

II. RESEARCH

Performance and Management Indicators

The performance and management indicators are as indicated in the Strategic Plan. Because the Center has been functioning for such a very short period of time, it is unrealistic to attempt to draw sweeping conclusions concerning performance; however, all indicators would suggest that the Research Component is well ahead of schedule and that the research management structure is functioning effectively. Research successes have attracted national attention and have motivated decisions in both industry and the Federal government. Material and device benchmarks appear to be either met or exceeded; however, because of the very early stage of research and knowledge/tranfer of research products, it would seem unwise to revise indicators at this time. The performance benchmarks and management indicators outlined in the Strategic Plan were carefully developed in a consultative manner with participation of STC personnel, the Strategic Advisory Board, industrial input, and input from NSF panels and staff. We are confident that only minor adjustments (if any) are required and these are best considered after the site visit review on July 7-8, 2003.

No problems have been encountered that have impeded progress toward the Center's Research Goals. Indeed, as noted above, progress is either as anticipated or exceeding expectations. For the sake of completeness in this report, we note that the following issues are being addressed during this reporting period.

The anticipated move of Professors Marder, Perry, Brédas, and Kippelen to Georgia Institute of Technology is being actively accommodated. The Center Management Team has been actively involved in assuring that this move does not affect in any negative way the research (or other critical functions) of this Center. Proactive management appears to be turning this event into an important opportunity for the Center to expand its impact in research, education, outreach, knowledge transfer and technology transfer.

The device development efforts involving ring microresonators, superprisms, photonic crystal structures, and controlled critical coupling structures are novel and, as such, critical materials processing issues had not been addressed. These were truly "new" efforts and effective teams of material scientists and device engineers had to be assembled and coordinated into a force that could quickly adapt to specific problems such as materials integration on the nanometer scale. In truth, anticipated problems have been quickly addressed and surprisingly successful results are being realized. Effective exchanges of personnel are occurring between universities and between universities, participating industries, and government laboratories.

While we anticipate future problems (both of scientific and management natures), the resources and management structure of an STC appears to provide a very effective paradigm for dealing with problems that would be much more challenging if encountered in a single investigator format.

THRUSTS

Thrust Name	Organic Electro-Optic and All Optical Switching Materials and Devices
PI Name	Thrust Leader: Alex Jen

Goals and Benchmarks:

The vision in this thrust is to develop “disruptive” E-O and AOS materials and devices for lightweight, low drive voltage, and ultrahigh-speed information processing. This will be achieved through “end-to-end” cross-disciplinary collaboration in theory, material synthesis, processing, and device design and fabrication. The E-O activity of materials will be significantly enhanced through improved poling efficiency of dendrimers that are developed through theory-guided structural design to overcome deleterious inter-chromophore interactions. Five-year goals of the thrust are to: (i) develop materials with high E-O activities ($r_{33} > 100$ pm/V); (ii) develop traveling wave and resonant E-O devices and processes to increase bandwidths (> 100 GHz-cm) and lower drive voltages (< 0.7 V); (iii) demonstrate long-term thermal stability at 85°C and photochemical stability (input power of 20 mW) of the operating devices. Ten-year goals are to (i) further enhance E-O activities ($r_{33} > 200$ pm/V), increase bandwidths (> 200 GHz-cm), and lower drive voltages (< 0.3 V); (ii) scale-up the synthesis of high performance E-O materials; (iii) demonstrate AOS device feasibility; (iv) integrate E-O devices with organic electronic circuitry developed in the Center; and (v) develop highly integrated modules that satisfy the standards of the Telecommunications Industry (Telecordia standards).

Connection of Thrust to STC Goals: This thrust provides a linkage between advanced optical materials and innovative processing techniques to develop powerful new photonic devices.

Industrial Participants: Agilent, Boeing, Corning, DuPont, Intel, IPITEK, Lucent, Lockheed-Martin, Lumera, Motorola.

Activities, Highlights, Outcomes, and Future Plans

(1) Development of Improved Electro-Optic Chromophores: A number of new chromophores have been prepared and evaluated. Paradigms for the systematic improvement of molecular first hyperpolarizability have been identified through effective coordination with the **Theoretical Thrust**. These include the following:

- (a) Replacement of methyl groups on the cyanofuran acceptor (of FTC and CLD type chromophores) with one or two trifluoromethyl groups leads to factors of 1.5-2.0 improvement in molecular hyperpolarizability (β).
- (b) Replacement of one or two cyano groups of the cyanofuran acceptor with strong acceptor groups like nitro groups or the sulfonyl trifluoromethyl groups leads to factors of two improvements in molecular first hyperpolarizability. These observations suggest the paradigm of mixed ligand acceptors for improving beta.
- (c) Development of gradient bridge structures (containing a thiophene moiety on the electron donor half of the bridge and a thiazole moiety on the electron acceptor half of the bridge) leads to improved molecular first hyperpolarizability.
- (d) Development of new acceptors (e.g., replacement of the methylene ether moiety of the cyanofuran acceptor with an amide moiety) leads to significant improvement of molecular first hyperpolarizability.
- (e) Preliminary success has been realized in developing new donor segments.

