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S. A. Jenekhe, A. J. Bard, S. H. Chen, P. T. Hammond,
L. J. Rothberg, S. Scheiner, and T. M. Swager

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)
University of Washington, Department of Chemical Engineering,
Box 351750, Seattle, WA 98195-1750

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13. ABSTRACT (Maximum 200 words)

This multidisciplinary university research initiative (MURI) program investigated tunable optical polymer systems suitable for large-area color-switchable coatings and devices, displays, sensors, and other electronic applications. The synthesis and properties of new electrochromic polymers are described. Electrochromic devices incorporating conjugated polymers have been fabricated and found to be durable past 100,000 cycles. Black-red, yellow-red, blue-black color-switchable all-plastic electrochromic devices were demonstrated. Fast-responding, bright red light-emitting diodes based on ruthenium (II) complexes were fabricated and investigated. Efficient voltage-tunable multicolor light-emitting diodes based on bipolar blends of polyquinoline and MEH-PPV or poly(octylthiophene) were developed. New quinoline-functionalized dendrimers have been found to be efficient electron transport materials, leading to bright LEDs with high external efficiencies (2.6-6.0%). Blue LEDs with good spectral stability were developed from polyfluorene blends with high glass transition polymers. Red-blue-white tunable LEDs with a brightness of up to 4000 cd/m^2 (3.7 cd/A) and 3.1% external quantum efficiency have been developed from blends of conjugated polymers. Polarized blue LEDs have been developed from ogliofluorene with a dichronic ratio of 15-18.0 and a luminous efficiency of 0.5-5.9 cd/A. Novel chiral-nematic glass forming liquid crystals were synthesized and found to exhibit 100% selective reflection of ultraviolet, visible, and infrared light. High performance n-channel thin film transistors were developed from ladder polymer semiconductors.

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Tunable optical properties; electrochromism; electroluminescence; tunable electroluminescence; selective reflection; conjugated polymers; color-switchable devices; smart materials; displays; polymer chemistry; chromogenic polymers; self-assembly; electrostatic self-assembly; aggregation; ruthenium (II) complexes; liquid crystals; thin film transistor; oligofluorene; polyfluorene; ladder polymer; polyquinoline; dendrimer; smart window; light-emitting diode; plastic electronics; poly(hexylthiophene); polyphenothiazine; polyaniline; macrocycles; oligoanthrazoline.

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Submitted by

Principal Investigator:
Professor Samson A. Jenekhe
Department of Chemical Engineering
University of Washington
Benson Hall, Box 351750
Seattle, WA 98195-1750
Phone: (206) 543-5525
Fax: (206) 685-3451
E-mail: jenekhe@u.washington.edu

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1. Background and MURI Program Objectives

Chromogenic phenomena (for example: electrochromism, photochromism, thermochromism, piezochromism, and magnetochromism, i.e. color changes induced respectively by applied electric, optical, thermal, pressure and magnetic fields) provide many processes for achieving real time tunability of optical properties of materials. Photochromism and electrochromism in polymeric and organic materials have been widely investigated, finding applications in areas such as self-adjusting sunglasses, filters for optical sensors, medical thermographic recording media, self-adjusting rear-view car mirrors, and color-switching ski jackets. However, the full potential of chromogenic materials--e.g., in large-area information display, optical information storage, holographic recording, smart windows, photoresistive transducers, and large-area color-tunable wallpaper--has not been realized. Among the challenges and barriers to achieving large-scale and high impact technological applications of various chromogenic materials include materials issues such as stability of materials under long term cycling, the speed with which optical changes can be effected, the amount of energy required to achieve optical tunability, satisfactory color contrasts, durability, the processability of the chromogenic materials into suitable forms (conformal coatings, multilayers, etc), and realization of a variety of necessary properties beyond optical tunability (e.g. mechanical strength).

A better fundamental understanding of these chromogenic phenomena and associated materials issues will enable the design and development of the next generation of chromogenic materials. As a class, low cost and easily producible optically tunable (i.e. chromogenic) polymers or hybrid organic-inorganic nanocomposites hold a great potential for the development of new concepts for various displays and intelligent sensors/detectors. Such materials also facilitate implementation of novel concepts for smart/interactive textiles, environmentally responsive protective clothing, environmentally- and time- sensitive packages for food, drugs, and perishables. Nanostructured, tunable optical polymer systems represent potential model systems for exploring a range of new concepts of intelligent/self-repairing materials and systems, nanoelectromechanical systems, and various nanofunctional devices. Therefore, we believe that the next generation of chromogenic polymer systems will have important implications for and the potential to meet several of the needs of Force XXI, especially those in the areas of the Soldier System.

The main mission and objectives of our focused research and education program under this MURI on *Tunable Optical Polymer Systems* (TOPS) were: (i) the development of the knowledge base for the design, synthesis, processing, and characterization of new generations of optically tunable polymeric materials suitable for various photonic and optoelectronic applications; (ii) the development of the fundamental understanding of the physical/chemical mechanisms underlying chromogenic phenomena, especially electrochromism, photochromism, photoelectrochromism, thermochromism, tunable luminescence, and tunable reflection, in polymeric materials; and (iii) incorporation of these materials in appropriate device structures and evaluation of their performance in standardized test beds; It is our intent to provide a realistic appraisal of tunable optical polymer systems in photonic and optoelectronic applications. To achieve these objectives, we explored several new concepts of optically tunable polymer systems at the electronic structure, molecular structure, supramolecular structure, nanostructure, and macroscopic device and systems levels. Some of the main results are highlighted in the following sections. The complete details of the results can be found in the numerous publications cited in this report.

2.1. Electrochromic Materials And Devices

2.1.a Electrochemical Characterization and Device Properties of Optically Tunable Materials

The main objectives were: (i) the electrochemical characterization of new generations of optically tunable polymeric materials suitable for various photonic and optoelectronic applications; (ii) the development of the fundamental understanding of the physical/chemical mechanisms and dynamics underlying electrochromism, electrogenerated chemiluminescence and electroluminescence in suitable materials; and (iii) the development of prototype electrochromic and electroluminescent devices for photonic and optoelectronic applications.

Phenothiazine-Phenylquinoline donor-acceptor small molecules and polymers. The new quinoline-containing compound, 3,7-[bis[4-phenyl-2-quinolyl]]-10-methylphenothiazine (BPQ-PTZ), was synthesized and used to generate electrogenerated chemiluminescence (ECL) emission from phenothiazine without the addition of a coreactant or a second compound. Semiempirical MNDO calculations of this compound determined that the phenylquinoline was twisted 77.5° relative to phenothiazine and indicated no molecular orbital overlap between these two groups. This molecular geometry, therefore, favors localization of the negative charge of the individual radical anions of the dianion onto each quinoline group and of the positive charge of the radical cation onto phenothiazine. As a result, the oxidation and reduction potentials of BPQ-PTZ were very similar to the constituent compounds, 2-phenylquinoline (2-PQ) and 10-methylphenothiazine (10-MP). The covalent linkage of the phenylquinoline groups to the 10-MP enables one to generate the radical anion at potentials far less negative than those for solvent reduction. This, along with charge separation, facilitated the electron transfer between the two electrochemically generated radical ions of BPQ-PTZ, thus eliminating the need to add a coreactant or a second compound. More importantly, the energy of this annihilation reaction is sufficient enough to generate the singlet-excited state and corresponding ECL emission of BPQ-PTZ.

A new molecule, 7,7'-bis-(6-hexyl-4-phenylquinolin-2-yl)-10,10'-dimethyl-10*H*,10*H*'-[3,3']biphenothiazinyl (BHQ-BPZ), was synthesized and shown to be a new donor-acceptor compound capable of ECL. The presence of phenothiazine dimer as the electron donor and phenylquinoline groups as the electron acceptors allows the generation of ECL without the addition of a coreactant or a second compound. On the basis of semiempirical MNDO calculations of this compound, the phenylquinoline group is twisted 82.5° relative to phenothiazine, indicating no molecular orbital overlap between these two groups. This molecular geometry, therefore, favors localization of the negative charge of the individual radical anions of the dianion onto each quinoline group and of the positive charge of the individual radical cation onto each phenothiazine group. In addition, the first phenothiazine is twisted 46.5° relative to the adjacent phenothiazine group, suggesting a possible delocalization of charge between these two moieties. However, this interaction is not strong enough to cause a pronounced effect in its photophysics. As a result of this slight interaction between the two phenothiazine groups, the oxidation of the first phenothiazine group creates a slight energetic barrier to the oxidation of the adjacent phenothiazine group, characterized by two closely spaced one-electron oxidation waves. Overall, BHQ-BPZ showed electrochemical, photophysical, and ECL properties similar to those of its parent compound, BPQ-PTZ. Most importantly, the energy of the annihilation reaction for

BHQ-BPZ is sufficient to generate the singlet-excited state and corresponding ECL emission. Donor-acceptor block architectures such as this may provide a general approach to designing new materials exhibiting efficient ECL.

Electrochemical studies showed that a new phenothiazine-phenylquinoline donor-acceptor copolymer, poly(2,2'-(10-methylphenothiazine-3,7-diyl-6,6'-bis(4-phenylquinoline)) (PPTZPQ), as a thin film undergoes a reversible electrochemical oxidation accompanied by a color change. The reduction behavior is unstable and causes loss of the electrochromic effect. The PPTZPQ spectroelectrochemical behavior was interpreted as a combination of the properties of individual donor and acceptor moieties. The construction of all-plastic PPTZPQ-based electrochromic cells with interesting color changes showed the potential use of PPTZPQ as an electrochromic material as well as flexible all-plastic electrochromic devices. Further work is still necessary to improve the spectroelectrochemical characteristics of these cells by optimizing their charge capacity ratio and particularly the composition of the polymeric electrolyte.

New electrochromic polymeric materials. A study of poly(7,14-diphenylacenaphtho[1,2-*k*]-fluoranthene) electrodeposited as a film on Pt or ITO surfaces showed electrochromic properties. These included changes in film color and in resistance (over two to three orders of magnitude) by varying the potential of the working electrode. The film characterization was carried out by electrochemical, AFM, SECM, EQCM and resistance measurements.

Films of semi-ladder and ladder poly(benzobisimidazobenzophenanthroline) (BBB and BBL) spin-coated on ITO electrodes showed brilliant changes in film color and in resistance with varying the potential of the working electrode. Film characterization was performed by electrochemical, SECM, AFM, and resistance measurements. These conjugated ladder and semiladder polymers constitute an interesting class of electrochromic and electron transport materials.

