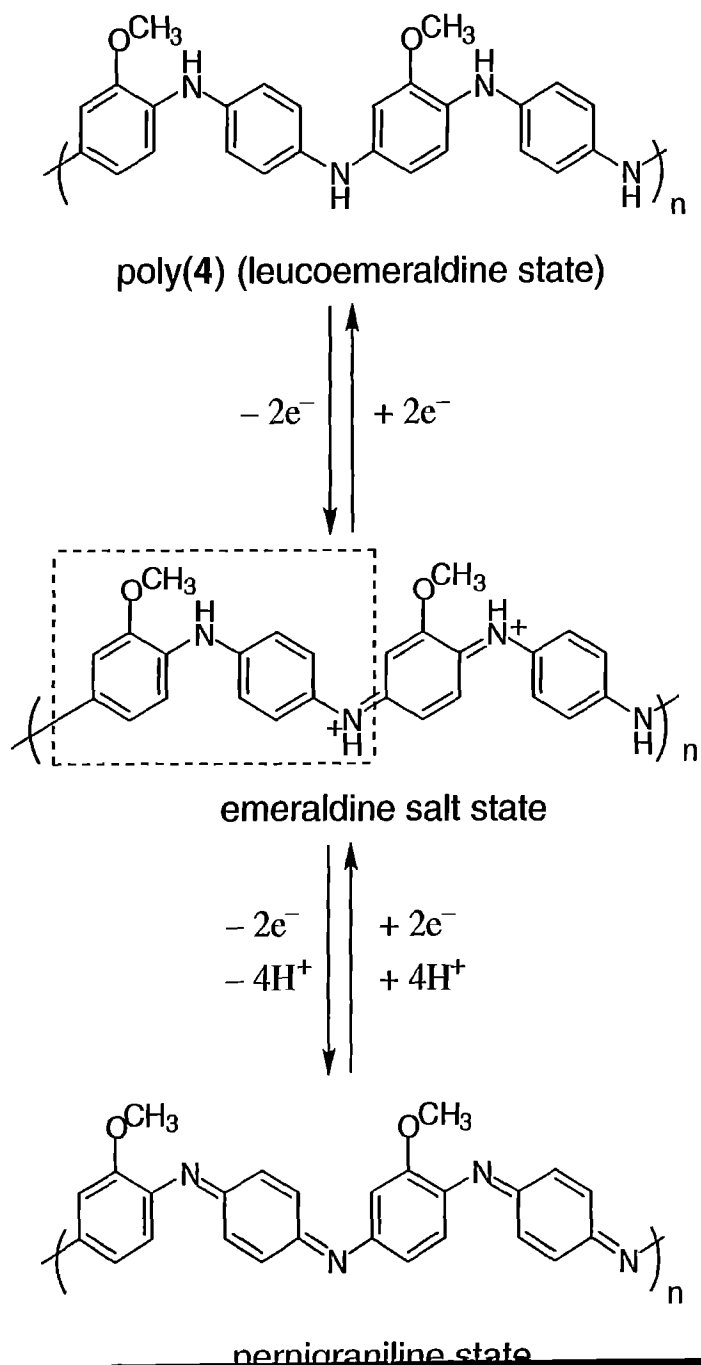


(a) Equal Amounts
(b) 2:1 (Aniline Excess)

Broader Electrochemistry
Slightly Lower Conductivity



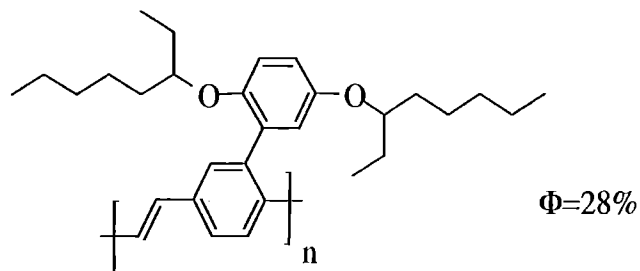
Resonance Structures and The Charged States of Co-Polyanilines



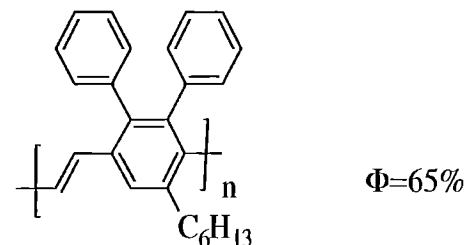
An Organic Chemist's View



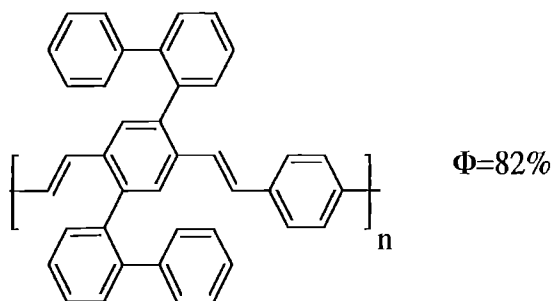
Examples of Highly Luminescent PPVs



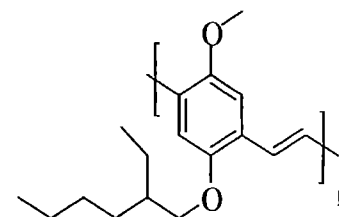
Johansson, D. M.; Srdanov, G.; Yu, G.; Theander, M.; Inganäs, O.; Andersson, M. R. *Macromolecules* **2000**, 33, 2525-2529.



Hsieh, B. R.; Yu, Y.; Forsythe, E. W.; Schaaf, G. M.; Feld, W. A. *J. Am. Chem. Soc.* **1998**, 120, 231-232.



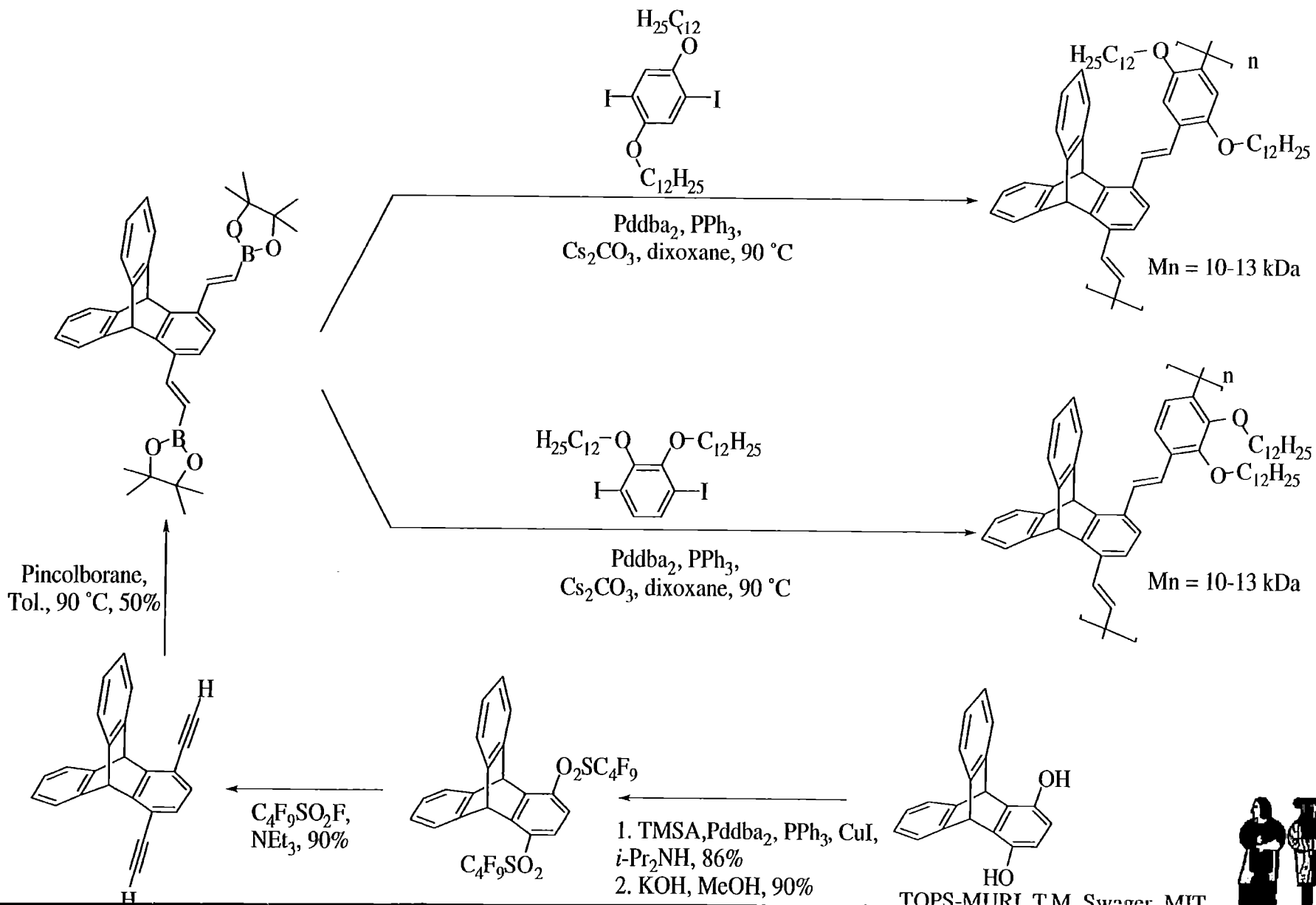
Peng, Z.; Zhang, J.; Xu, B. *Macromolecules* **1999**, 32, 5162-5164.