Individually the above advances have already led to record electro-optic activity with coefficients greater than 100 pm/V (100-130 pm/V) realized at both 1.3 and 1.55 microns telecommunication wavelengths. These values are 3-4 times greater than those of lithium niobate. When implemented together, these theoretically inspired chromophore modifications may lead to still further improvement in molecular first hyperpolarizability. Long-term stability at 85°C has been demonstrated for these chromophores in a high glass transition polyquinoline (PQ-100) host polymer. Future research will focus on combining the above-mentioned strategies together with

synthesizing, in some cases, longer versions of the above chromophores. This activity should lead to further improvements in molecular first hyperpolarizability. Chromophores will be incorporated into a variety of hardened lattice structures (see below) and the resulting materials will be transitioned to device prototyping after synthetic production has been optimized.

(2) Development of New Synthetic Methodology Including Microwave Synthesis Techniques: A number of synthetic reaction scheme improvements have been realized by **Jen** and **Dalton** that increase the yield in the synthesis of electro-optic chromophores; however, the most important general advance in the synthetic area has involved the application of microwave synthesis techniques. Microwave synthesis has permitted dramatic improvements in reaction yields and the shortening of reaction times for a number of coupling, protection/deprotection, etc. reactions central to the preparation of electro-optic chromophores. Moreover, microwave-assisted synthesis techniques have permitted, for the first time, isolation of the key imine intermediate crucial to the synthesis of mixed ligand acceptor chromophores. The outcome has been the production of chromophores exhibiting record hyperpolarizability. Future plans call for increased utilization of microwave synthesis and ultimately translating the capability to scale-up conditions. Commercial suppliers of microwave synthetic equipment have become very interested in our success; support both for research and educational purposes may become available from these suppliers.

(3) Development of New Capabilities for Improved Measurement of Beta: The STC currently houses perhaps the only remaining active HyperRayleigh Scattering (HRS) measurement facility available for the characterization of molecular first hyperpolarizability. This facility has been upgraded and is being modified for wavelength agile measurement capability in the infrared (0.7-2.5 microns) by **Reid** and **Dalton**. Previous facilities typically permitted measurement only at one fixed wavelength such as 1.06 microns. Our new instrumentation has been utilized for hyperpolarizability measurements on the chromophores synthesized by researchers of this STC. Measurements have also identified problems with values determined for traditional reference standards and an attempt is being made to obtain improved values for commonly used reference standards. The basis of the improved capability is the fundamental advance in laser, detector, and parametric amplifier components realized over the past five years. This facility will likely become a national resource for the characterization of molecular first hyperpolarizability. Future work calls for affecting measurement of chromophores synthesized so as to understand factors contributing to both molecular hyperpolarizability and the translation of that hyperpolarizability to macroscopic electro-optic activity. Beta must be known if order parameters are to be defined from macroscopic electro-optic activity coefficients. Future plans call for complementing HRS measurements with other related measurements.

(4) Synthesis of Electro-Optic Dendrimers and Dendronized Polymers: A variety of electro-optic chromophores containing dendrimers and dendronized polymers have been prepared by **Jen** and **Dalton** that lead to significant (e.g., factors of 2 or 3) improvements in electro-optic activity compared to the same chromophores existing in chromophores/polymer composite materials. Values of over 100 pm/V have been achieved even for chromophores available at the start of this STC. Such materials have also been found to lead to improved optical transparency (reduced optical loss) and to improved stability (both thermal and photochemical). Important integrated activities between nanometer scale materials synthesis and processing and the statistical mechanical calculations of the Theory Thrust have resulted in dramatic improvements in ferroelectric chromophore order (acentric order parameters). A great breakthrough in the realization of ferroelectric order for nanostructured materials are being achieved that could ultimately lead to electro-optic materials exhibiting activity of many hundreds of picometers/volt. Future work will focus on (1) exploring new supramolecular material architectures (working with

theorists of the Theory Thrust) with the aim of increasing acentric order parameters and perhaps even achieving perfect ferroelectric order and (2) incorporating new and improved chromophores into currently identified dendrimer and dendronized polymer architectures. The new integrated theory/synthesis team effort would seem a sure-fire approach to the realization of five-year objectives. As particularly successful architectures are identified consideration will be given to optimizing the chemistries leading to those materials and to the scale up of the reactions. Of course, new materials will be transitioned to device efforts and there will clearly be pressure for accelerating this process for new DARPA/NRO/MDA device programs.