2.1.b Tunable Electrochromic Multilayers

The efforts from the Hammond laboratory revolved around two goals, both of which were directed toward the implementation of a simple, low cost processing method, layer-by-layer assembly, in electrochemical devices, particularly for reflective displays. The first objective was the development of tunable chromic polymer thin films utilizing the electrostatic layer-by-layer method. In the relatively new technique of electrostatic LBL assembly, substrates are alternately exposed to solutions containing polyelectrolytes of opposite charges. This approach enables the use of chromophores immobilized in stable ultrathin flexible polymer films which exhibit high contrast and provide the opportunity to create multichromic systems without the need for sophisticated synthetic approaches. Because nonlithographic patterning of these thin films has also been mastered in the Hammond group, the formation of thin patterned functional films on a range of surfaces opens up the potential for portable large area reflective displays for disposable electronics, electronic paper, and fast smart windows using a low cost but stable technology. A second, fundamental focus of the project was the development of a multilayered solid electrolyte which can be employed within fully solid-state electrochromic devices (ECDs) to achieve faster switching performance and a greater device lifetime; many other applications exist for ultrathin films that exhibit high ionic transport, including applications in the power and energy storage areas. These systems should be applicable to plastic and flexible substrates, and can be incorporated into a number of device applications. Highlights of this work include the increase in contrast of electrochromic systems to an unusually high level of 82%, which outperforms almost all other organic polymer systems reported thus far, the introduction of the first multiple color LBL electrochrome, and development of ionically conductive LBL thin films for electrochemical applications. Other new developments in the project include the development of new thin films based on nanoparticles formed from transition metal cyanoferrates, including Prussian Blue, which are capable of strong coloration, and allow the formation of films with a range of colors, including cyan, purple, and yellow states achieved with different metal compounds.

Electrochromic LBL polyelectrolyte thin films with enhanced contrast. We have successfully introduced extremely high contrast in these thin films by creating LBL systems in which the polycation and polyanion species are both cathodically coloring electrochromic species. The cation species, poly(hexyl viologen) (PXV) is colored in the reduced state due to the formation of a charge transfer complex, while the anion species, the poly(3,4-ethylene dioxythiophene):poly(styrene sulfonate) colloidal dispersion (PEDOT:SPS, available as BAYTRON P from Bayer) derives color upon reduction from undoping of the transparent conducting state. Both polymers become dark blue when reduced. In Figure 1, the spectroelectrochemistry of the combined composite clearly shows three broad absorption peaks: two due to PXV at 550 nm and 620 nm, and one due to PEDOT at approximately 670 nm. The separation of redox potentials within this composite *provides unique control over the grayscale of coloration, with adjustable absorption over the entire potential range studied*. Due to the wide band absorption unique to the composite of these two films, thick PXV/PEDOT:SPS films appear blue-black at negative potentials. Synthetic polymer efforts have reported Δ%T (T=transmittance) measurements up to 78% for polymer films synthesized specifically for electrochromic applications. The maximum achievable contrast from a PXV/PEDOT:SPS film is Δ%T = **82.1%** at 525 nm. Because of the very wide band absorption, Δ%T is greater than 50% over the entire range of 450 nm to 700 nm. *The performance of this readily assembled LBL composite is on par with or exceeds that of materials synthesized by far more intricate strategies.*

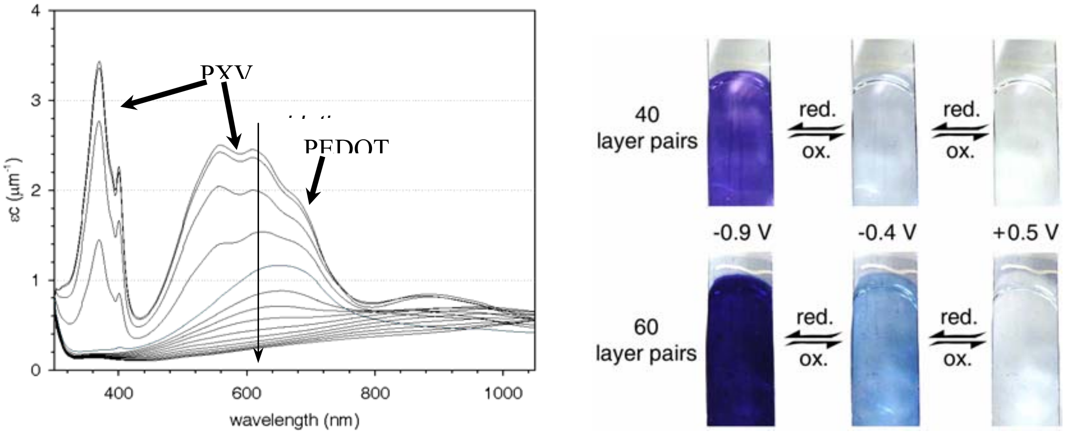

Figure 1. (left) Spectroelectrochemisty of PXV/PEDOT:SPS dual electrochrome and (right) colors displayed on reduction and bleaching cycles.

Multiple coloring anodic electrochromes. Similar work involving the alternation of two different coloring systems within an LBL film have led to *multihue anodic coloring thin films* from polyaniline (PANi) and a form of Prussian Blue (Iron(III) Hexacyanoferrate(II)) that can be prepared as a water based dispersion. Figure 2 indicates the color changes induced on oxidation –

from a clear, transparent bleached state, to a green color at 0.2 V, to a blue color at 0.6 V. Further development of multichromic systems has continued, and includes the development of new colors. The use of nickel in the place of iron results in a yellow electrochrome, whereas the use of a ruthenium hexacyanoferrate leads to a purple color that approaches the color of magenta. These three colors are shown together in Figure 3. The development of these multiple colors is advantageous for the development of a full color reflective display; patterning methods are being applied to device construction. The Prussian blue nanoparticle films also exhibits novel release characteristics when cycled to higher voltages.

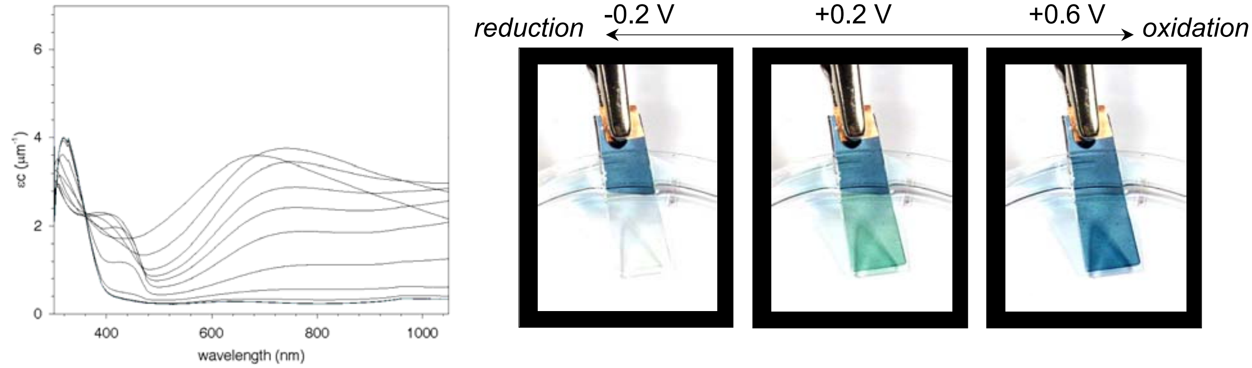

Figure 2. Spectroelectrochemistry and color changes observed in PANi/Prussian Blue LBL multilayer films.

Figure 3. Array of colors obtained through the layer-by-layer assembly of different metal hexacyanoferrate nanoparticles with LPEI (a polycation). From left to right, thin nanocomposite films of iron, nickel and ruthenium hexacyanoferrate nanoparticles.

Ionically conductive thin films. The applications of LBL films have been extended to solid state polymer electrolytes for the first time, with the development of new LBL composites with ionic conductivity levels appropriate for many electrochemical applications. Key to this work was the use of strongly acidic and/or hydrophilic polyelectrolytes, and the ability to manipulate adsorption conditions to obtain the optimal effective crosslink density and free volume for ion transport. LPEI/PAMPS was discovered to assemble through two different types of interactions, which can be selectively screened to create films with different ion conduction properties, including a film assembled from weak interactions that displays ion conductivity of 10^{-5} S/cm at intermediate hydration (52% RH). The LPEI/PAA(polyacrylic acid) system *exhibited very high ionic conductivity* similar to LPEI/PAMPS at high hydration (100% RH), and *also possessed excellent mechanical properties, being stable to flowing water and high ionic strength solutions.*

The addition of salt to LBL films was shown to enhance ion conduction at intermediate hydration.

Development of solid polymer electrolyte for solid-state ECDs. Very recent developments include the investigation a solid polymer electrolyte film formed from hydrogen bonding layer-by-layer (LBL) assembly; the resulting thin films outperform previously reported LBL assembled films and approach integration capability for a number of electrochromic, sensing and micropower/battery applications. Films were fabricated by alternating deposition of poly(ethylene oxide) (PEO) and poly(acrylic acid) (PAA) layers from aqueous solutions. *Ionic conductivity of 5 x* 10^{-5} *S/cm is achievable after short exposure to 100% relative humidity (RH) for plasticization.* Adding free ions by exposing PEO/PAA films to lithium salt solutions enhanced conductivity to greater than 10^{-5} S/cm at only 52% RH, and tentatively greater than10^{-4} S/cm at 100% RH. The excellent stability of PEO/PAA films even when exposed to 1.0 M salt solutions led to an exploration of LBL assembly with added electrolyte present in the adsorption step. *Dry ionic conductivity was enhanced in films assembled in the presence of salt as compared to films that were merely exposed to salt after assembly*. These results reveal clear directions for the evolution of these promising solid polymer electrolytes; ongoing projects now examine them for power storage and generation applications, including fuel cells and batteries. Finally, the electrolyte has been used successfully as the electrolyte in an all layer-by-layer electrochromic device, work which is currently in preparation for an upcoming paper.

2.1.c Electronic Structure of Chromic Macrocycles

The overall objective of this subproject was the analysis of several different molecular systems for tunable optical properties. Fundamental understanding required an in-depth analysis of the electronic structures and configurations of each system of interest, and how they are affected by certain perturbations.