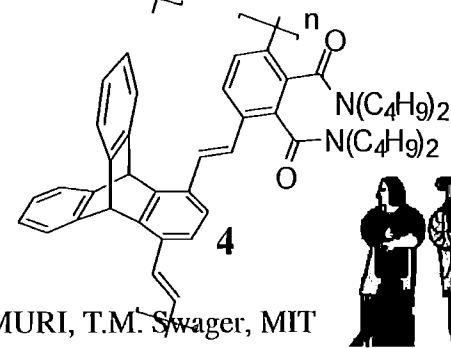
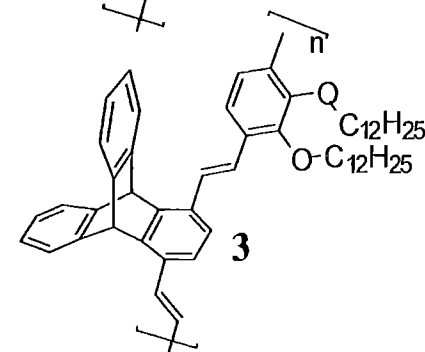
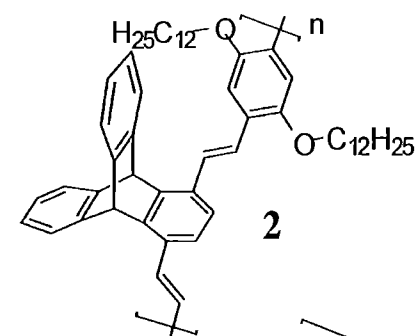
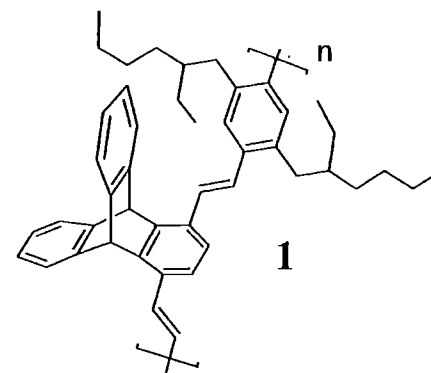
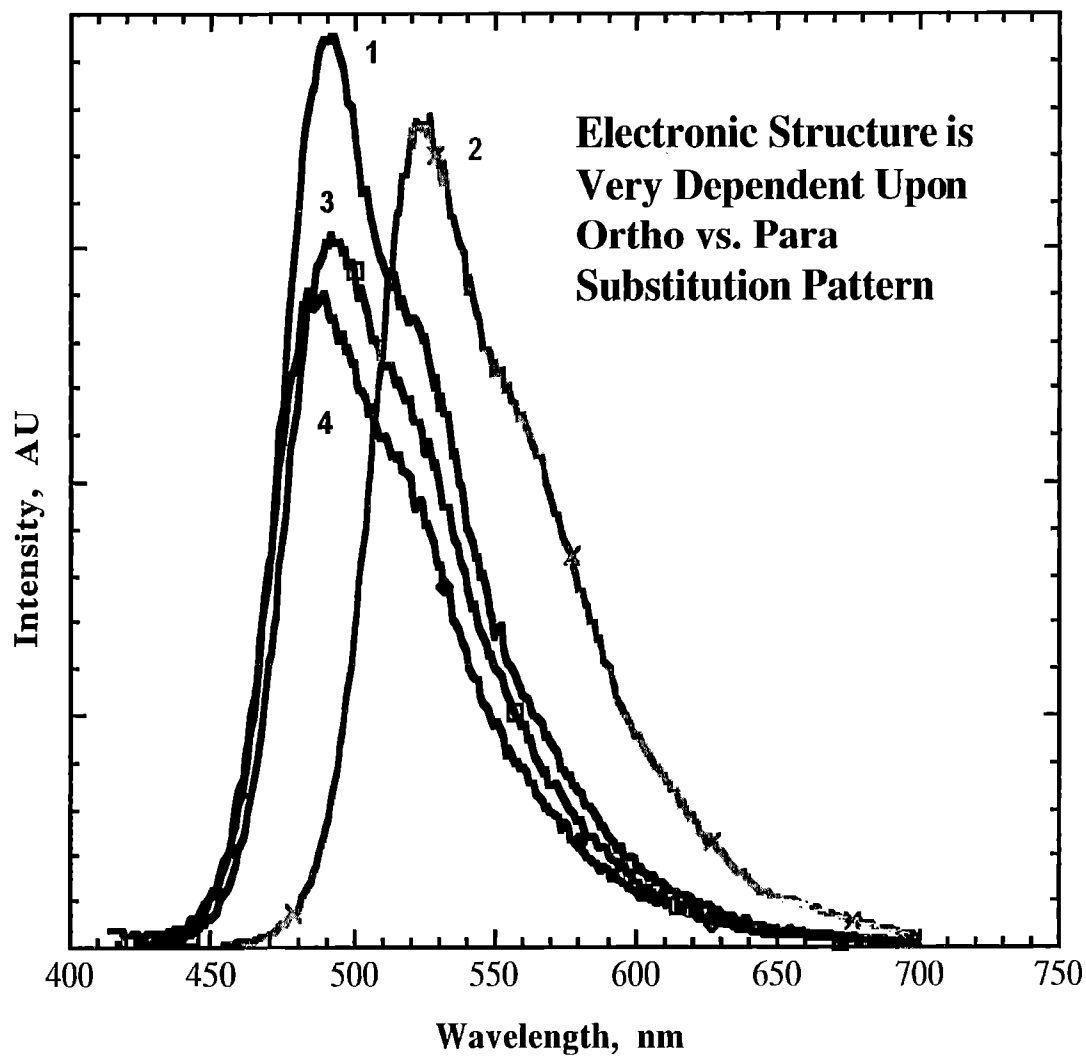
Braun, D.; Heeger, A. J.; *Appl. Phys. Lett.* **1991**, 58, 1982