(5) Development of Hardened Electro-Optic Materials: A variety of new lattice hardening (crosslinking) schemes have been developed by **Jen** group including protocols based on reaction of trifluorovinyl ether moieties for forming perfluorocyclobutane bridged polymers and based on the reverse Diels-Alder reaction. These protocols have led to hardened materials with thermal stability (assessed by the dynamic assay method) on the order of 200°C and have led to materials characterized by low optical loss. The outcome of this effort is the production of materials that appear to meet Telcordia standards. Future research will involve utilizing these protocols with new and improved chromophores and with new nanostructured material components (dendrimers and dendronized polymers).

(6) Exploration of Photochemical Stability: Singlet oxygen scavengers were shown to significantly enhance the photochemical stability of organic electro-optic materials. The addition of these materials to composite materials produces some plasticization of the polymer lattice. This plasticization facilitates oxygen diffusion and leads to accelerated photochemical decomposition of chromophores once the scavengers are consumed. Simple packaging to reduce oxygen exposure, together with the use of small concentrations of scavengers by **Dalton** and **Steier** groups, leads to dramatic enhancement of photochemical stability. The outcome of various accelerated studies of photochemical instability is the identification of several paradigms for dramatically improving photochemical stability of electro-optic materials and certainly improving materials to the point of adequate stability for commercial application. Future work will involve the combination of various identified methods of improvement (use of singlet oxygen quenchers, lattice hardening, chromophore modification including the use of steric protection of reactive sites) by **Dalton** and **Jen**. Knowledge gained will be applied to the utilization of new and improved chromophore materials.

(7) Investigation of Optical Loss: A number of studies of optical loss associated with absorption and scattering mechanisms were carried out by **Jen** and **Dalton** in a variety of collaborative studies both within the STC and external to the STC (e.g., photothermal deflection measurements on electro-optic materials produced within the STC but carried out by **Barto** at Lockheed Martin, Palo Alto). Partial fluorination of chromophore-containing dendrimers was shown to lead to significantly reduced absorption loss at telecommunication wavelengths. The trifluorovinyl ether crosslinking reagent (discussed above with respect to lattice hardening) not only leads to significantly enhanced thermal stability but also to low optical loss (e.g., to values as low as 0.1 dB/cm when coupled with significant fluorination of the electro-optic material). Detailed studies of optical loss were carried out in stripline and ring microresonator structures. Three loss mechanisms were identified for ring microresonators constructed from organic electro-optic materials and organic cladding materials: Material loss, scattering loss (from waveguide surface roughness), and bending loss. The former two loss mechanisms contribute about 1 dB of loss while the last mechanism dominates. Indeed, the last mechanism ultimately defines the size of ring microresonators that can be utilized. The outcome of this investigation of optical loss is a dramatically improved understanding of optical loss mechanisms in a variety of device structures. Moreover, optical loss values for devices fabricated from organic materials

are beginning to approach loss values for the best inorganic materials and dramatically smaller than the best loss values achieved for gallium arsenide (and related) electro-absorptive modulators. Future studies will focus on characterizing loss in new materials and new device structures including superprisms and photonic bandgap structures.

(8) *Waveguide Development with Soft Lithography:* We have successfully used soft-lithography to pattern channel waveguide structures for device fabrication. Several novel passive waveguide structures such as 1x4 coupler and array waveguide gratings have been fabricated by **Jen/Xia** and **Yariv** groups using a very low optical loss polymer (0.12 dB/cm @ 1.55 micron) developed by STC researchers. The outcome is an alternative to waveguide patterning by reactive ion etching (RIE) and photolithographic methods. Future studies will involve the utilization of newly developed materials and adaptation of the approach to the fabrication of active device structures.

(9) *Hybrid Material Waveguides:* Both hybrid polymer/sol-gel waveguide modulators and hybrid polymer/glass waveguide modulators have been successfully fabricated through the collaboration between the **Peyghambarian** and **Jen** groups. The hybrid approach overcomes certain limitations associated with an all-polymeric modulator approach, such as efficient and reliable coupling between single-mode fibers and modulators, reduced propagation losses, elimination of waveguiding instability, and better adaptability to general optical polarization conditions. We have demonstrated efficient vertical transition between sol-gel waveguide and electro-optic polymer, with similar results in ion-exchanged glass. We also have our first preliminary results on E-O modulation using hybrid E-O polymer/selectively buried sol-gel. This successful demonstration enabled inexpensive device fabrication, stable waveguiding, and easy fiber connection. Future studies will involve newly developed electro-optic chromophores and supramolecular (dendrimer and dendronized polymers) as the organic component of hybrid materials.