Summary of the most important results. We began with a 1996 paper by a Japanese team that had found interesting redox properties of complexes between several transition metals and phthalocyanine (Pc) in thin films. Reversible electrochromism had been observed for certain metals, irreversible for others. Our calculations revealed that all metals considered were strongly bound to the phthalocyanine ring. Whereas Fe and Co phthalocyanines have $^3A_{2g}$ and ^2E_g ground states, respectively, these states are changed upon interaction with strong-field axial ligands. The valence electronic structures of Fe and Co phthalocyanines differ significantly from those of the others. The HOMOs in Fe, Co, and Cu phthalocyanine are metal 3d-like, whereas in Ni and Zn phthalocyanines, the HOMO is localized on the phthalocyanine ring. The first ionization removes an electron from the phthalocyanine a_{1u} orbital in all cases, with very little sensitivity of the ionization energy to the identity of the metal. Whereas the first reduction in Fe and Co phthalocyanine occurs at the metal, it is the phthalocyanine that is reduced upon addition of an electron to the other systems. Fe, Ni, and Cu phthalocyanines have smaller HOMO-LUMO separations than do Zn and Co phthalocyanine.

The porphyrin family holds great promise for its optical tuning potential. We began with a sample of such molecules in which iron was the central atom, specifically a series of unligated and ligated Fe^{II} porphyrins (FeP). Unligated four-coordinate iron porphyrins have a $^3A_{2g}$ ground state that arises from the $(d_{xy})^2(d_{z^2})^2(d_\pi)^2$ configuration. For the six-coordinate Fe-P(L)$_2$, the strong-field axial ligands raise the energy of the Fe d_{z^2} orbital, thereby making the iron porphyrin diamagnetic. The ground-state configuration of FeP(2-methylimidazole) was confirmed to be high-spin $(d_{xy})^2(d_{z^2})^1(d_\pi)^2(d_{x^2-y^2})^1$.

We next compared porphyrin (P) with porphyrazine (Pz), and phthalocyanine (Pc), again with metals Fe, Co, Ni, Cu, and Zn. The calculations provided a clear elucidation of the ground states for the MP/Pz/Pc molecules and for a series of $[MP/Pz/Pc]^{x-}$ and $[MP/Pz/Pc]^{y+}$ ions. For FeP/Pz and CoP/Pz, the first oxidation occurs at the central metal, while it is the macro-ring of FePc and CoPc that is the site of oxidation. The smaller coordination cavity results in a stronger ligand field in Pz than in P. However, benzo annulation produced a surprisingly strong destabilizing effect on the metal-macrocycle bonding. The effects of Cl axial bonding upon the electronic structures of the iron(III) complexes of P, Pz, and Pc were examined, as was the bonding of pyridine (py) to NiP, NiPz, and NiPc. The porphinato core size played a crucial role in controlling the spin state of Fe^{III} in these complexes. FePc(Cl) was predicted to be a pure intermediate-spin system, whereas $NiPz(py)_2$ and $NiPc(py)_2$ are metastable in high-spin (S = 1) states. The $NiPz/Pc-(py)_2$ binding energy curve has only a shallow well which facilitates decomposition of the complex. The $NiP-(py)_2$ bond energy is small, but the relatively deep well in the binding energy curve ought to make this system stable to decomposition.

Particularly when studying metals low in the periodic table, relativistic effects may play a significant role, so it was necessary to study them explicitly. DFT calculations were performed on four-coordinate metal porphyrins MP and their six-coordinate adducts $MP(py)_2$ and MP(py)(CO) (py=pyridine) with M = Fe, Ru, and Os. FeP and OsP have a $^3A_{2g}$ ground state, while this state is nearly degenerate with ^3E_g for RuP. Without relativistic corrections, the ground states of both RuP and OsP would be ^3E_g. For the six-coordinate adducts with py and CO, the strong-field axial ligands raise the energy of the M d_z2-orbital, thereby making the M^{II} ion diamagnetic. The difference between RuP(py)(CO) and OsP(py)(CO), in terms of site of oxidation, is due to relativistic effects.

In order to derive insights with potentially important implications for a broader range of systems, calculations were performed on a series of β-substituted copper porphyrins, CuP-X, with particular regard to substituent effects upon the relative energies of two frontier occupied, nearly degenerate a_{2u} and a_{1u} orbitals. Substitution by electron-withdrawing groups only slightly enlarged the a_{2u}-a_{1u} separation of CuP. Electron-donating groups CH_2OH and OCH_3 raised the energies of a_{2u} and a_{1u} uniformly. In contrast, SH and NH_2 reverse the normal ordering; these $[CuP\text{-}X]^+$ cation radicals are mainly a_{1u} in character.

The list of metals bonded to porphines was expanded to Group 4A Si, Ge, Sn, and Pb. All the divalent MP's, including SiP and GeP, were non-planar with the metal atom considerably out of the porphyrin plane. Each MP has a closed-shell $(3a_1)^2$ ground state, but the HOMO $3a_1$ is *not* a metal-np_z orbital (as proposed in the literature). For PbP the HOMO ($3a_1$) is almost made up of the porphyrin $2a_{2u}$ orbital, which accounts for the fact that PbP undergoes initial oxidation at the ring. For the second oxidation step of $[PbP]^+ \rightarrow [PbP]^{2+}$, the electron is removed initially from the HOMO, and then an internal redistribution of electrons takes place, i.e. two electrons transfer from the metal to the ring: $Pb^{II} \rightarrow Pb^{IV}$. The $3a_1 \rightarrow \pi^*$ transition has the lowest excitation energy; the B_1 and B_2 bands assigned early in the experimental spectra of Sn^{II} and Pb^{II} porphyrins are actually the Q and B bands, respectively.

Heavier metals (actinyls U, Np, and Pu) were studied next, in their interactions with alaskaphyrin (AP), an expanded porphyrin. For UO_2 and NpO_2, the ground state is altered by relativistic effects, but it remains unchanged for PuO_2. The nonrelativistic ground states of the AnO_2AP complexes are all high spin, where the AP HOMO b_{2g} is singly occupied. At the relativistic level, there are two electrons in b_{2g}. The bonding characteristics in AnO_2AP were examined by calculations of the AnO_2–AP binding energy and charge distribution on AnO_2. The predicted spectroscopic constants for NpO_2, PuO_2, NpO_2AP, and PuO_2AP will aid in future spectroscopic studies of these molecules.

2.2 Light Emitting Polymers and Devices

2.2.a New n-Type Materials for Organic Light-Emitting Diodes

The *Jenekhe* group previously found large enhancements in efficiency and brightness of polymer light-emitting diodes (LEDs) using polyquinolines and polyanthrazolines as n-type (electron transport) layers for poly(*p*-phenylenevinylene) (PPV). However, these rigid-rod polyquinolines and polyanthrazolines are soluble primarily in protonic acids such as formic acid which limits their use in optoelectronic devices. The main objective of our studies under the MURI program was the development of new organic solvent-soluble n-type organic semiconductors, both low molar mass and polymeric, that can be used in organic LEDs as electron transport materials (ETMs) or as emissive materials.

Diphenylanthrazolines and Quinoline-based dendrimers. A series of diphenylanthrazolines **1a-1e** (Chart 1) and quinoline-based dendrimers with high electron affinity were synthesized and used as ETMs in bilayer LEDs with poly(2-methoxy-5-(2'-ethyl-hexyloxy)-1,4-phenylene vinylene) (MEH-PPV). The new light-emitting conjugated dendrimers were based on a benzene core, poly(phenylenevinylene) dendrons, and diphenylquinoline peripheral groups. These materials are soluble in a wide range of common organic solvents and in protonic acids. Estimated electron affinities (LUMO levels) of compounds **1a-1e** and the dendrimers were 2.90-3.10 eV and 2.5-2.6 eV, respectively. As the emissive layers in single-layer LEDs, relatively moderate brightness and efficiencies were observed using either the diphenylanthrazolines **1a-1e** or quinoline-based dendrimers. Bilayer LEDs using compounds **1a-1e** as the electron-transport layer and MEH-PPV as the emissive layer had a maximum external quantum efficiency (EQE) of 3.1% and a brightness of up to 965 cd/m^2 in ambient air. These results represent enhancements of up to 50 times in EQE and 17 times in brightness when using **1a-1e** as the ETMs in polymer LEDs. Similar large improvements in bilayer LED performance were obtained using the dendrimers as the ETMs with MEH-PPV emissive layer. The performance increased with dendrimer generation and number of electron-acceptor peripheral groups, reaching a maximum EQE of 5.0%, a power efficiency of 1.3 lm/W, and a brightness of up to 2000 cd/m^2 in ambient air using aluminum cathode. This represents enhancements of up to 167 times in EQE and 35 times in brightness compared to single-layer MEH-PPV diodes. These results demonstrate that the new diphenylanthrazolines and quinoline dendrimers can be used as efficient electron transport and hole blocking materials to improve the performance of polymer LEDs.

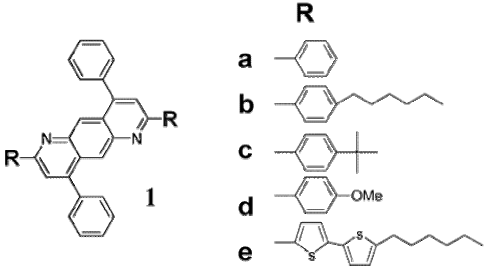

Chart 1. Molecular structure of anthrazoline oligomers

Regioregular head-to-tail poly(4-alkylquinoline)s. The objective of this study was the regiocontrolled synthesis and investigation of new regioregular n-type π-conjugated polymers for optoelectronic devices. Five poly(4-alkylquinoline-2,6-diyl)s (P4AQs), having 100% head-to-tail regioregularity, were synthesized by self-condensation polymerization of new AB-type monomers. The P4AQs were organic solvent soluble and had an electron affinity (2.6 eV) that was independent of alkyl chain length. X-ray diffraction studies showed that solution-cast films of the regioregular P4AQs have self-organized lamellar structures with an interchain π-stacking distance of 3.9-4.1 Å (Figure 4) and an interlayer *d*-spacing that varied linearly from 13.4 Å for butyl to 22.3 Å for tridecyl side chains. As emissive materials in LEDs, yellow electroluminescence with a luminance of up to 86 cd/m^2 and an external quantum efficiency of up to 0.6% was observed for the P4AQs. Improvement in performance of MEH-PPV-based LEDs by factors of up to 100 (a luminance of up to 700 cd/m^2 and an EQE of up to 3.0%) was observed when the P4AQs were used as the electron transport materials. These results demonstrate that the new regioregular P4AQs are promising n-type conjugated polymers for polymer LEDs and other optoelectronic devices.