PPVs with Alternate Triptycene Units



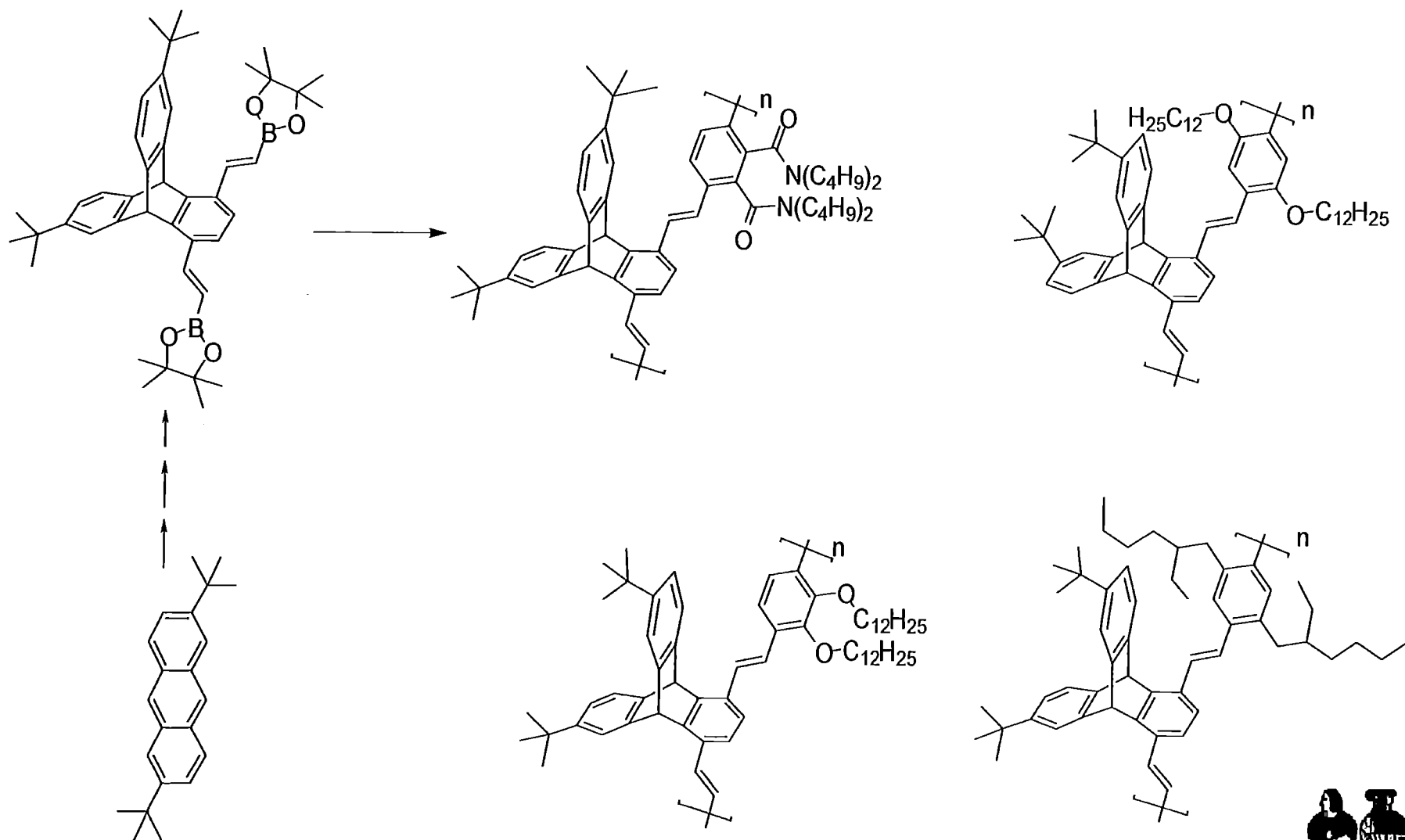
Emission Spectra



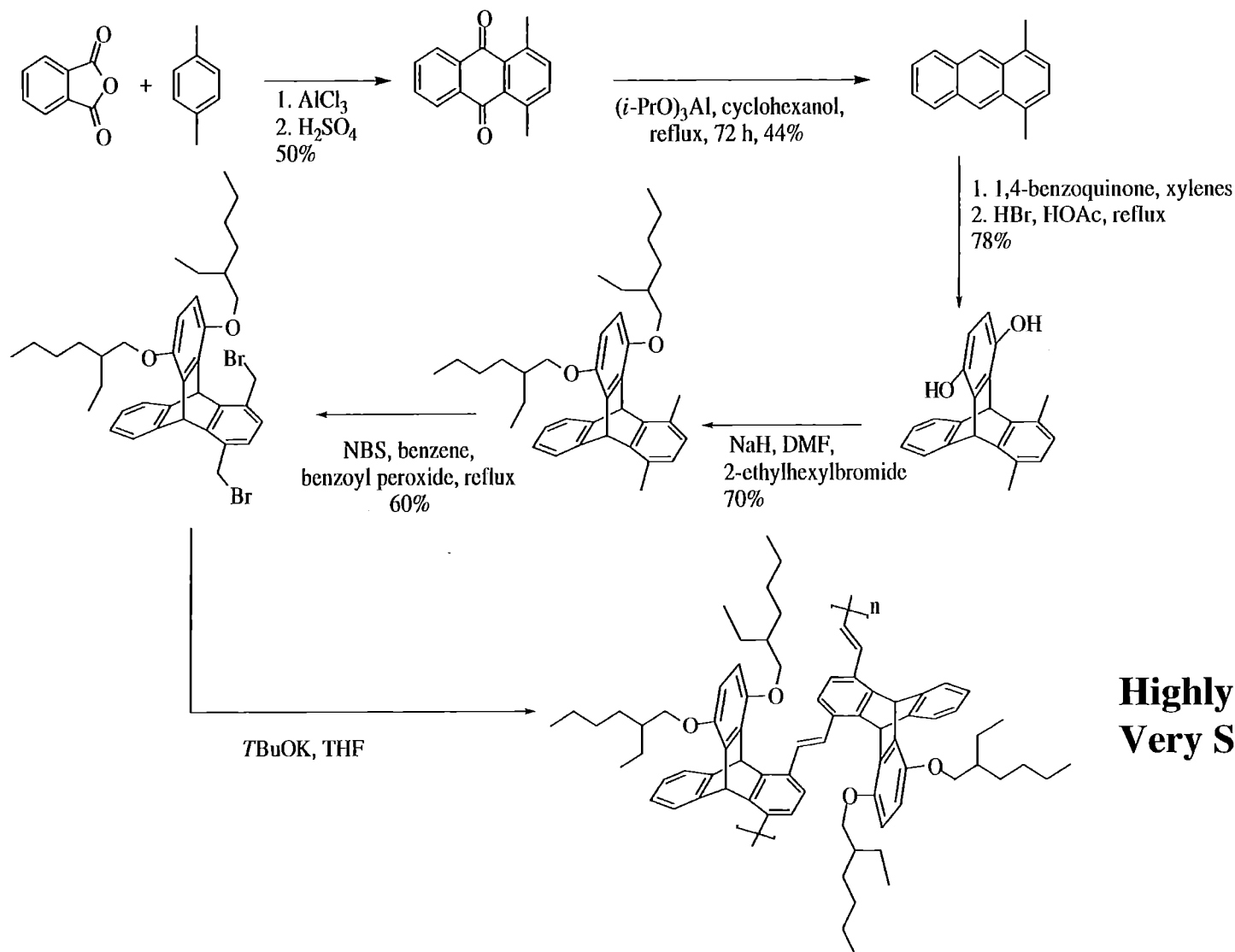
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PPVs with Greater Larger Interchain Distances