(10) *Integration of Photonic and Electronic Components:* **Steier** and **Dalton** have developed the methods to integrate the polymer devices with other photonic and electronic components and circuits into a single integrated module. We are studying the applications of polymers in an optical computer back-plane. During the period we have:

- Demonstrated an integrated Mach Zehnder modulator which uses the EO polymer only in the arms of the interferometer and uses low loss polymers elsewhere. This greatly reduces the chip loss and the fiber coupling loss.
- Demonstrated both single and two coupled polymer ring resonators and their application for a widely tunable optical source.
- Initiated a study of devices and waveguides for optical backplanes operating at 850 nm and 980 nm.

Future studies will utilize new materials developed within the STC and will involve increasing interaction with industrial research efforts including those at Intel, IBM, Agilent, Boeing, and Lockheed Martin as well as a number of smaller companies.

(11) *Exploration of Ring Microresonator Device Structures:* Well-established computational models and analyses have been used by **Steier** and **Dalton** to design polymer based waveguide-microresonator devices. The fabrication methods we have developed to create these devices are, in themselves, novel to EO polymeric optical devices. Initial work on single ring microresonators, which involved utilizing 2000 year vintage CLD/APC electro-optic materials, resulted in devices with free spectral range (FSR) values of 300 GHz to 1 THz and per channel modulation bandwidths of 12-18 GHz (Q values on the order of 1 million lead to wavelength discrimination of 0.01 nanometer at telecommunication wavelengths). Drive

voltages as low as 1 volt were used to effect manipulation of both digital and analog data at both 1.3 and 1.55 micron telecommunication bands. Double ring microresonator devices were fabricated by **Steier** that permitted tuning of an oscillator across the band of the erbium amplifier (1520-1560 nm). A voltage tuning of 0.04 nm/V and thermal tuning of 0.6 nm/mW was demonstrated. Side mode suppression was greater than 30 dB. A distinct advantage of organic microring resonators is that both thermal and athermal designs can be implemented. Microring resonators can be used for active wavelength division multiplexing (single chip rates of 500 Gb/s is a realistic short term goal), active wavelength selective filtering, 3-D optical interconnection, wavelength tuning of optical sources, and pulse storage & manipulation devices. Preliminary results have led to research support from Intel Corporation in the amount of \$75,000/year. Future work will focus on utilizing new active and passive materials (for realization of greater index of refraction contrast between active and cladding materials). Future studies will also explore a variety of new device designs including athermal designs. Device packages based on multiple resonators (e.g., WDM transmitter/receiver resonators) integrated on a single chip will be explored.

(12) Exploration of Photonic Bandgap Waveguide Structures: A collaborative study involving STC researchers at UW (**Dalton**), Caltech (**Scherer**), and USC (**Steier**) together with researchers at Boeing, Motorola, and Northwestern are exploring the incorporation of electro-optic and all-optical materials into very high Q photonic bandgap waveguide, ring nanoresonator, and superprism structures. A variety of deposition techniques (spin casting, vapor phase, and sequential self-assembly synthesis) are being explored. Theoretical and experimental studies are being correlated to define the maximum index change that can be achieved with different device structures. Preliminary results have supported a successful application to the DARPA chip scale wavelength division multiplexing (CS-WDM) for mobile platforms BAA. In this program, organic materials are directly incorporated into silicon device structures. Potential applications include analog and digital data management and a new generation of sensor technology. Future work will continue all of the studies that have been commenced, will compare the stability of photonic bandgap devices with standard stripline devices, and will incorporate newly developed materials into such devices.

(13) Exploration of Voltage-Controlled Critical Coupling Device Structures: Preliminary studies of device structures that effect data management by voltage control of critical coupling have been carried out. Work to the present has focused on proof of concept of device designs (which has been successfully demonstrated) and on incorporation of active materials into device structures. Future studies will focus on methods of incorporating active EO materials into device structures and on utilizing new electro-optic materials.

(14) Terahertz Signal Generation and Detection: Professor **Hayden**, University of Maryland Baltimore County (a seed project) has demonstrated successful generation and detection of terahertz signals utilizing organic electro-optic materials. The demonstrated performance exceeds that of any known inorganic materials. Future studies will focus on incorporating new electro-optic materials into device structures. Future studies will also focus on the issue of fabricating the thick film devices necessary for terahertz signal generation and detection.