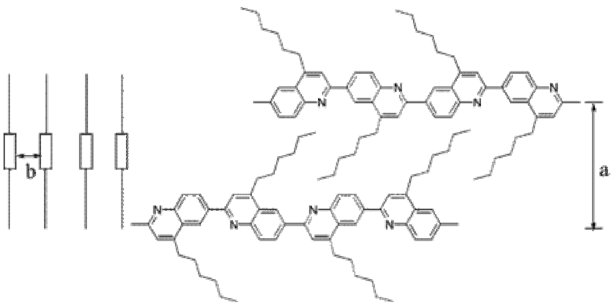

Figure 4. Schematic of layered and π-stacking structures of regioregular poly(4-alkylquinoline)s exemplified for poly(4-hexylquinoline).

Phenylquinoline-based alternating copolymers. We synthesized a series of five new soluble, head-to-head regioregular, poly(2,2'-(3,3'-dialkyl-2,2'-bithienylene)-6,6'-bis(4-phenylquinolines)) (PxBTQ), in which the alkyl chain length is varied from butyl to dodecyl. The copolymers were soluble in common organic solvents in addition to protonic acids. The high electron affinity (2.88-2.97 eV), robust thermal stability (T_g = 161-256 °C), suitable solution processability, and weak-to-moderate intrinsic electroluminescence of the copolymers make them attractive for use as electron transport materials in organic LEDs. Using the copolymers as electron transport materials in bilayer MEH-PPV LEDs resulted in substantial enhancement in device performance under ambient air conditions (1.4% external quantum efficiency, 2170 cd/m^2 brightness) compared to most current electron transport polymers for LEDs.

Conjugated oligoquinolines. A new oligoquinoline 6,6’-Bis(2,4-diphenylquinoline) (BDPQ), was successfully synthesized and employed as both a blue-emitting and an electron-transport material in a simple bilayer device architecture to achieve pure blue electroluminescence with high efficiency in air. Stable blue EL with a peak at 453 nm, CIE coordinates of (0.15, 0.12), and a maximum brightness of 925 cd/m^2 was obtained. The observed 4.1% external quantum efficiency at 100 cd/m^2 is among the highest reported to date for blue OLEDs. The high T_g (133 °C) of the oligoquinoline renders the molecule extremely stable in the amorphous form leading to the observed blue spectral stability. Since the oligoquinolines are readily synthesized and purified, derivatives of BDPQ are excellent candidates for further synthesis and development as blue emitters and electron transport materials for blue OLEDs.

2.2.b Color-tunable Polymer LEDs

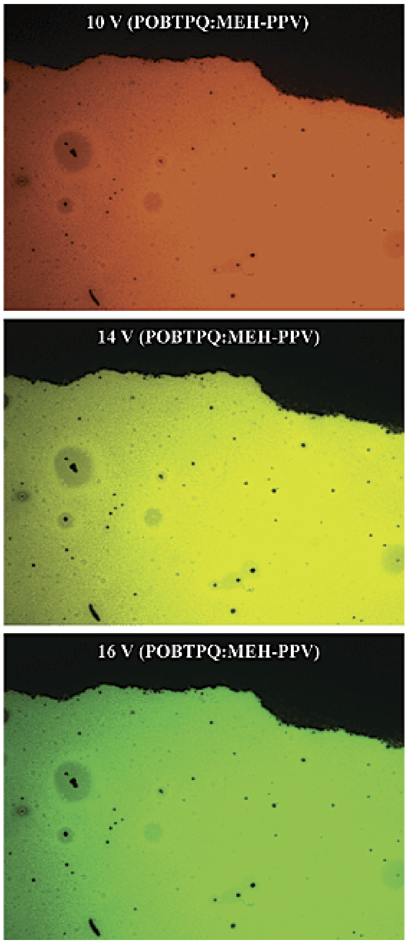

Figure 5. EL micrographs (×10) of a POBTPQ:MEH-PPV (30:70 wt %) blend LED.

Nanophase-separated blends of acceptor and donor conjugated polymers. Although electroluminescence (EL) from blends of emissive conjugated polymers has been reported, all of the prior blends have been *unipolar* in the sense that the components were of the same type: either *all-p-type or all-n-type.* Prior reports of blends of donor (p-type) and acceptor (n-type) conjugated polymers showed that they generally undergo photoinduced charge transfer and separation, leading to quenching of EL and enhancement of photovoltaic properties. We observed efficient EL in LEDs from binary blends of the acceptor conjugated polymer poly(2,2'-(3,3'dioctyl-2,2'-bithienylene)-6,6'-bis(4-phenylenequinoline)) (POBTPQ) with donor conjugated polymer poly(2-methoxy-5-(2'-ethylhexyloxy)-1,4-phenylenevinylene) (MEH-PPV) or poly(3-octylthiophene) (POT). To our knowledge, there is no prior literature report of EL from blends of donor and acceptor conjugated polymers. Efficient Forster energy transfer was observed in both blend systems. Voltage-tunable orange-red↔yellow↔green EL (Figure 5) was observed in the POBTPQ:MEH-PPV blend diodes at a composition of 10-80 wt % MEH-PPV. Only red emission characteristic of POT was observed from POBTPQ:POT blend devices due to efficient energy transfer from POBTPQ. The different EL characteristics of the two blend systems resulted from the different nanophase-separated morphologies revealed by AFM; the POBTPQ:MEH-PPV blends had a spinodal decomposition type morphology with 90-120 nm domains, whereas nucleation and growth type morphology was seen in the phase-separated POBTPQ:POT blends. Our results demonstrate that efficient EL can be achieved in bipolar blends of conjugated polymers by judicious selection of the blend components such that efficient energy transfer rather than charge transfer occurs. Additionally, nanophase-separated morphology is essential to voltage-tunable multicolor light emission in the blend LEDs.

2.2.c Polyfluorene-Based Blue and Green LEDs

Polyfluorenes are attractive electroluminescent conjugated polymers for blue LEDs. One of the major current challenges in developing the polyfluorenes for blue LEDs is the poor spectral stability under normal device operation with a broad EL band centered at 530-540 nm evolving with passage of current, changing the pure blue emission to an undesired blue-green color. Various approaches have been tried to minimize or eliminate this undesirable long-wavelength emission band in polyfluorene-based LEDs. Additionally, the origin of the green emission band has been controversial and remains not fully understood. However, it is vital to understand the exact origin of the green emission, because this would dictate the future methodologies, both synthetic and device fabrication-related, for stabilizing the blue emission and paving the way for commercial realization of blue and full-color polymer LEDs.

Blue LEDs with good spectral stability based on blends of poly(9,9-dioctylfluorene). Spectrally stable blue electroluminescence (EL) was obtained from single-layer polymer LEDs fabricated from binary blends of poly(9,9-dioctylfluorene) (PFO) with either thermally stable poly(vinyl diphenylquinoline) (PVQ) or polystyrene. The additional green emission observed in the EL spectra of pure PFO devices was substantially suppressed in the blend LEDs. The origin of the spectral stability lies in the improved thermal stability of the binary blends due to the high glass transition temperatures (T_g) of PVQ (185 °C) or polystyrene (101 °C) relative to PFO (75 °C). Thus, we can make the electroluminescent material less susceptible to molecular rearrangements due to the applied electric field and related heat effects. Additionally, the brightness and EL efficiency of the polymer blend LEDs were enhanced by a factor of 5-14 compared to the PFO homopolymer devices. The electrical characteristics of the diodes and electric-field-modulated PL spectroscopy results indicated increased spatial confinement induced exciton stability and electron-hole recombination efficiency in the blend devices. These results demonstrate that blending of PFO with high T_g charge transport or charge blocking polymers is a simple strategy to overcoming the problem of poor spectral stability of blue-emitting polyfluorenes.

Origin of the green emission and bright green LEDs based on fluorenone-containing polyfluorenes. The additional low-energy emission band in blue-emitting polyfluorenes has been generally attributed to the formation of aggregates and/or interchain excimers in the polyfluorene films, and more recently to emissive keto (fluorenone) defect sites produced due to thermo- or electro-oxidative degradation of the polyfluorene backbone. So far, no clear verdict has been made on the exact nature of the controversial green emission band in polyfluorenes. We systematically investigated the photophysics of a series of four new copolymers of 9,9-dihexylfluorene and 9-fluorenone with well-defined structures and a new fluorene-fluorenone-fluorene trimer model compound (Chart 2) to elucidate the origin of the undesired green emission. The oligofluorene trimer, 2,7-bis(2'-9',9'-dihexylfluorenyl)-9-fluorenone (BFF), was shown to be an excellent model of the active green-emitting chromophore in polyfluorenes. Our steady-state PL data in conjunction with the PL decay dynamics of all fluorenone-containing copolymers and oligomer allowed us to conclude that the controversial 535-nm green emission of the polyfluorenes originates from the fluorenone defects in single-chain polymers, definitively ruling out interchain aggregate or excimer emission. Our results also suggest that some of the current methods of stabilizing the blue emission of polyfluorenes, such as dendronization and blending, likely impede the oxidation process that forms the fluorenone defects. In addition, bright green EL was achieved from single-layer copolymer LEDs with aluminum cathodes in air, with brightness levels in the range of 1600-3340 cd/m^2. These results demonstrate that although the fluorenone defects in the polyfluorenes

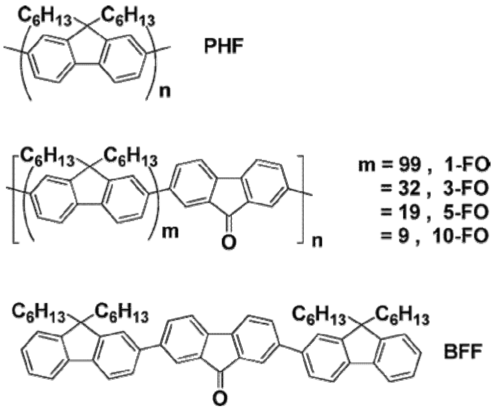

Chart 2. Molecular structure of fluorenone-fluorene copolymers and model compound BFF.

completely destroy the normal blue emission, the materials can instead be used as efficient green electroluminescent materials in LEDs.