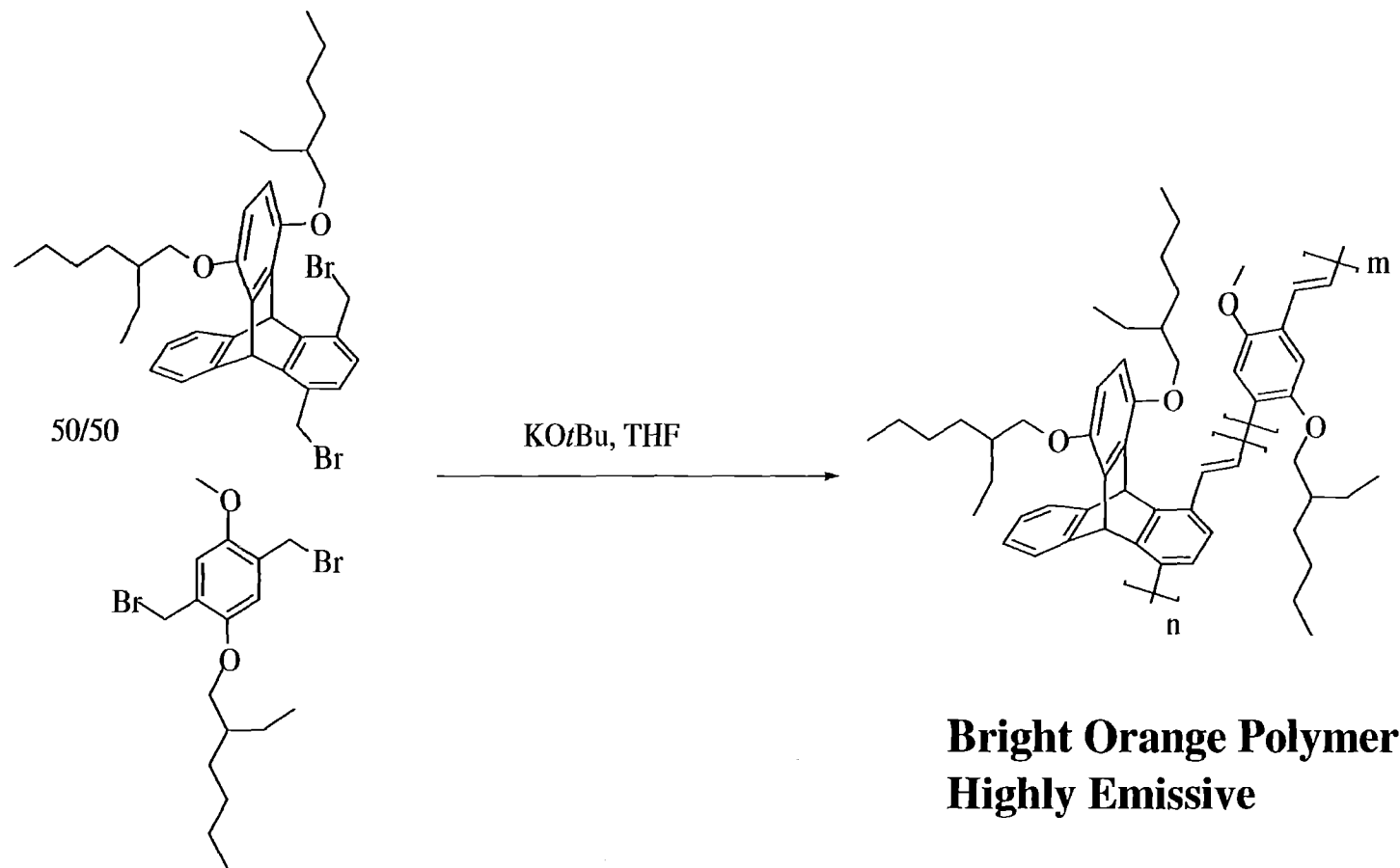
Synthesis of Triptycene PPV



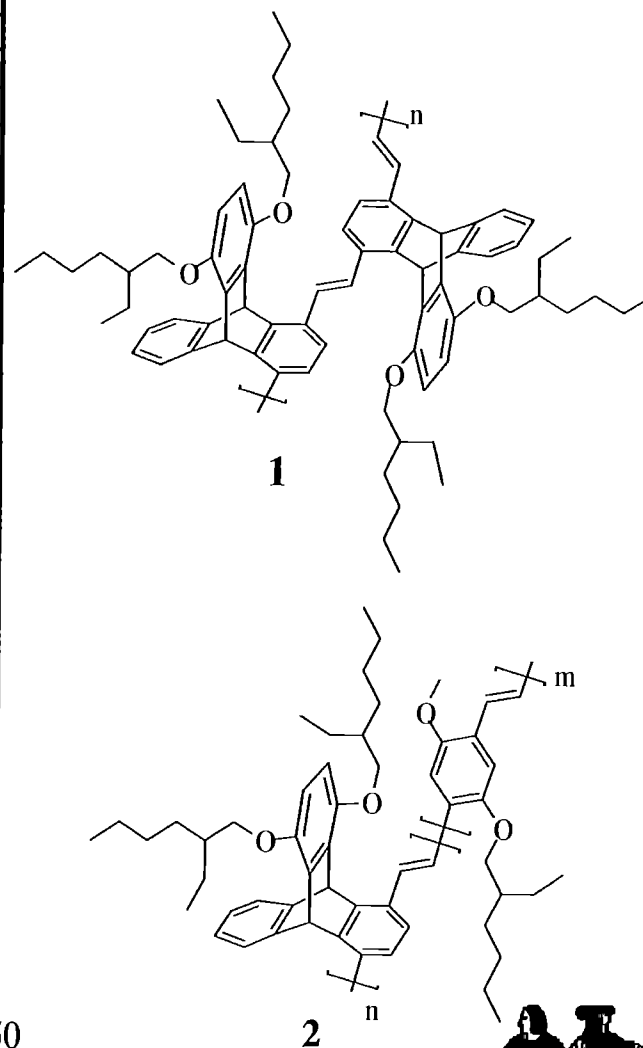
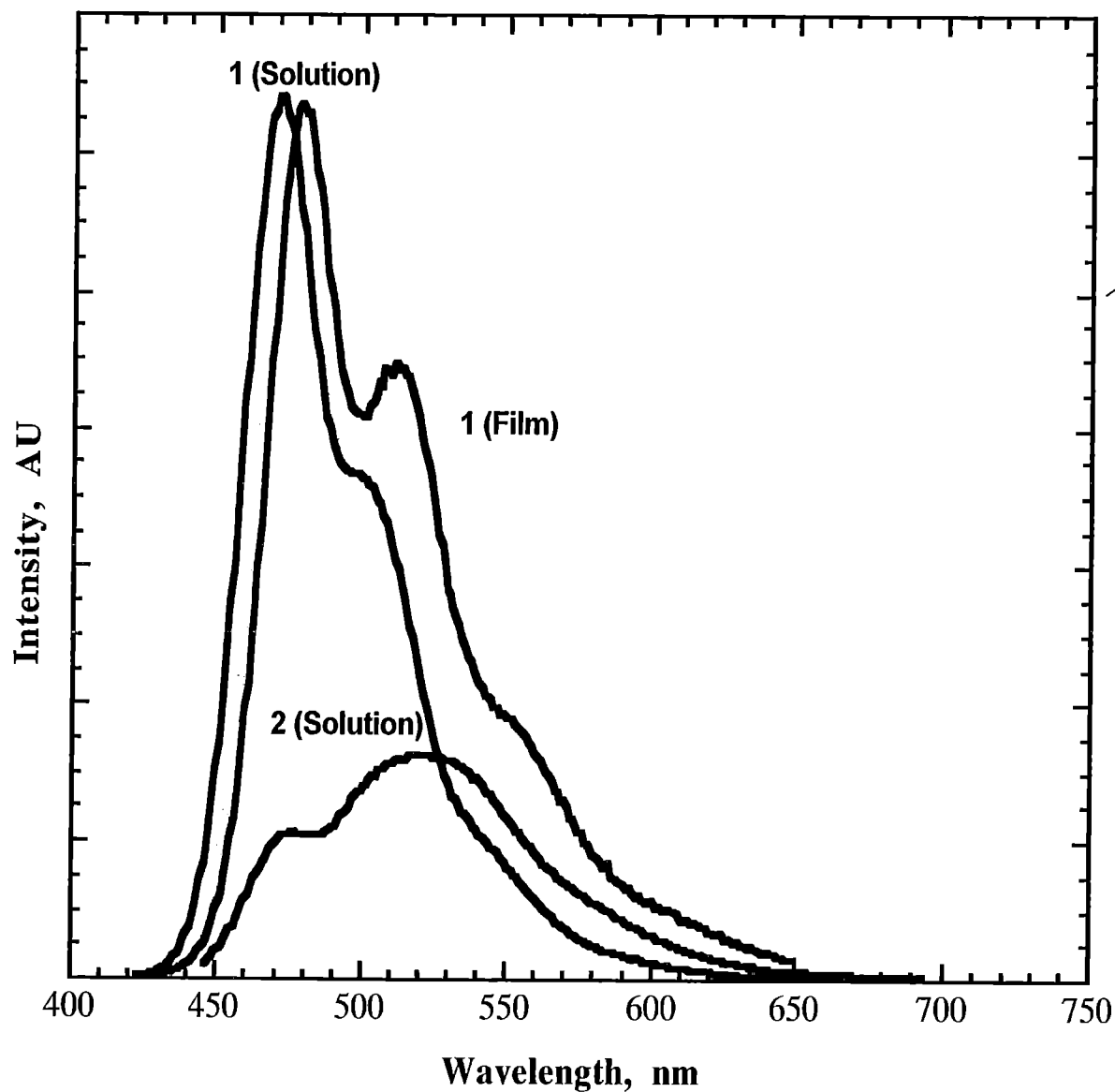
Highly Emissive
Very Stable