(15) Fabrication of Low Insertion Loss Coupling Structures: A variety of low insertion loss coupling strategies have been explored with the outcome of achieving per facet coupling of better loss than 1 dB (as low as 0.1 dB) per facet. Professor **Lipson** of the Department of Electrical Engineering, Cornell University has joined this effort exploring tapered transition structures. Future work will involve continuation of the research which has been initiated.

(16) Improvement of All-Optical Materials: Integrated theoretical and experimental efforts have resulted in materials with improved third order optical nonlinearity. The results have contributed to the successful realization of additional support from DARPA for this area. Materials are being provided to Professor **Scherer** of Caltech for incorporation into photonic bandgap device structures. Future studies will continue this integrated research program and seek preliminary incorporation of materials into device structures (both fiber and resonated structures).

In addition to the above results, materials were provided to a number of research efforts external to the STC including the optical gyroscope program at China Lake Naval Weapons Laboratory/Army Redstone Arsenal; the electro-optic device program at the Air Force Research Laboratory (AFRL) at Wright Patterson AFB; the electro-optic device program at AFRL at Rome, NY; the electro-optic device program at Boeing, Seattle; the electro-optic device program at Lockheed Martin, Palo Alto; the electro-optic device program at University of Texas-Austin; the electro-optic device program at Photonics Systems; the electro-optic device program at Lumera Corporation; and to an electro-optic device program sponsored by Intel Corporation.

Thrust Name	Theory
PI Name	Thrust Leader: Bruce Robinson

Goal

The goal of the theoretical thrust is to provide the computational tools for the end-to-end design of materials and devices having unprecedented performance. This requires improved theory at all levels ranging from first-principles molecular quantum mechanics, to statistical mechanics for intermediate length scales, to the simulation of devices at the micrometer scale. In the early stages, the thrust will focus on fundamental quantum mechanical theory of individual molecules and its use to model charge transport in organic media and to develop force fields for use in statistical mechanical modeling. A short-term goal is the validation of models and codes by simulating properties of well-characterized materials. Five year goals are to (i) develop and use codes for simulating the properties of target materials to be used in the fabrication of new devices, and to (ii) develop codes that integrate quantum mechanical and statistical mechanical treatments of materials at the molecular level with electromagnetic wave propagation for simulating the performance of devices. Ten year goals of the thrust are to (i) produce and disseminate codes that are useful tools for the chemical design of materials and the engineering design of devices including codes for calculation of dielectric properties, nonlinear optical properties, charge transport, large structure optimization, molecular dynamics, and device response, and to (ii) evaluate the accuracy of the codes on test data sets and demonstrate use of the codes in systematically improving the performance of materials and devices. The goals of the theory thrust have not changed.

Management Indicators

In the first year, one of our management indicators has been the staffing of the individual groups that comprise the components of the theory thrust. Specifically, one of our major management goals has been the staffing of each group with qualified and well-trained individuals. As mentioned under problems, finding these individuals has been difficult. However, we have made progress in this area. In particular, bringing Bruce Eichinger from Accelrys into the project has been a major accomplishment. He is a polymer theoretician with an international reputation and has experience with DFT calculations and condensed matter theory. He has proven to be an important addition to the team. The Rehr group has added a new graduate student and is

still interviewing people for a postdoctoral position in their group. All other groups are fully staffed and ready.

Graduate student recruitment is highly competitive at the present time and while several offers were made, students chose to pursue their studies at other locations. After more extensive searching we have recruited and hired several extremely talented students.

The theory thrust provides fundamental understanding for the design of new EO and AO materials developed by the other thrust areas. The Brédas group works closely with the Marder, Perry, and Kippelen groups at the University of Arizona and more recently with synthesis and processing groups at the University of Washington. The Prezhdo and Robinson groups work closely with the Dalton and Jen groups at the University of Washington and more recently with groups across the STC. In both cases the theory groups calculate the energetics and the optical properties of proposed or recently synthesized structures to determine whether there are any flaws in the structures and whether the structures are likely to lead to new materials with improved properties. These theory groups compare methods and results on different test molecules, as will be discussed below.

Another indicator of success of the theory thrust is the development of a variety of computational techniques that are all compared among each other and with experimental data. As this comparative work continues, it will allow us to determine the best methods to use to interpret and validate the optical properties of the newly developed chromophores for the electro-optical materials. These codes will enable the development of materials with tuned optical properties and enable experimentalists to design devices having predictable optical characteristics.

The developments in the current year have moved on a broad front to tune the properties of individual chromophores, understand the advantages of dendrimer synthesis, optimize optical response conditions and concentrations, begin to cross check among different computational approaches, and finally to treat the problem of light interacting with ordered arrays of chromophores and with ordered patterns of chromophore and non-chromophore arrangements to determine the photonics properties of materials.