2.2.d Thin Film Solid-State Electroluminescent Devices Based on tris(2,2'-bipyridine)ruthenium-(II) Complexes

The behavior of tris(2,2'-bipyridine)ruthenium-(II)-based light-emitting devices was investigated and shown to depend strongly on the nature of mobile ions. Moreover, traces of water in the tris(2,2'-bipyridine)ruthenium(II) film seemed to be intimately linked to the existence of mobile ions. A simple semiquantitative electrochemical model is proposed for describing both the transient and the steady-state behavior of light-emitting devices based on tris(2,2'-bipyridine)ruthenium(II) and light-emitting electrochemical cells in general. A model describes well the transient behavior of these electroluminescent devices, proving that they are, in fact, light emitting electrochemical cells. The experimental data correlated with simulation results indicated that for low applied voltages, electrons are the main carriers in tris(2,2'-bipyridine)ruthenium(II) light-emitting devices, while for larger voltages, the device becomes bipolar.

The stability of tris(2,2'-bipyridine)ruthenium-(II)-based light-emitting devices is greatly improved when they are produced and operated under drybox conditions. The proposed mechanism of the light-emitting device degradation involves formation of a quencher in a small fraction of tris- (2,2'-bipyridine)ruthenium(II) film adjacent to a cathode, where light generation occurs. The formation of a quencher was also accompanied by an increase in device resistivity. Observed for the first time, the electroluminescence profile in tris(2,2'- bipyridine)ruthenium(II) device constructed on interdigitated electrode arrays demonstrated that the charge injection in such devices is highly asymmetric because of more efficient hole injection. A microscopic study of photo- and electro-luminescence profiles of planar light-emitting electrochemical cells was shown as a useful approach for studies of charge carrier injection into organic films.

2.2.e Spectroscopy and Photophysics of Luminescent Polymers

Understanding relationship between polymer morphology and fluorescence spectrum and quantum yield. *Pei Wang* and *Jui-Hung Hsu* did a variety of experiments under TOPS MURI support to verify the "two species" hypothesis and to identify the structure of the two species. This model suggests that there are primarily two configurations of the polymer, namely the well-packed form and the more extended solution-like form. Film spectra are a composite of these and, because the solution-like sites have much higher quantum yield, the amount of them represented in a film spectrum is a good indicator of quantum yield. This was verified by systematic studies of phenylenevinylene polymers and oligomers in mixed solvents. Poor solvents were introduced to controllably initiate packing and the resulting spectroscopic changes were studied by absorption, luminescence, transient absorption, NMR and excitation spectroscopy. All of these could be understood quantitatively in terms of the model. In addition, NMR shows that the main structural difference between the two forms of the polymer is that backbone motion is suppressed in the packed form. This leads to less shaking of the pi cloud and apparently longer conjugation length. This explanation of the red shift is in contrast to literature that cites interchain species in the phenylenvinylenes. The model was verified directly in beautiful transient pump dump experiments done by *Pei Wang* and selective photooxidation experiments, each of which showed that the two species could be addressed independently. *Jui-Hung Hsu* further showed that the model applies well to trimers of MEH-PPV. He also did excellent studies of chain length dependence of the photophysics that was coupled with theoretical work done at the Institute of Atomic and Molecular Sciences in Taipei.

A second important discovery with regard to polymer photophysics was made in transient bleaching and gain experiments by *Pei Wang*. His work showed that some fraction of the excited population undergoes rapid internal conversion to the ground state. This has potentially important implications for the efficiency of electroluminescent devices. It has been widely assumed that recombination of electrons and holes injected into organic light-emitting diodes recombine to form excited singlet or triplet states. We think it is likely that the process that explains the rapid internal conversion we observe is interchain charge generation followed by rapid recombination to form the ground state directly (some of the charges may no longer have the energy to re-form the excited singlet). If this is the case, it suggests a third pathway for recombination of electrons and holes, one that also does not lead to light emission. The statistical recombination hypothesis that one forms 25 % singlet and 75 % triplet excited states does not allow for this additional possibility and would place additional constraints on design of solid-state organic emitters.

Another important conclusion that can be inferred from Wang's experiments is that a measurement of the photoluminescence quantum yield Φ_{PL} is *not* a measurement of the singlet excited state's probability to fluoresce Φ_F. This is often assumed to be the case in measuring photoluminescence yield Φ_{PL} with the idea of relating it to the maximum possible electroluminescence efficiency $\chi\Phi_F$ where χ is the fraction of recombination events that form excited state singlets. Wang's results make it clear that there are large populations of species other than singlets formed by photoexcitation so that the relationship between Φ_{PL} and Φ_F is not simple.

Reduction in efficiency of organic LEDs with increasing drive current. We decided to address this problem, brought to our attention by colleagues at Kodak, using an electroabsorption testbed that was set up for the MURI. *Arabinda Chowdhury* adapted this to do charge modulation spectroscopy in model OLEDs made at Kodak. He and *Terri Haskins* tested the hypothesis that the efficiency roll-off with drive current in OLEDs is caused by Förster transfer by the emissive species to nonemissive cations in the device. The initial studies were in hole-only devices with the structure ITO/IG/Alq_3:DCJTB/Alq_3/Mg:Ag where IG is a current blocking layer, Alq_3 is hydroxyquinolinealuminum and DCJTB is a highly fluorescent cyanine dye.

We have recently completed single pulse measurements where we study the charge injected and fraction of photoluminescence that is quenched simultaneously. From these data, we have extracted plots of the quenching versus cation concentration. Using the emission spectra of the DCJTB and the absorption of the cation from the charge modulation spectra, we have verified reasonably good agreement with the Forster model. This conclusion tells us how to most effectively choose dyes that will not suffer from current quenching from their spectroscopy.

We also observed a new hysteresis phenomenon, namely that traps are more effective at quenching during the extraction than during the injection cycle. We hired a local high school student *Aaron Burberry* for the summer to study this slow PL quench recovery and hysteresis. He was able to show that the trap release rate as measured by PL quench recovery depends on the host matrix HOMO level as expected, being much faster in NPB than Alq_3. We are currently testing models for the hysteresis in the device behavior.

Photophysics of highly emissive oligofluorenes. *Jane Wesely* has been studying the delayed emission from the efficient blue-emitting glassy oligofluorene F(MB)10F(EH)2 prepared by Chen's group. These oligomers have been used to make the best blue polymer LEDs yet reported. The delayed emission is due to charge photogeneration and later recombination and is much weaker than in analogous phenylenevinylenes our group has studied. The reduced amount of interchain charge generation allows for higher exciton survival rates and fluorescence quantum yields. Jane has observed temporal power law decay ($\sim t^{-1.4}$) of the emission from pristine F(MB)10F(EH)2 out to milliseconds, remarkable data that span seven to eight decades in time and intensity. The long-lived PL in the pristine sample has the same spectrum as the steady state emission and its linear intensity dependence makes the charge separation and recombination mechanism clear.

Beyond this, we have observed different delayed emission for photooxidized samples. Oxidation sites are known to be quenching defects in conjugated polymers and quite small concentrations can cause substantial quenching. The ability to see the emission spectra for these defects is therefore of great interest. Previous work has identified "keto defects" with fluorenone-like emission in polyfluorenes. We show that the situation is more complex in photooxidized F(MB)10F(EH)2. We observe two different emissions with different temporal behavior and temperature dependence. We tentatively assign the red band at 590 nm that has not previously been observed to emission from an exciplex between oxidation defects and the host material. Our group has collaborated with Chen’s group on a number of studies of oligofluorenes over the course of the MURI.

Finally, we completed the testbeds for which we were responsible and made those available to MURI collaborators. These include spectroscopic ellipsometry, current-voltage measurements for devices, an electroabsorption and saturated photovoltage apparatus, a facility to measure photoluminescence yields and a device fabrication set up.

2.2.f Monodisperse Oligofluorenes for Polarized Blue Emission

Under the TOPS-MURI sponsorship, our research aimed to develop glassy liquid crystals comprising well-defined molecular structures with a low to medium molecular weight. This material class is uniquely characterized by its ability to self-organize into ordered fluid films at an elevated temperature and to preserve molecular orientation in the solid state by way of glass transition without encountering crystallization. The key idea is to prevent packing of liquid crystal molecules into a three-dimensional crystalline lattice through both molecular and supramolecular considerations. This is an innovative approach to the preparation of macroscopically ordered solid films for photonics and electronics. To meet the TOPS-MURI program objectives, we focused on glassy liquid crystals potentially useful for tunable reflective coloration and polarized electroluminescence. Activities range from molecular design and material synthesis, processing of ordered films, and exploration of photonic device concepts. The most significant accomplishments are summarized below.

(i) Monodisperse Oligofluorenes Forming Glassy Nematic Films for Strongly Polarized and Efficient Blue Organic Light-Emitting Diodes, OLEDs. The first series of monodisperse glassy nematic oligofluorenes has been synthesized following a divergent-convergent approach. With optimized structural parameters, a T_g close to 150 ^{o}C and a T_c beyond 375 ^{o}C were achieved. These oligofluorenes were employed for the fabrication of strongly polarized and efficient, deep blue OLEDs. The requisite uniaxial molecular alignment was accomplished by spin-casting oligo(fluorene)s onto a PEDOT/PSS conductive alignment layer with subsequent thermal annealing under relatively mild conditions. Superior chemical purity and ease of material processing into monodomain films resulted in the highest EL dichroic ratio ever observed in polarized OLEDs. Furthermore, the polarized OLEDs using monodisperse oligo(fluorene)s showed a deeper blue emission with a higher luminance yield than those prepared with poly(fluorene)s. At roughly the same film thickness, the EL dichroic ratio increases with an increasing chain length because of the higher degree of uniaxial molecular alignment. For a given oligo(fluorene) sample, the thinner the film, the higher the EL dichroic ratio because of the stronger surface anchoring furnished by the rubbed conductive alignment layer.

(ii) Monodisperse Glassy-Nematic Conjugated Oligomers with Chemically Tunable Polarized Light Emission. A novel series of monodisperse conjugated oligomers were synthesized by inserting varied segments into blue-emitting oligofluorenes to complete the color gamut of light emission. These conjugated oligomers were lightly doped into a heptafluorene film for the construction of polarized OLEDs that generate green, red and white light via intermolecular Förster energy transfer. At a current density of 20 mA/cm^2, an emission peak polarization ratio up to 26, an integrated polarization ratio up to 19, and a luminance yield up to 6.4 cd/A have been accomplished. Compared to the previously reported polarized green and red OLEDs, the donor-acceptor approach resulted in superior polarization ratio and luminance yield. The first ever polarized white-light OLED has been achieved with an integrated polarization ratio of 16 and a luminance yield of 4.5 cd/A. All the CIE coordinates were found to be essentially independent of current density up to 100 mA/cm^2. Highly polarized OLEDs are potentially useful as an efficient light source for liquid crystal displays, for electroluminescent displays with improved viewing quality, projection displays, and stereoscopic imaging systems. In addition, efficient electroluminescence via energy transfer using monodisperse conjugated oligomers could lead to low threshold solid-state organic lasers with an added advantage of high polarization.