Random Triptycene/MEH PPV Copolymers



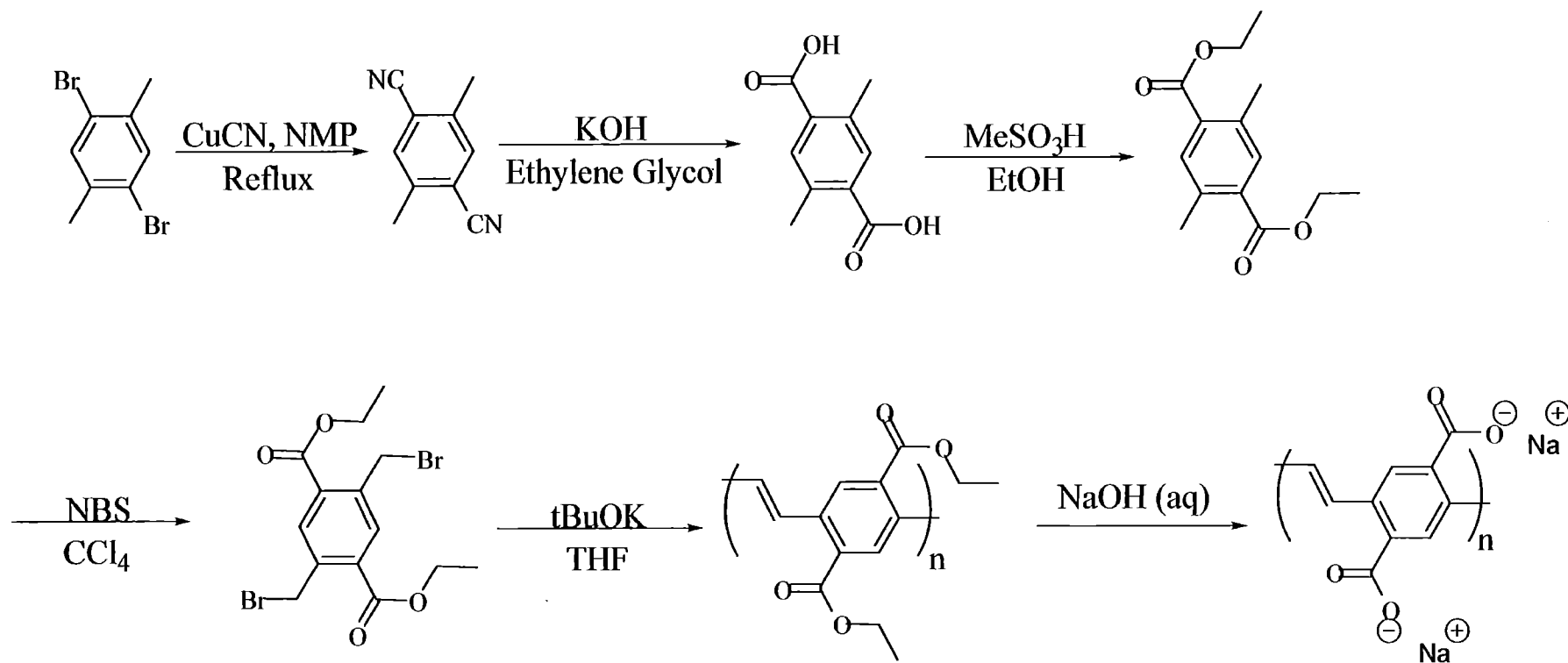
Emission of Triptycene PPV and Copolymer



TOPS-MURI, T.M. Swager, MIT



New Water Soluble PPVs



Carboxylates: Electron Withdrawing
Excellent for Functionalization



**ROUTING AND ACTION
MEMORANDUM**

ROUTING

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(Kiserow, Douglas)
Report is ATTACHED for review.

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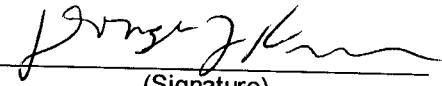
TITLE: Thermotropic Chiral-Nematic Poly(P-Phenylene)s as a Paradigm of Helically Stacked pi-Conjugated Systems

ACTION TAKEN BY DIVISION

☒ Report has been reviewed for technical sufficiency and ☒ IS ☐ IS NOT satisfactory.

☒ Material has been given an OPSEC review and it has been determined to be nonsensitive and, except for manuscripts and progress reports, suitable for public release.

☐ Further action requested:

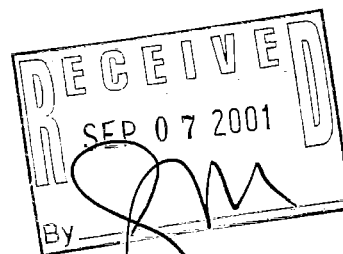

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Thermotropic Chiral–Nematic Poly(*p*-phenylene)s as a Paradigm of Helically Stacked π -Conjugated Systems

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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, visible, 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.¹ In particular, feasibility has been demonstrated with amorphous or crystalline conjugated polymers for light-emitting diodes,² organic lasers,³ thin film transistors,⁴ photoconductors,⁵ and

nonlinear optical devices.⁶ 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 π -conjugated segments has been shown to enhance electrical conductivity by orders of magnitude⁷ and to induce linearly polarized light emission.⁸ 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 present⁹ 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,¹⁰ circularly polarized luminescence,¹¹ and electrochromism inherent to π -con-

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^{||} Laboratory for Laser Energetics.

(1) Salaneck, W. R.; Lundström, I.; Rånby, B., Eds. *Conjugated Polymers and Related Materials*; Oxford University Press: Oxford, 1993.

(2) Burroughes, J. H.; Bradley, D. D. C.; Brown, A. R.; Marks, R. N.; Mackay, K.; Friend, R. H.; Burn, P. L.; Kraft, A.; Holmes, A. B. *Nature* 1990, 347, 539.

(3) Tessler, N.; Denton, G. J.; Friend, R. H. *Nature* 1996, 382, 695.

(4) Horowitz, G. *Adv. Mater.* 1998, 10, 365.

(5) Blei, H. In *Organic Materials for Photonics*; Zerbi, G., Ed.; Elsevier: Amsterdam, 1993; p 77.

(6) Marder, S. R.; Kippelen, B.; Jen, A. K.-Y.; Peyghambarian, N. *Nature* 1997, 388, 845.

(7) Akagi, K.; Shirakawa, H. *Macromol. Symp.* 1996, 104, 137.

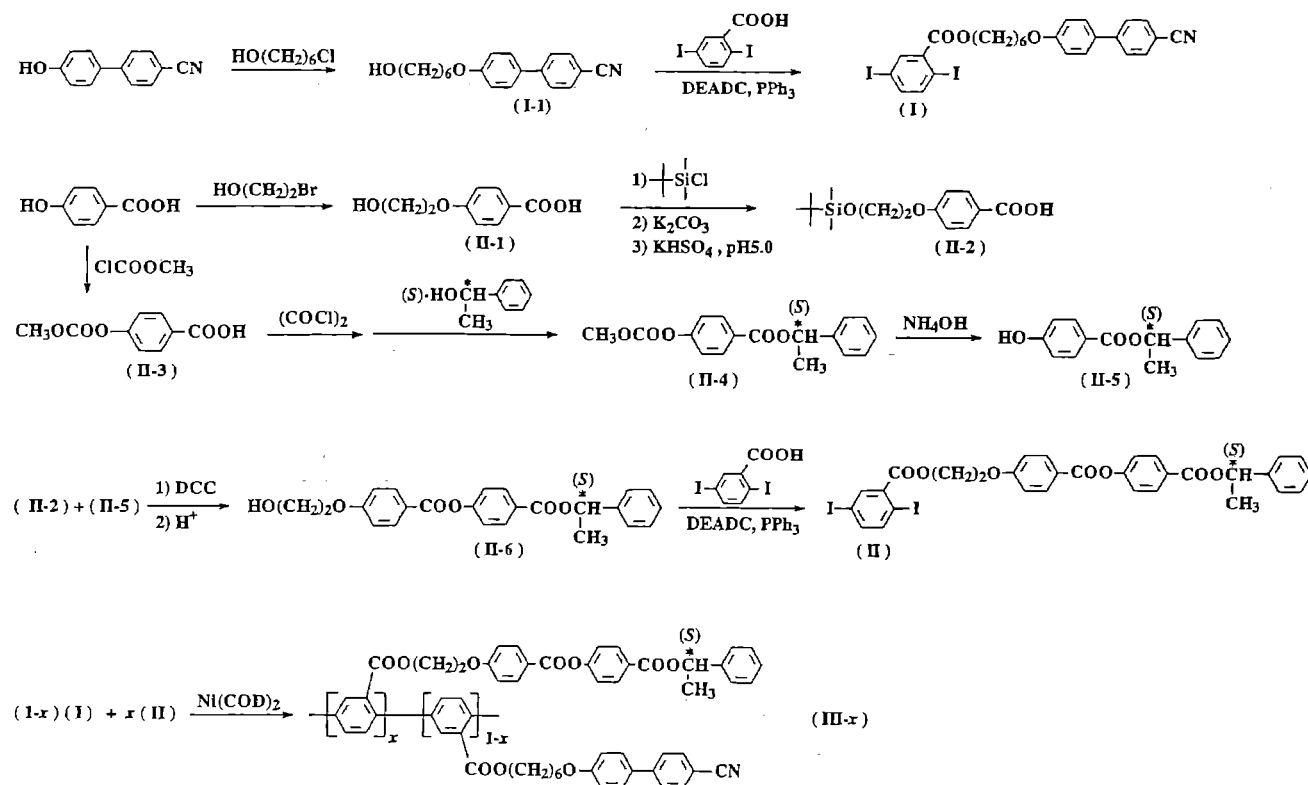
(8) Weder, C.; Sarwa, C.; Montali, A.; Bastiaansen, C.; Smith, P. *Science* 1998, 279, 835.