Theoretical guidance for the improvement of molecular hyperpolarizability:

Semi-empirical calculations of molecular first hyperpolarizability (β) have explained experimental observations made by researchers of this STC (see **Electro-Optic and All-Optical Materials Thrust**), researchers at Lockheed Martin, and researchers at Corning and have led to novel molecular architectures for development of next generation electro-optic materials.

The Brédas group, using a semi-empirical quantum theory codes -- Modified Intermediate Neglect of Differential Overlap (MINDO), has determined the optimal arrangement of acceptor groups on chromophores, when considering the placement of three acceptors which can be either -CN or -NO₂ moieties. The Robinson group has developed the Accelrys DMOL programs, which use DFT to determine the optical polarization parameters μ , α and β for a series of test molecules as well as novel molecules developed by the Jen and Dalton groups.

(a) The observation (by Dalton/Jen, Lockheed Martin, and Corning) that replacement of the methyl groups of the cyano furan acceptor (of FTC and CLD type chromophores) by trifluoromethyl methyl groups leads to improvement of molecular first hyperpolarizability has been simulated by several different types of quantum mechanical calculations.

(b) Quantum mechanical calculations predicted that replacement of the methylene ether segment of the cyanofuran acceptor with an amide moiety should lead to a factor of two improvement in molecular first hyperpolarizability. This prediction was subsequently verified by both hyper-Rayleigh scattering (HRS) and electro-optic measurements. Indeed, an electro-optic coefficient of 101 pm/V (at 1.55 microns wavelength) was recorded for a moderately short chromophore containing the new acceptor. Identification of this new acceptor represents a significant advance in the development of improved electro-optic materials.

(c) Quantum mechanical calculations and experimental measurements have confirmed that replacement of one or two of the cyano groups of the cyanofuran acceptor group with other strong acceptors such as nitro groups lead to significant improvements in molecular first hyperpolarizability. This new paradigm for developing improved chromophores can be described as exploiting "mixed ligand acceptors".

(d) Quantum mechanical calculations are being used to investigate new donors and bridge segments as well as acceptor segments. Preliminary results suggest several new paradigms for further improvement of electro-optic materials.

The outcome has been the simulation and development of dramatically improved chromophores. Future studies will consider chromophore structures that involve combinations of the above modifications.

Modified Atomistic Monte Carlo Calculations of Multi-Chromophore Containing Dendrimers:

The statistical mechanical methods developed by Robinson and Dalton have been extended to treat multi-chromophore-containing dendrimers. The approach is to develop modified atomistic Monte Carlo methods. Relatively rigid segments (e.g., electro-optic chromophores) of the supramolecular dendrimers are treated as rigid objects while flexible segments are treated in an atomistic manner. The Monte Carlo techniques include the effects of dipoles and van der Waals type forces. Calculations suggest that the motional restrictions associated with covalent bonds of dendrimer structures can assist the realization of acentric (near-ferroelectric) ordering under electric field poling. The outcome has been the realization of nanostructured materials leading to record electro-optic activity (greater than 100 pm/V at all telecommunication wavelengths and 3-4 times that of lithium niobate). Future studies will involve studies of dendronized polymers as well as further studies of multi-chromophore containing dendrimers.

The Robinson and Prezhdo groups have used these Statistical Mechanical methods to determine the most stable configurations for the 3 and 4 arm junction dendrimer-based chromophores developed by the Jen and Dalton groups. The results show why the 3 arm structure should give improved electro-optic properties (as confirmed by experiment). The Prezhdo group has reinforced these results by taking a different theoretical approach: Self-consistent, mean field theory has also explained the collective structures of chromophores and has shown the different phases that arrays of chromophores can adopt. In particular, they estimate that the 3 arm structure should be twice as effective as a simple chromophore (at comparable concentration) without the dendrimer connections. The Robinson and Prezhdo groups are comparing different methods to determine whether they give comparable explanations.

Standardizing the calculations

Of considerable importance is the use of a common molecular architecture among the various groups. The structure, a model chromophore developed and used by the Brédas group, is being used by the Robinson and Rehr groups as well now. With this structure the three groups are comparing the optical properties determined by the various, different computational

techniques. The Rehr group is developing codes to study the optical properties of large-scale arrays of chromophores. In particular, it is difficult to determine how a material with dynamic, light dependent refractive indices will respond to the light field and how it will scatter or bend light. Of considerable importance therefore, is to have a reference chromophore that has been optimized by many different methods.