(iii) Origin of Strong Chiroptical Activities in Films of Nonafluorenes with a Varying Extent of Pendant Chirality. Novel nonafluorenes with a varying extent of pendant chirality were synthesized for an investigation of the origins of chiroptical activities in neat films. Thermal annealing of 4-μm-thick sandwiched films and of 90-nm-thick spin-cast films, all on surface-treated substrates, produced monodomain glassy films characterized as a right-handed cholesteric stack with a helical pitch length ranging from 180 to 534 nm and from 252 to 1151 nm, respectively. The observed strong circular dichroism, CD, and the degree of circularly polarized emission, g_e, as functions of helical pitch length in single-substrate monodomain glassy cholesteric films were quantitatively interpreted with a CPF theory accounting for light absorption, emission, and propagation in a cholesteric stack. Although intertwined molecular helices were likely to be present, cholesteric stacking of rod-like molecules seemed to be the predominant contributor to the strong chiroptical activities. All the cholesteric stacks comprising a polydomain glassy film on an untreated substrate were found to contribute to CD and g_e largely to the same extent as in a monodomain film. A circularly polarized blue OLED containing a nonafluorene film resulted in a g_e of 0.35 with a luminance yield of 0.94 cd/A at 20 mA/cm^2, the best performance to date.

2.3 Tunable Reflective Materials and Devices

2.3.a Deterministic Synthesis and Optical Properties of Enantiomeric Glassy Chiral-Nematic Liquid Crystals

A new series of morphologically stable, glassy chiral-nematic liquid crystals were synthesized following three distinct deterministic approaches. A glass transition temperature from 67 to 82 ^{o}C and a clearing temperature from 175 to 225 ^{o}C were accomplished. A helical pitch length from 188 to 210 nm emerged with enantiomeric 1-phenylethylamine as the chiral precursors, yielding selective reflection in the UV-region. With (+)-estrone as the chiral moiety, a selective reflection in the near infrared was observed. The concepts of high-performance circular polarizers, optical notch filters and reflectors were illustrated with a mixture of enantiomeric glassy chiral-nematics. Selective reflection wavelength can be readily tuned by varying chemical composition in terms of the ratio of enantiomers or that of chiral-nematic to nematic components.

Novel Glassy-Nematic Liquid Crystals for Nondestructive Optical Memory and Photonic Switching. The first morphologically stable glassy-nematic liquid crystal comprising a dithienylethene core has been successfully designed and synthesized to achieve elevated phase transition temperatures. One of the salient features of this material class is its ability to form a macroscopically ordered solid film in which the photoresponsive core's electronic transition moment is spontaneously aligned with the nematic director. As a result, refractive indices and optical birefringence can be modulated to a large extent by photochemical means. The selected dithienylethene core is characterized by its thermal stability, fatigue resistance, high quantum yields, and a fast response. Therefore, glassy-nematic liquid crystals present new opportunities for nondestructive rewritable optical memory and high-speed photonic switches, including spatial light modulators, filters, polarizers, and beam splitters for optical communication and image processing.

2.3.b Development of environmentally responsive materials

This program developed fundamental approaches for the design of optical materials capable of absorbing and emitting light. Materials that respond to electrical, chemical and photochemical simulation were investigated. Novel molecular designs were explored to best optimize these properties.

Detailed descriptions of our innovations can be found in previous annual reports and our publications. We summarize here important results in different areas of research.

Chemically Responsive Materials. The development of materials that undergo rapid easily detectable responses to toxic chemicals is an important first step that can guide the development of methods that can protect soldiers from chemical weapons. With this in mind we have developed indicator chromophores that respond as shown in Figure 6 to a reactive phosphate, diisopropyl-fluorophosphate. These indicators can be placed in thin polymer films to create coatings that are capable of being instrumented to give sensors. This continued development is being performed by Nomadics Inc. which has licensed this technology.

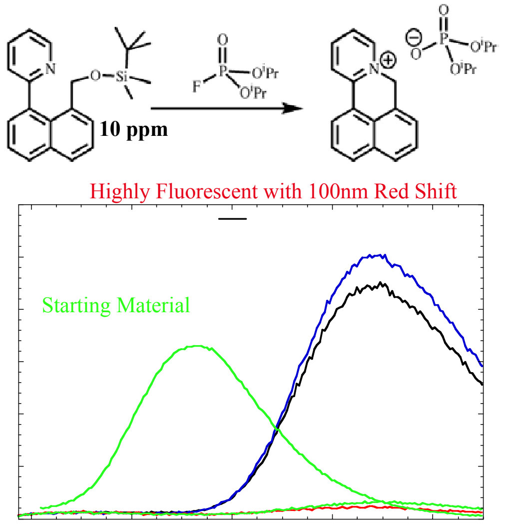

Figure 6. Indicator that undergoes highly sensitive fluorescence and absorption responses shown to reactive phosphates.

Supramolecular Architectures for Optimized Emissive Polymers. The central design paradigms of highly luminescent organic semiconductive polymers have focused on avoiding interchain interactions (3-D electronic interactions) due to the fact that these interactions almost universally give rise to dramatic reductions (> 100 fold attenuation) in their emission quantum yields. A downside to avoiding extended interpolymer electronic interactions is that it dramatically reduces the mobility of charges and energy throughout the medium. This has restricted the performance of semicondutive polymers in most electrooptic applications. We have developed an alternative novel method that produces stable highly fluorescent chiral 3-D grids using interlocking structural elements. In terms of optimizing fluorescent polymers for sensor, photovoltaic, and electroluminescent applications we believe these design principles are some of the most significant breakthroughs in the last few years. We have further shown that these chiral assemblies provide superior sensory properties for the detection of explosives and are excellent at discriminating between chiral molecules.

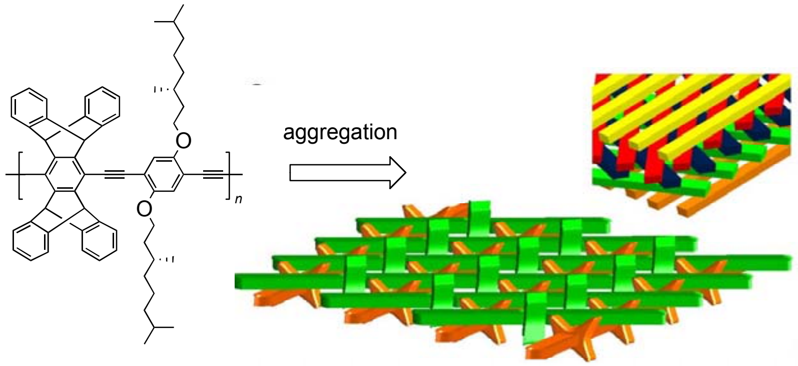

Figure 7. Aggregation of this chiral polymer creates grids that have 3-dimensional electronic structures and improved exciton and carrier mobility.

Methods for Aligning Polymers and Chromophores. Most optical methods for data presentation require highly anisotropic materials. To produce high performance optical materials we have developed a fundamental new method for generating high alignment of solutes in liquid crystals and polymers. The principle is based upon using rigid frameworks that promote specific orientations of solutes in order to minimize the amount of free volume in the composite structure. We investigated nematic liquid crystalline solutions of highly emissive semiconductive poly(phenylene vinylene)s and poly(phenylene ethynylene)s. The liquid crystalline solvent (a wide variety of nematics are acceptable) has the important feature that it creates an extended chain conformation that is highly aligned (S ranges between 0.7 and 0.8). As can be seen from simple switching studies in Figure 8 the poly(phenylene vinylene)s can be reoriented with the nematic host by application of electric fields. Additionally the polymers have greatly enhanced conjugation lengths in nematic LC solutions. Methods to extend conjugation lengths in electronic polymers are critical to optimize their transport properties.

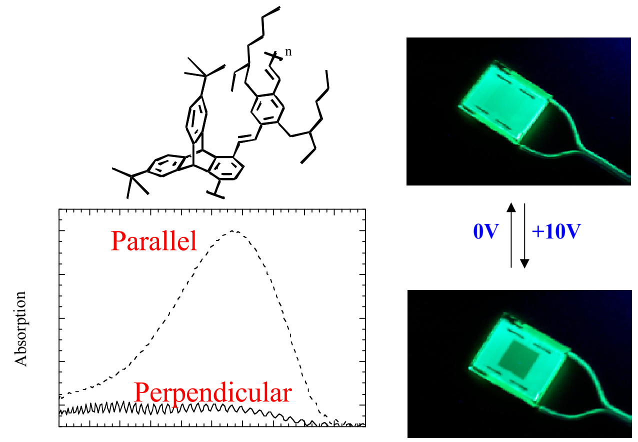

Figure 8. A 4-(*trans*-4-pentylcyclohexyl) benzonitrile nematic solution of the poly(phenylene vinylene) shown. The absorption spectra reveal that the backbone is aligned and the response in a test cell indicates that it tracks the nematic director.

Ultrastable Electrochromic Materials

In search of highly stable electrochromic materials, we have developed synthetic methods for the incorporation of polycyclic aromatic residues into a conjugated polymer backbone. Our process shown in Figure 9 involves a tandem cyclization-polymerization mechanism to produce aromatized monomers *in situ* prior to oxidative polymerization. Within this context a pendant thienyl monomer undergoes an oxidative cyclization to provide an aromatized material containing a bithiophene repeat unit planarized by a bridging benzeno segment. As shown this process can be used to create electrochromic materials that undergo reversible changes throughout the visible and near IR regions of the spectrum. These materials were remarkably stable relative to simple polythiophenes. This stability is attributed to the polycyclic aromatic structure. The tandem-cyclization-polymerization method in general can has been applied to a variety of other thiophenes and pyrrole monomers.