(9) Chen, S. H.; Conger, B. M.; Mastrangelo, J. C.; Kende, A. S.; Kim, D. U. *Macromolecules* 1998, 31, 8051.

(10) Schadt, M.; Fünfschilling, J. *Jpn. J. Appl. Phys.* 1990, 29, 1974.

(11) Chen, S. H.; Katsis, D.; Schmid, A. W.; Mastrangelo, J. C.; Tsutsui, T.; Blanton, T. N. *Nature* 1999, 397, 506.

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



jugation.¹² Nonetheless, no existing conjugated polymers possess a tight enough pitch to show selective wavelength reflection in the visible region. In what follows we report on the synthesis and characterization of tightly pitched, chiral-nematic conjugated polymers with supramolecular structure fully characterized by polarized photoluminescence and infrared dichroism.

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 until blue and then distilled. Silica gel 60 (EM Science, 230–400 mesh) was used for liquid chromatography.

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

4-(6-Hydroxyhexyloxy)-4'-cyanobiphenyl (I-1). 4-Hydroxy-4'-cyanobiphenyl (4.92 g, 25.2 mmol), 6-chloro-1-hexanol (4.40 g, 32.2 mmol), cesium carbonate (9.18 g, 28.1 mmol), and potassium iodide (0.43 g, 2.6 mmol) were dissolved in 65 mL of DMF. The reaction mixture was stirred at 80 °C for 5 h. The resultant salt was removed by hot filtration. The filtrate was slowly added to 600 mL of water, and the crude product was collected for recrystallization from methanol to produce 5.75 g in 76% yield.

2,5-Diiodobenzoic Acid, 6-[4-(4'-Cyanobiphenyl)oxy]hexyl Ester (I). 2,5-Diiodobenzoic acid (6.65 g, 17.8 mmol), triphenylphosphine (5.33 g, 20.3 mmol), and I-1 (5.00 g, 16.9 mmol) were dissolved in 85 mL of anhydrous tetrahydrofuran, to which diethyl azodicarboxylate (DEADC; 4.43 g, 25.4 mmol)

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 8.08–7.00 (m, aromatic, 11H), 4.38 (t, COOCH₂, 2H), 4.04 (t, ArOCH₂, 2H), 1.86 (m, COOCH₂CH₂(CH₂)₂CH₂CH₂OAr, 4H), 1.58 (m, COOCH₂CH₂(CH₂)₂CH₂CH₂OAr, 4H). Anal. Calcd: C, 47.95; H, 3.56; N, 2.15; I, 38.97. Found: C, 47.98; H, 3.34; N, 2.21; I, 39.40.

4-(2-Hydroxyethyloxy)benzoic Acid (II-1), 4-[2-[(tert-Butyldimethylsilyl)oxy]ethoxy]benzoic acid (II-2), 4-Methoxycarbonylbenzoic Acid (II-3), 4-Methoxycarbonylbenzoic 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)benzoyloxy]benzoate (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, 35.8 mmol), and 4-pyrrolidinopyridine (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

(12) Hyodo, K. *Electrochim. Acta* 1994, 39, 265.

(13) Krishnamurthy, S. Ph.D. Thesis, University of Rochester, Rochester, NY, 1992, pp 97–99.

(14) Katsis, D.; Chen, P. H. M.; Mastrangelo, J. C.; Chen, S. H.; Blanton, T. N. *Chem. Mater.* 1999, 11, 1590.

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

2,5-Diiodobenzoic Acid, 4'-{4''-[(*S*)-(-)-1'''-Phenylethyl]benzyloxy]benzyloxy}-2-ethyloxy Ether (II). Chiral monomer II was prepared following the same procedure as for the nematic monomer I, except recrystallization from a 20/80 mixture of acetone and ethanol to obtain a 86% yield. ^1H NMR: δ 8.20–7.00 (m, aromatic, 16 H), 6.16 (q, $-\text{COOCH}(\text{CH}_3)$, 1H), 4.75 (t, COOCH_2 , 2H), 4.43 (t, ArOCH_2 , 2H), 1.70 (d, CHCH_3 , 3H). Anal. Calcd: C, 48.84; H, 3.17; N, 0.00; I, 33.29. Found: C, 49.03; H, 2.98; N, 0.00; I, 33.69.

Nematic and Chiral-Nematic Polymers III-x. The procedure for Ni(0)-mediated polymerization is illustrated with copolymer III-0.23 as follows. Bis(1,5-cyclooctadiene)nickel(0) ($\text{Ni}(\text{COD})_2$; 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 DMF. To this solution were added I (0.90 g, 1.38 mmol) and II (0.45 g, 0.59 mmol). Precautions 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 ethanol, basic EDTA, acidic EDTA, water, and ethanol. The resultant solid was slurried in methylene chloride, and the insolubles were filtered off. The methylene chloride solution was washed sequentially with basic EDTA, acidic EDTA, water, and brine before being dried over anhydrous MgSO_4 . The solution was reduced to 6 mL in volume for precipitation into 80 mL of methanol. A 0.61 g (59%) of copolymer III-0.23 was collected. (III-0.00) ^1H NMR: δ 8.50–6.80 (m, aromatic, 11H), 4.50–3.70 (m, $\text{COOCH}_2(\text{CH}_2)_4\text{CH}_2\text{OAr}$, 4H), 2.00–1.00 (m, $\text{COOCH}_2(\text{CH}_2)_4\text{CH}_2\text{OAr}$, 8H). Anal. Calcd: C, 78.56; 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, $x(26\text{H}) + (1-x)(11\text{H})$), 6.14 (br, $-\text{COOCH}(\text{CH}_3)$, $x\text{H}$), 4.70–3.70 (m, $\text{COOCH}_2-(\text{CH}_2)_4\text{CH}_2\text{OAr}$ and $\text{COO}(\text{CH}_2)_2\text{OAr}$, $x(4\text{H}) + (1-x)(4\text{H})$), 1.90–1.10 (m, $-\text{CH}_3$ and $\text{COOCH}_2(\text{CH}_2)_4\text{CH}_2\text{OAr}$, $x(3\text{H}) + (1-x)(8\text{H})$). Anal. Calcd: C, 78.07; 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, $x(26\text{H}) + (1-x)(11\text{H})$), 6.13 (br, $-\text{COOCH}(\text{CH}_3)$, $x\text{H}$), 4.70–3.70 (m, $\text{COOCH}_2(\text{CH}_2)_4\text{CH}_2\text{OAr}$ and $\text{COO}(\text{CH}_2)_2\text{OAr}$, $x(4\text{H}) + (1-x)(4\text{H})$), 1.90–1.10 (m, $-\text{CH}_3$ and $\text{COOCH}_2(\text{CH}_2)_4\text{CH}_2\text{OAr}$, $x(3\text{H}) + (1-x)(8\text{H})$). Anal. Calcd: C, 77.77; H, 5.68; 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, $x(26\text{H}) + (1-x)(11\text{H})$), 6.14 (br, $-\text{COOCH}(\text{CH}_3)$, $x\text{H}$), 4.70–3.70 (m, $\text{COOCH}_2(\text{CH}_2)_4\text{CH}_2\text{OAr}$ and $\text{COO}(\text{CH}_2)_2\text{OAr}$, $x(4\text{H}) + (1-x)(4\text{H})$), 1.90–1.10 (m, $-\text{CH}_3$ and $\text{COOCH}_2(\text{CH}_2)_4\text{CH}_2\text{OAr}$, $x(3\text{H}) + (1-x)(8\text{H})$). Anal. Calcd: C, 77.55; H, 5.63; N, 2.86. Found: C, 76.87; H, 5.77; N, 2.67. (III-0.23) ^1H NMR: δ 8.50–6.50 (m, aromatic, $x(26\text{H}) + (1-x)(11\text{H})$), 6.14 (br, $-\text{COOCH}(\text{CH}_3)$, $x\text{H}$), 4.70–3.70 (m, $\text{COOCH}_2(\text{CH}_2)_4\text{CH}_2\text{OAr}$ and $\text{COO}(\text{CH}_2)_2\text{OAr}$, $x(4\text{H}) + (1-x)(4\text{H})$), 1.90–1.10 (m, $-\text{CH}_3$ and $\text{COOCH}_2(\text{CH}_2)_4\text{CH}_2\text{OAr}$, $x(3\text{H}) + (1-x)(8\text{H})$). 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, Whitesboro, NY) and FTIR (Nicolet 20 SXC) and ^1H and ^{13}C NMR (Avance-400, Bruker) spectroscopic techniques. Thermal transition temperatures were determined by differential scanning calorimetry (Perkin-Elmer DSC-7) with a continuous N_2 purge at 20 mL/min. Liquid crystal mesomorphism was characterized with a polarizing optical microscope (DMLM, Leica) equipped with a hot stage (FP82, Mettler) and a central processor (FP90, Mettler); the nematic and cholesteric mesomorphisms were identified with the threaded textures and oily streaks, respectively. Three PLgel mixed-C, 7.5×300 mm columns (Polymer Laboratories) were used in a size-exclusion chromatograph equipped with serially arranged UV-vis absorbance detector, 15° and 90° light scattering detector, differential viscometer, and differential refractometer, as described previously.¹⁵ The size-exclusion chromatograph system was operated at 35 °C with uninhibited tetrahydrofuran as the eluent at a flow rate of

0.1 mL/min. A universal calibration curve was constructed using 15 polystyrene standards with a molecular weight ranging from 580 to 2 300 000. Samples in 100 μL were injected at a concentration of 2 mg/mL. The weight-average molecular weight was calculated from the 15° light scattering with correction for anisotropic scattering.