Finding Super-Ordered States

The Robinson group has been exploring organization of dipoles to find arrangements that give enhanced order over the simple cubic lattice at the same density. They have found that placing the dipoles closer on the axis common with the poling field and further apart on the other axes (still keeping the overall density fixed) can increase the ordering by a factor of two. This increase comes in around 10% loading. The group is now looking for modified dipoles to extend the range of order up to 20% loading. At that point, one is competitive with conventional methods. If the trend continues then there will be a factor of two improvement. This architecture will then be converted into structures that will take advantage of this spatial arrangement of chromophores.

Understanding the ratio of singlet vs. triplet exciton formation in electroluminescent polymers.

The Brédas group has examined the cross-sections for intra- and inter-molecular recombination of a pair of positive and negative polarons into singlet and triplet excitons in model phenylenevinylene conjugated chains. The relative efficiency for singlet versus triplet exciton generation is found to be mainly determined by the energy separation, Δ_s , between the initial charge-separated state and the lowest-lying S_1 singlet excited state. The group will test whether these results transfer to larger conjugated polyenes that are of direct interest to experimentalist.

Plans for the next year

Quantum Calculations on new chromophores

The Brédas group will explore other chromophores for better optical properties. The Goddard group will use a set of chromophores, already developed as a test set, to give classical charge distributions, and convert them into united atom potentials. The Prezhdoo group will compare mean field and Monte Carlo approaches to understand the basis of both. The Robinson group will calculate electronic and optical properties of newly synthesized multichromophoric molecules, develop united atom Monte Carlo methods to look for super ordered arrays and optimum geometries of chromophores. The Hayden group will study the interaction of chromophores and polymers to understand solvent interactions using all-atom, kinetic Monte Carlo methods. The Rehr group will develop all-optical scattering codes to predict optical properties of arrays of chromophores. The Bertsch and Goddard groups will collaborate to develop time dependent DFT codes to study excited state properties of molecules, needed to understand electron transport in EO and AO materials.

The statistical mechanical modeling

The Robinson and Prezhdoo groups are collaborating to describe molecules with different levels of a "United Atom type" approach that currently includes dipolar and van der Waals forces. It is important to use more realistic, classical potentials for the molecules. To this end, the Goddard group is developing a reactive force field description of molecules, ReaxFF, that describes both ground state and transition states for reactions. ReaxFF will be validated by comparing to experimental and quantum mechanical results. The ReaxFF will be used to provide potentials needed by the Robinson group for use in statistical mechanical calculations. Additionally, in

collaboration with Brédas at UA, the Goddard group will integrate semiempirical excited state capabilities into ReaxFF to incorporate exciton behavior into these simulations.

Excited State Codes

The Goddard group will implement TD-DFT approaches for excited states of molecules and solid polymers into existing quantum software [Jaguar (developed in collaboration with Schrödinger Inc) for finite molecules and SeqQuest (developed in collaboration with Sandia National Laboratories)] for periodically infinite polymers and will test this methodology by comparing to experiment and to other *ab initio* methods of describing excited states. The development and application of this TD-DFT functionality will be in collaboration with George Bertsch at UW and Jean-Luc Brédas at UA. These methods will be applied to the various Electric Optic Materials being pursued experimentally in this project, including the chromophore containing dendrimers. In a similar development, to look at electron injection and electron transfer properties, the Prezhdo group is modeling ultra-fast electron transfer (ET) dynamics across chromophore-semiconductor interfaces. They have already developed an initial version of the non-adiabatic molecular dynamics code that will be used to study the ET process across chromophore-semiconductor interfaces in real time and at the molecular level. The code, when tested against a system typical of the chromophore-semiconductor systems in Graetzel-type cells, reproduced the time-resolved experimental data on the electron injection rate. The codes will be improved and used to understand the processes of electron injection needed in the devices being developed by the Scherer group at Caltech and the Steier group at USC.

Determining Optical Properties for NLO chromophores

The Robinson and Prezhdo groups have examined various QM methods to calculate optical properties of pNA and other known molecules and conclude that the correct geometry is best obtained by high level calculations but that the best polarizations and hyperpolarizations are found from minimum basis sets, and DFT works about as well as MP2 for determining the optical properties. When examining larger chromophores, more typical of the types being made, it was found that the best agreement was obtained with large basis sets using DFT. We are up to speed on getting polarizabilities and hyperpolarizabilities using DMOL by Accelrys but only at zero frequency. We need to develop methods to obtain these parameters at other frequencies, particularly the 1.0 to 1.6 micron wavelength range which is the telecom communications range and the light fields often used in optical experiments such as EFISH and hyper-Rayleigh scattering. These groups will use direct time dependent quantum calculations (using the GAMES codes) and TD-DFT to compare more exact calculations with time dependent perturbation techniques currently employed by the Brédas group.