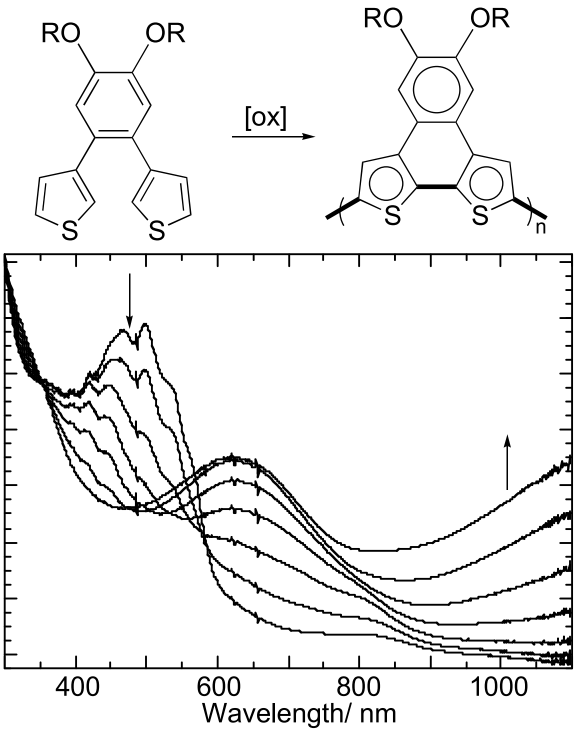

Figure 9. Reaction scheme showing the formation of the polycyclic aromatic polymer structure with oxidative polymerization and electrochromic behavior of the polymer. The large long wavelength absorption is consistent with a highly conductive material.

2.4 Thin Film Transistors for All-Plastic Electronics

Hole transport and p-channel polymer FETs. Since the regioregular poly(3-alkylthiophene)s have the highest reported hole mobilities (0.02-0.1 cm^2/Vs) and have been the most widely studied polymer semiconductors for thin film transistors, we initially used them to learn to fabricate and characterize polymer field effect transistors (FETs). The poly(3-hexylthiophene) (PHT) thin films (20-30 nm) spin coated from chloroform solution onto a SiO_2 surface on a Si substrate were revealed to be nanocrystalline by atomic force microscopy (AFM) and to have electrical properties characteristic of a p-channel FET. The field-effect hole mobility determined from the linear and saturation regions was 0.02 cm^2/Vs and the on/off current ratio was 10^4. This value of the hole mobility in regioregular PHT is comparable to the highest values previously reported for this polymer. The hole mobilities of the series of regioregular (> 98.5 % H-T linkages) P3ATs with different alkyl chain lengths from n-butyl to n-dodecyl were also determined. The mobility varied from 1.2×10^{-3} cm^2/Vs for poly(3-butylthiophene) (PBuT) and 2×10^{-1} cm^2/Vs for PHT to 2.4×10^{-5} cm^2/Vs for poly(3-dodecylthiophene) (PDDT). Contrary to a previous report which was based on *thick-film* (1-2 μm) FETs with poor on/off current ratios (<15), our repeated measurements showed that the hole mobility μ_h is not a decreasing exponential function of the alkyl chain length. In fact, we observed PHT to have the highest mobility in the series. It is likely that the n-hexyl side chain is optimum for charge transport because of better self-organization in PHT compared to PBuT with n-butyl side chains. These results underscore the fact that the structure-carrier mobility relationships in even the most widely studied polymer FETs, i.e. poly(3-alkylthiophene)s, remain to be fully understood.

Our most interesting new results in the area of hole transport in conjugated polymer semiconductors came from the first studies of *FETs based on polymer blends*. We investigated 5 different binary blend systems. Each of the series of blends contained regioregular PHT which has a high mobility: PHT/poly(3-decylthiophene) (PDT); PHT/poly(9,9-dioctylfluorene) (PFO), PHT/poly(2-methoxy-5-(2'-ethylhexyloxy)-1,4-phenylenevinylene) (MEH-PPV); PHT/ poly(4-hexylquinoline) (PHQ); PHT/polystyrene (PS). A number of interesting new phenomena were discovered in the polymer blend FET including: a novel “stair step” hole mobility dependence on blend composition in some of the blends; relatively high and constant hole mobilities over a broad blend composition range; and a large variation in the hole mobility depending on the dipole moments of the blend components, demonstrating large dipolar effects on the field-effect mobility of charge carriers in blends of conjugated polymers. These results clearly demonstrate that blends of conjugated polymers are alloy semiconductors capable of having high charge carrier mobility depending on the components and blending should also be considered a viable supramolecular engineering approach to enhancing or controlling the carrier mobility in conjugated polymer semiconductors

Electron transport and n-channel polymer FETs. Our initial studies of *electron* transport and the *field-effect mobility of electrons* in polymer semiconductors have focused on a ladder polymer poly(benzobisimidazobenzophenanthroline) (BBL). We discovered that by controlled BBL thin film processing the intrinsic electron mobility can be increased to 5×10^{-4} cm^2/Vs, *demonstrating for the first time n-channel polymer FETs with electron mobilities exceeding* 10^{-4} cm^2/Vs. Initial study of other n-type conjugated polymers such as poly(*p*-phenylene benzobisthiazole) (PBZT) and the polyquinolines PPQ and PHQ showed no FET activity. We therefore investigated n-channel polymer blend FETs made from BBL/PBZT blend system. The measured field-effect mobility of electrons in the BBL/PBZT blend system showed “stair-step” composition-dependence similar to our other blend FETs. The estimated electron mobility in PBZT was 2×10^{-7} cm^2/Vs.

Our most exciting breakthrough in polymer FETs to date is the recent fabrication of air-stable n-channel field-effect transistors from a solution spin coated, nanocrystalline, conjugated ladder polymer BBL and observation of electron mobilities as high as 0.05 to 0.1 cm^2/Vs and on/off current ratios of up to $5x\ 10^5$ (Babel, A.; Jenekhe, S. A. *J. Am. Chem. Soc.* **2003**, *125*, 13656). These results were achieved as a result of advances in the controlled thin film processing of the ladder polymer. In conjunction with the present FET studies, we used atomic force microscopy (AFM) to examine the morphology of BBL thin films (35-40 nm) processed under identical conditions as used for the FET fabrication. The AFM images reveal nanoscale sheets that are randomly oriented within the film (Figure 10a). We consider these films to be polycrystalline with nanocrystalline grains in view of the AFM images, prior X-ray diffraction results on similar BBL thin films and our unpublished electron diffraction results. Typical n-channel FET output characteristics were observed as exemplified in Figure 10b for a device with channel width (W) and length (L) of 1500 and 30 µm, respectively.

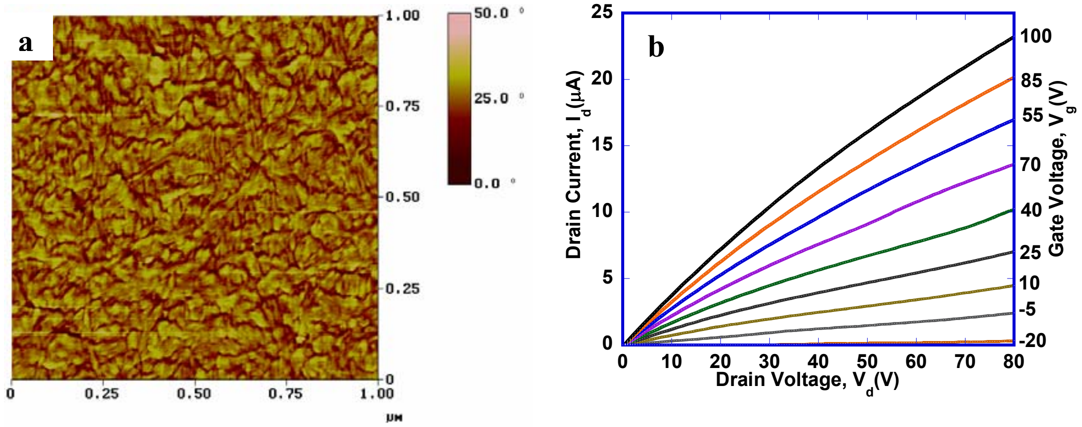

Figure 10. BBL thin films: (a) AFM image and (b) output characteristic of a BBL FET.

Ambipolar polymer blend thin film transistors. Ambipolar thin film transistors based on a series of air-stable, solution-processed, blends of an n-type polymer poly(benzobisimidazobenzophenanthroline) (BBL) and a p-type small molecule, copper phthalocyanine (CuPc) have been demonstrated, where all fabrication and measurements were performed under ambient conditions. The hole mobilities were in the range of 6.0×10^{-6} to 2.0×10^{-4} cm^2/Vs and electron mobilities were in the range of 2.0×10^{-6} to 3.0×10^{-5} cm^2/Vs, depending on the blend composition. UV-Visible spectroscopy and electron diffraction showed crystallization of CuPc in the metastable α-crystal form within the semicrystalline BBL matrix. These CuPc domains developed into elongated ribbon-like crystalline nanostructures when the blend films were processed in methanol, but not when they were processed in water. On methylene chloride vapor annealing of the blend films, a phase transformation of CuPc from the α−form to the β−form was observed, as shown by optical absorption spectroscopy and electron diffraction. Ambipolar charge transport was only observed in the blend films where CuPc crystallized in the elongated ribbon-like nanostructures (α-form). Ambipolar behavior was not observed with CuPc in the β-polymorph. Unipolar hole mobilities as high as 2.0×10^{-3} cm^2/Vs

were observed in these solution processed blend FETs on prolonged treatment in methanol, comparable to previously reported hole mobilities in thermally evaporated CuPc FETs. These results show that ambipolar charge transport and carrier mobilities in multicomponent organic semiconductors are intricately related to the phase-separated nanoscale and crystalline morphology (Babel, A.; Wind, J. D.; Jenekhe, S. A. *Adv. Funct. Mater*. **2004**, *14*, 891).

3. Publications

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(d) Manuscripts submitted, but not published

1. Kwon, T. W.; Alam, M. M.; Jenekhe, S. A. "n-Type Conjugated Dendrimers: Convergent Synthesis, Photophysics, Electroluminescence, and Use as Electron-Transport Materials for Light-Emitting Diodes," *Chem. Mater.* **2004**, *Special Issue on Organic Electronics*, ASAP (published on web 06/05/04).

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5. Kulkarni, A. P.; Tonzola, C. J.; Babel, A.; Jenekhe, S. A. "Electron Transport Materials for Organic Light Emitting Diodes," *Chem. Mater., Special Issue on Organic Electronics*, **2004**, Accepted.

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10. Kulkarni, A. P.; Zhu, Y.; Jenekhe, S. A. "Quinoxaline–Containing Polyfluorenes: Synthesis, Photophysics, and Stable Blue Electroluminescence," *Macromolecules*, Submitted.