Preparation of Films and Characterization of Optical Properties. Optical elements for the order parameter measurement were fabricated using optically flat, calcium fluoride substrates (1.00 in. diameter $\times$ 0.04 in. thickness, Optovac) 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 $\times$ 1/8 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 T_c , followed by annealing 20 °C below T_c 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 chloroform solution 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 (Nicolet 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 normal) at 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 spectrofluorometer (Photon Technology International Quanta Master C-60SE). A liquid light guide (2 mm diameter $\times$ 1 m long, Photon Technology International) was used to direct the UV excitation source onto 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 (CPPL), polarization analysis was performed via a circular analyzer with maximum polarization efficiency greater than 99% at 425 nm. At 560 nm the efficiency dropped to 90%. In the case of linearly polarized photoluminescence (LPPL), two identical UV-vis 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 (both LPPL and CPPL) spectra were corrected for both the efficiency and the transmission dispersion of the analyzer. The order parameter governing the poly(*p*-phenylene) backbone was determined by the LPPL and CPPL 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

(15) Mourey, T. H.; Balke, S. T. *J. Appl. Polym. Sci.* 1998, 70, 831.

Table 1. Number- and Weight-Average Molecular Weights and Thermotropic Properties of Poly(*p*-phenylene)s

polymer	$\bar{M}_n^a$ (SEC)	$\bar{M}_w^a$ (SEC)	DP ^b	$\bar{M}_w^c$ (LS)	DSC (°C) ^d
III-0.00	3380	6320	9	6760	G 66 N 165–196 I
III-0.07	5440	10000	13	10600	G 72 Ch 168–195 I
III-0.12	7050	14500	17	15200	G 75 Ch 162–192 I
III-0.17	3900	8100	9	8170	G 70 Ch 147–175 I
III-0.23	4610	10400	11	10300	G 73 Ch 153–181 I

^a Number- and weight-average molecular weights, $\bar{M}_n$ and $\bar{M}_w$, calculated from the molecular weight distribution measured by SEC with universal calibration using polystyrene standards.

^b Number-average degree of polymerization, $DP = \bar{M}_n/\bar{M}_1$, where $\bar{M}_1$ is the nominal molecular weight of a "chiral-nematic repeat unit", i.e., the molecular weights of chiral and nematic repeat units weighted with mole fraction. ^c $\bar{M}_w$ evaluated with the integrated 15° LS signal and the mass injected; agreement between SEC and LS indicating the absence of polymer aggregation. ^d Samples preheated to 200 °C with subsequent cooling to room temperature for gathering heating scans at 20 °C/min on a differential scanning calorimeter; glass transition temperature, T_g , reported as the inflection point across the step change, and clearing temperature, T_c , as the range over which nematic or cholesteric mesomorphism vanishes into an isotropic fluid.

poly(*p*-phenylene)s **III-x** were elucidated with analytical as well as ¹H NMR spectral data. The chiral mole fraction, x , was calculated from the intensities of the two sets of ¹H NMR signals centered around δ 6.14 and between δ 4.70 and δ 3.70 ppm. The structures of poly(*p*-phenylene)s were further elucidated with ¹³C NMR spectra of **I**, **II**, **III-0.00**, and **III-0.23**, which are provided as Supporting Information. On the basis of the accepted Ni(0)-catalyzed polymerization mechanism¹⁶ and reduction with hydrogen chloride as part of the workup procedure,¹⁷ it is believed that the resultant poly(*p*-phenylene)s are terminated with hydrogen atoms. In the presence of ester linkages other than those directly attached to the backbone, the degree of regio-regularity could not be assessed with ¹H NMR or ¹³C NMR spectroscopy. However, a multitude of peaks between δ 166.0 and δ 168.8 in the ¹³C NMR spectrum of nematic homopolymer **III-0.00** seems to indicate the absence of regioregularity¹⁸ in the resultant polymers. The average molecular weight of a repeat unit in **III-x**, $\bar{M}_1$, was calculated using the molecular weights of monomers **I** and **II** less iodine atoms. Number- and weight-average molecular weights, $\bar{M}_n$ and $\bar{M}_w$, were determined from the molecular weight distribution measured with size-exclusion chromatography (SEC) based on universal calibration using polystyrene standards. The ratio, $\bar{M}_n/\bar{M}_1$, yields the number-average degree of polymerization, DP. The light scattering (LS) signal observed at 15° was employed for an independent evaluation of $\bar{M}_w$. The results are presented in Table 1. The fact that the $\bar{M}_w$ values measured by size-exclusion chromatography agree with those by light scattering to within $\pm 5\%$ on average suggests the absence of aggregation in solution. The depicted polymer structures are consistent with analytical data for which the calculation was performed using the chiral mole fraction determined with ¹H NMR spectroscopy and the number average degree of polymerization determined with size-

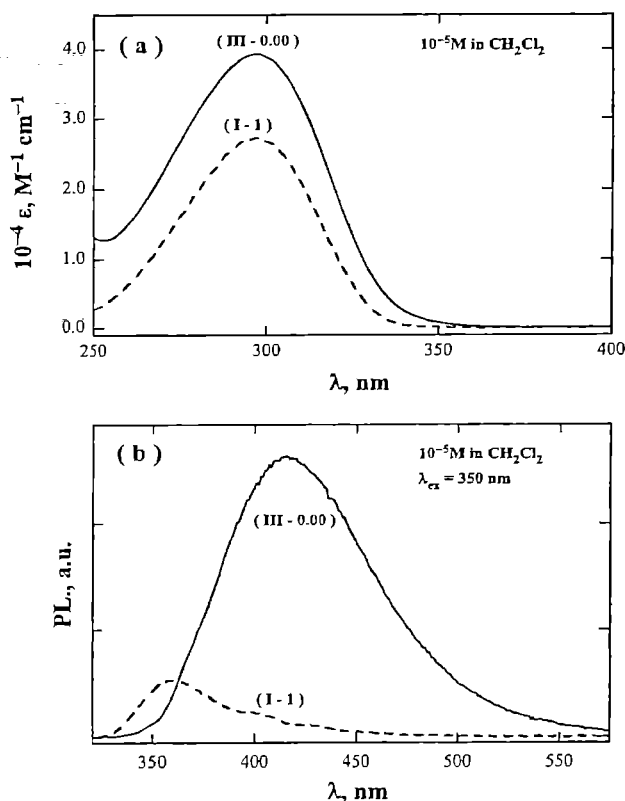


Figure 1. Absorption (a) and photoluminescence (b) spectra of nematic pendant, **I-1**, and nematic homopolymer, **III-0.00**, in methylene chloride at 10^{-5} M repeat units.

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 temperature, T_g , and the nematic-to-isotropic or cholesteric-to-isotropic transition (i.e., clearing) temperature, T_c , based on 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 pendants 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 two 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 achieved in the mesomorphic melt state (viz., between T_g and T_c) 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. The chiral precursor **II-7** is not included in Figure 1 because it was found to have a UV absorption cutoff at 325 nm and to be nonfluorescent with excitation at 350 nm. Figure 1a

(16) Yamamoto, T. *Bull. Chem. Soc. Jpn.* 1999, 72, 621.

(17) Grob, M. G.; Feiring, A. E.; Auman, B. C.; Percec, V.; Zhao, M.; Hill, D. H. *Macromolecules* 1996, 29, 7284.