11. Wesely, E. J.; Rothberg, L. J.; Chen, S. H.; Geng, Y. H.; "Population of and emission by photooxidation defects in an oriented oligofluorene," *J. Chem. Phys*., Submitted.

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14. Liao, M. S.; Kar, T.; Scheiner, S. "Effects of Peripheral Substituents and Axial Ligands on the Electronic Structure and Properties of Iron Phthalocyanine," *Inorg. Chem*., Submitted.

(e) Technical reports submitted

None.

4. Scientific Personnel and Honors/Awards/Degrees

A. Senior Personnel

S. A. Jenekhe (UW), A. J. Bard (UT), S. H. Chen (UR), P. T. Hammond (MIT), L. J. Rothberg (UR), S. Scheiner (USU), and T. M. Swager (MIT).

B. Postdoctoral Research Associates:

Maksudul M. Alam (UW), now a post-graduate researcher at The Crump Institute for Molecular Imaging, University of California, Los Angeles; **Mihai Buda** (UT), now at the "Politehinca" University of Bucharest, Romania; **Arabinda Chowdhury** (UR), is now a professor at a University in India; **Fernando Fungo** (UT), now at Universidad Nacional De Rio Cuarto, Dept. of Chemistry; **Frank G. Gao** (UT), now at Broadley-James Corporation, California; **Yanhou David Geng** (UR), now a Professor of Polymer Chemistry, Changchun Institute of Applied Chemistry; **Sergiu M. Gorun** (USU), now at New Jersey Institute of Technology; **Dr. Jui-Hung Hsu** (UR), is now a Research Associate at a University in Taiwan; **Dr. Dimitris Katsis** (UR), now a Senior Engineer, Microdisplay Corporation, San Pablo, California; **Dongwahn Lee** (MIT), now an Assistant Professor at Indiana University; **Wenming Li** (UR); **Yun Lu** (USU), now a faculty member at Southern Illinois University, Edwardsville; **David T. McQuade** (MIT), now an Assistant Professor at Cornell University; **John C. Mastrangelo** (UR), now at Naval Research Laboratory, Washington D. C.; **Jocelyn Nadeau** (MIT); **Soley Ozer** (UT), now at Intel Corporation, Oregon; **Vernon D. Parker** (USU), now a Professor at Utah State University; **Donald Pile** (UT); **Anthony Pullen** (MIT), now a Research Chemist at A123 Inc.; **Maurizio Quinto** (UT), now at the Universita degli Studi di Froggia, Italy; **Takeshi Shioya** (MIT), now a Research Chemist at Mitsubishi Chemical Corporation, Japan; **Arkadi Vigalok** (MIT), now an Assistant Professor of Chemistry at Tel Aviv University in Israel; **Dr. Zhenjia Wang** (UR); **Shigehiro Yamaguchi** (MIT), now an Associate Professor at Nagoya U., Japan; **Steffen Zahn** (MIT); **Shi-Wei Zhang** (MIT), now a Research Chemist at a small start-up company; **Zhengguo Zhu** (MIT); now a Research Chemist at Kanarka Inc.

C. Graduate Students:

John P. Amara (MIT); **Amit Babel** (UW); **Paul Byrne** (MIT); **Philip Chen** (UR) is now an Assistant Professor at National Chiao-Tung University, Taiwan; **Sean W. Culligan** (UR); **Dean M. DeLongchamp** (MIT) is now at NIST as an NRC Postdoctoral Fellow; **Ankur Gupta** (UW); **Rebecca Lai** (UT); **Jinsang Kim** (MIT) is now an Assistant Professor at University of Michigan; **Abhishek Kulkarni** (UW); **Meng Sheng Liao** (USU); **Timothy M. Long** (MIT) is now a Postdoctoral Fellow at University of Illinois; **Aimee Rose** (MIT) is now a Research Chemist at Nomadics Inc.; **Chris Tonzola** (UW); **John D. Tovar** (MIT) is now a Postdoctoral Fellow at Northwestern University; **Jason Wallace** (MIT); **Pei Wang** (UR); **Jane Wesely** (UR); **Jordon H. Wosnick** (MIT) is now a Postdoctoral Fellow at University of Toronto; **Hsiao-Hua Yu** (MIT) is now a Senior Research Scientist at the Institute of Bioengineering and Nanotechnology in Singapore; **Nicole Zacharia** (MIT); **Yong Zhang** (UR); **Yan Zhu** (UW).

D. Undergraduate Students:

Bryan Bean (UW), **Angela Gifford** (UW), **Justin Kaffenberger** (UR), **Lisa Marshall** (UR), **Krista Novstrup** (UW).

E. Honors/Awards/Degrees

Senior Personnel

Samson A. Jenekhe (UW): Elected Fellow, American Association for the Advancement of Science (AAAS), 2003; Elected Fellow, American Physical Society (APS), 2003.

Allen J. Bard (UT): 2004 William H. Nichols Medal (NY-ACS); 2004 Welch Award in Chemistry; 2003 Presidential Citation (University of Texas at Austin); 2003 Honorary Doctorate

(Weizmann Institute of Science); 2001 Pittsburgh Analytical Chemistry Award; 2001 Career Research Excellence Award; 2002 Priestley Medal (American Chemical Society); 2000 Honorary Doctorate (Texas A&M University).

Paula Hammond (MIT): Mark Hyman, Jr. Associate Professor Chair, July 2003; Radcliffe Fellow, Harvard University, Fall 2003; Junior Bose Teaching Award January, 2000; Lloyd Ferguson Young Scientist Award, NOBCChE, March, 2000; GenCorp/Omnova Solutions Signature University Award, May, 2000; Joseph P. Mares Career Development Assoc. Chair, July, 2001; NSF Project Creativity Extension from Polymer Program, DMR, September, 2001.

Degrees:

Bryan Bean (B.S., 2003); Philip Chen (Ph.D., 2003); Dean DeLongchamp, Ph.D. (May 2003); Ankur Gupta (M.S., 2002); Rebecca Lai (Ph.D., 2003); Jinsang Kim (Ph.D., 2001); Timothy M. Long (Ph.D., 2002); Krista Novstrup (B.S., 2004); Aimee Rose (Ph.D., 2003); John D. Tovar (Ph.D., 2002); Pei Wang (M.S., 2000); Jordon H. Wosnick (Ph.D., 2004); Hsiao-Hua Yu (Ph.D., 2003);

5. Report of Inventions

1. Chen, S. H.; Fan, F. Y. "Glass-Forming Liquid Crystalline Compositions of Low Molar Mass and Optical Devices Formed Therefrom," U. S. Patent No. 6,730,242 B2; May 4, 2004.

2. Chen, S. H.; Geng, Y. "Light-Emitting Organic Oligomer Compositions," European Patent Application No. 02 747064.0, 19 February 2004.

3. Chen, S. H.; Chen, P. H. M. "Glassy Chiral-Nematic Liquid Crystals and Optical Devices Containing the Same," U. S. Patent Application No. 10/805,150, 19 March 2004.

4. Chen, S. H.; Geng, Y. "Monodisperse Conjugated Oligomers with Chemically Tunable Polarized Light Emission," U. S. Patent Application filed, 22 July 2004.

5. Chen, S. H.; Fan, F. Y. "Glass-Forming Liquid Crystalline Compositions of Low Molar Mass and Optical Devices Formed Therefrom," U. S. Patent No. 6,558,572 B2; May 6, 2003.

6. Culligan, S. W.; Geng, Y.; Chen, S. H.; Klubek, K. P.; Vaeth, K. M.; Tang, C. W. "Organic Light-Emitting Diodes for Production of Polarized Light," U. S. Patent Application filed, 28 February 2003.

7. Swager, T. M.; Zahn, S. "Emissive, High Charge Transporting Polymers," US Patent Application 60/396,028 July 16, 2003.

8. Swager, T. M.; Kim, T. –H.; Zhang, S. –W. "Detection of Chemical Species including Warfare Agents," US Patent Application 10/324,064, October 6, 2003.

9. Chen, S. H.; Geng, Y. “Light-Emitting Organic Oligomer Compositions,” U. S. Patent Application No. 10/199,099, 22 July 2002.

10. Culligan, S. W.; Geng, Y.; Chen, S. H.; Klubek, K. P.; Vaeth, K. M.; Tang, C. W. “Organic Light-Emitting Diodes for Production of Polarized Light,” U.S. Patent Application, February 2003.

11. Chen, S. H.; Chen, H. P.; Geng, Y. “Photoresponsive Glassy Liquid Crystals for Optical Memory and Photonic Switching,” U.S. Provisional Patent Application January 2003.

12. Hammond Cummingham, P. T.; DeLongchamp, D.; Tokuhisa, H. “Solid Polymer Electrolytes From Ethylene Oxide-Containing Layer-By-Layer Assembled Films,” Hammond Cummingham, P. T.; DeLongchamp, D. “Solid Electrolyte Created By Layer-By-Layer Assembly,” MIT Case Nos. 9722 and 9291. Patent application filed by MIT both domestically and internationally in Spring 2003.

13. Swager, T. M. Zhang, S. W. “Highly Specific Fluorescent Indicators for Chemical Warfare Agents,” 2003.

14. Jenekhe, S.A.; Zhang, X. “Tunable Multicolor Electroluminescent Device,” U.S. Patent 6,605,904, Aug. 12, 2003.

15. Swager, T. M.; Long, T. M., Zhu; Z. “Polymers with High Internal Free Volume” U.S. Patent Application, August 21, 2001.

16. Farhat, T. R.; Hammond Cunningham, P. T. “Fabrication of a Polymer Electrolyte Fuel Cell using the Layer-by-Layer Technology.”

17. Hammond, P.T.; DeLongchamp, D. “Solid Electrolyte Created by Layer-by-Layer Assembly,” Case No. 9291.

18. Hammond, P.T.; DeLongchamp, D. “Electrochromic Device Created by Layer-by-Layer Assembly,” Case No. 9292.

19. Hammond, P.T.; DeLongchamp, D. “Ethylene glycol/oxide and salt-containing solid electrolyte created by layer-by-layer assembly,” Case No. 9722.

20. Gao, F. G.; Liu, C-Y.; Buda, M.; Bard, A. J. Application Provisional Patent Application: “High Brightness and Low Voltage Operated LEDs Based on Inorganic Salts as Emitters and Conductive Materials as Cathodic Contacts,” Serial No. 09/872,163.