(18) Wang, Y.; Quirk, R. P. *Macromolecules* 1995, 28, 3495.

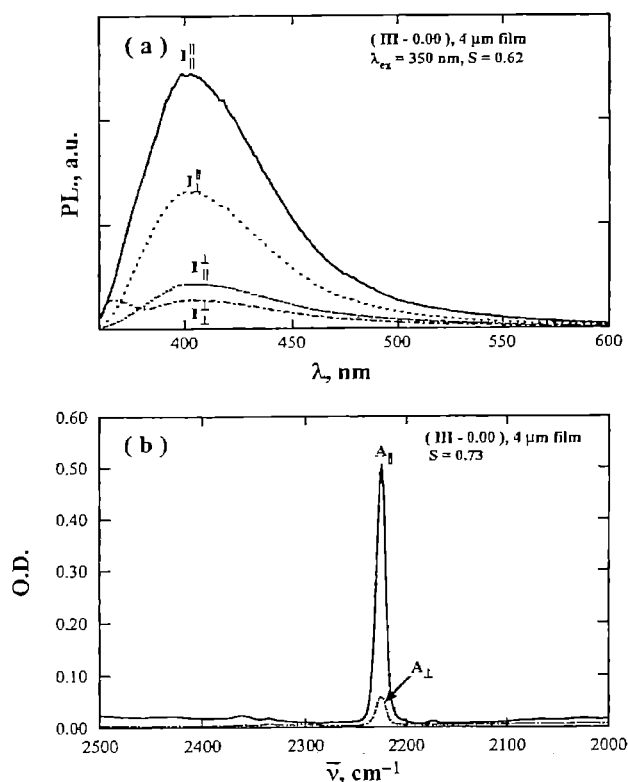


Figure 2. (a) Linearly polarized photoluminescence and (b) FTIR dichroism of a film of nematic homopolymer **III-0.00** for the evaluation of the orientational order parameter governing the conjugated backbone and the nematic pendant, respectively.

indicates that the nematic pendant is essentially non-absorbing above 340 nm in comparison to the backbone. Excited with $\lambda_{\text{ex}} = 350$ 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 surface-treated 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, $I_{||}^{||}$ 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,¹⁹ it is believed that the

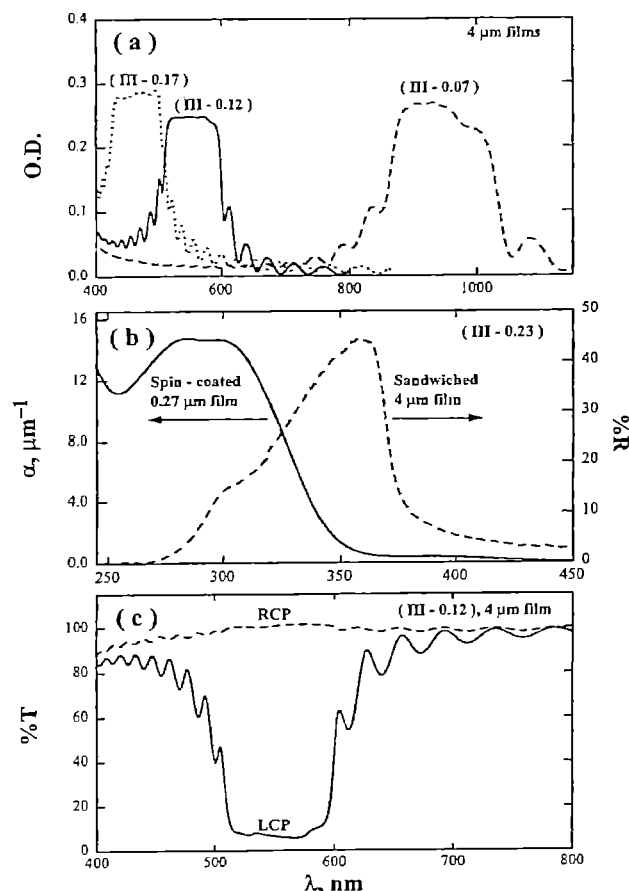


Figure 3. Optical properties of thin films prepared with chiral-nematic copolymers: (a) selective reflection spectra measured in terms of optical density for **III-0.17**, **III-0.12**, and **III-0.07**; (b) absorption coefficient, α , and reflection spectrum measured in terms of reflectivity, %R, for **III-0.23**; (c) transmittances of the right- and left-handed circularly polarized (RCP and LCP) light propagating through **III-0.12**.

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 ($A_{||}$) and perpendicular ($A_{\perp}$) to the nematic director were used to calculate the dichroic ratio, $R = A_{||}/A_{\perp}$, 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.²⁰ 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

(19) Gryczyński, Z.; Kawski, A. *Z. Naturforsch.* **1987**, 42a, 1396.

(20) Shi, H.; Conger, B. M.; Katsis, D.; Chen, S. H. *Liq. Cryst.* **1998**, 24, 163.

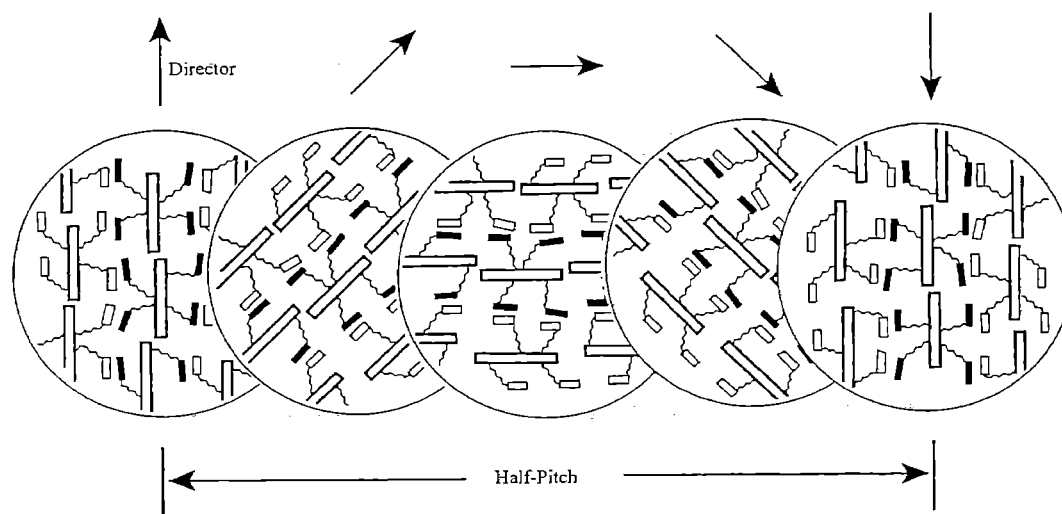


Figure 4. A schematic diagram of the supramolecular structure of a chiral-nematic film with its quasinematic director undergoing a counterclockwise rotation, as stipulated by the left-handed helical structure determined in Figure 3c. Within each layer, the backbone and the nematic pendant are oriented along the director. Note the antiparallel arrangement of nematic pendants, shown as small filled and open rectangles, from neighboring conjugated backbones. The pitch length is defined as the distance along the surface normal to quasinematic layers over which the director completes a 360° rotation.

with simultaneous circular polarization of incident unpolarized light.¹⁰ 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, λ_R , at a decreasing x value. At $x = 0.23$ 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.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.²³ 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 cyanobiphenyl 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, $g_e \equiv 2(I_L - I_R)/(I_L + I_R)$.

The experimental setup described previously²⁴ 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.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.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 ($\bar{n}$) and the optical birefringence (Δn) 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 previously⁹ served as the basis for parameter estimation: $\bar{n} = 1.75$ and $\Delta n = 0.30$ at 350 nm and $\bar{n} =$

(21) Khoo, I. C.; Wu, S.-T. *Optics and Nonlinear Optics of Liquid Crystals*; World Scientific: Singapore, 1993; p 64.

(22) De Gennes, P. G.; Prost, J. *The Physics of Liquid Crystals*; Clarendon Press: Oxford, 1993; p 264.

(23) Krishnamurthy, S.; Chen, S. H. *Macromolecules* **1991**, *24*, 3481.

(24) Katsis, D.; Schmid, A. W.; Chen, S. H. *Liq. Cryst.* **1999**, *26*, 181.

1.63 and $\Delta n = 0.25$ at 410 nm. In addition, the average absorbance per unit thickness reported previously⁹ for the nematic homopolymer, $0.651 \mu\text{m}^{-1}$ 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 ± 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 ^1H 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 $\text{C}\equiv\text{N}$ 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*)-(-)-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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