Photonics Properties of Active Materials

The Rehr group is developing codes to calculate the dielectric and optical response of the NLO chromophores. As a first step toward this objective they have extended the real-space multiple scattering codes (based on FEFF8 codes) to the optical regime with the assumption of energy independent transition matrix elements and other approximations. As learned from comparing with the experimental energy loss spectrum for Cu (and other systems) the agreement is in semi-quantitative agreement with experiment from the visible to the x-ray regime. The next step is to successively remove the various approximations used in codes in the initial phase. The improved codes will include the energy dependence in the transition matrix elements and hence provide a more quantitative theory in the optical regime. The Rehr group will also investigate the importance of local field effects, and plans to develop subroutines for the propagator matrix elements and scattering matrix for photons scattered by a dielectric sphere.

Thrust Name	Microfabrication and Nanoengineered Materials
PI Name	Thrust Leader: Joseph Perry

Thrust Description

This thrust will focus on the themes of assembling materials on multiple length scales, integration of EO polymers, $\chi^{(3)}$ polymers, organic gain materials into photonic and electronic devices, and free-form 3D mesoscale patterning. Our mission is to advance the fabrication and nanoengineering of photonic materials and devices, and to provide the tools needed to create a new generation of high-performance, low-cost active photonic and electronic devices for information technologies and telecommunications. Our vision is that this thrust, with theoretical and modeling support and working in an integrated manner with the EO materials and devices thrust and the organic light sources and electronics thrust, will lead to materials and microfabrication processes for the creation of new types of active photonic devices, in 2-D and 3-D photonic crystals with tunable characteristics, and in 3-D photonic circuits.

Thrust Projects and Collaborations

- ***2D and 3D Photonic Bandgap Structures: Jen, Perry, Scherer, Stucky, Xia***
- ***Patterned Self-Assembly Chemistry: Jen, Marder, Perry, Stucky, Xia***
- ***Materials Chemistry for Two-Photon Lithography: Jen, Marder, Perry***
- ***Macromolecular Data Storage: Marder, Mansuripur, Perry***
- ***Structural and Optical Characterization: Campbell, Perry, Scherer***

Collaborative team interactions have begun on a few projects within the thrust and good initial progress has been made. These interactions involve the participation by several faculty and direct interaction of students and post-docs undertaking the research work. Some of these activities involve interactions across thrusts and among members who are participating in two or more thrusts. For example, Scherer, Jen, and Dalton have begun a collaboration that aims to incorporate highly active electro-optic polymer materials into 2D silicon photonic bandgap structures with the goal of making the bandgap structures that are electrically tunable. Materials have been transferred and students have been exchanged between laboratories. Stucky, Perry, Marder and Xia are collaborating on the development of 3D photonic crystal structures through the use of two-photon 3D lithography and self-assembly or backfilling chemistry to incorporate high refractive index and optically active materials into polymeric or colloidal particle templates that have a form useful in photonic microdevices. Template structures have been transferred from the Perry group to the Stucky group and initial backfilling experiments have been performed. Students and post-docs are interacting directly, leading to enhanced training and education of students across different areas of expertise. Marder's group has transferred newly developed high-sensitivity, two-photon initiators to the Perry group for development of improved photopolymer systems for 3D lithography. Mansuripur, Perry, Marder, and Peyghambarian have teamed up to investigate macromolecular data storage that holds promise for ultrahigh density information storage. Microfluidic structures fabricated in the Perry and Peyghambarian group have been transferred to the Mansuripur group which has been fabricating nanopore based read/write stations for processing information on individual macromolecular chains. Initial experiments have demonstrated the ability to integrate microfluidic and nanopore structures and to measure distinct electrical transients from different types of polynucleic acid chains. Students are being exposed to highly cross disciplinary concepts and methods. While this is just the beginning, we believe that we are off to a very good start in the formation of integrative activities both within this thrust and among the different thrusts in the STC.

Objectives

Develop materials and microfabrication processes to create new types of active photonic devices, to provide tunability in 2D & 3D photonic crystals, and to take photonic devices into the 3rd dimension.

Milestones

The 5-year milestones for this thrust are 1) Materials and processes for 3D fabrication with 50 nm resolution over square centimeters. 2) Low loss (<1 dB) 3D tapered optical couplers. 3) New materials and methods for writing 3D optical circuits, 5x increase in a real waveguide density. 4) Large-area (1 cm²) 3D photonic crystal structures with well-defined defects. 5) Adding a “tuning knob” to 2D and 3D photonic devices with EO polymers. 6) Integration of EO, $\chi^{(3)}$, and amplifying polymers into microresonators devices. 7) Assess potential for integrated biological data storage. Looking to the future, we envision the following milestones over a 10-year period: 1) Integrated photonic chips based on integration of polymer and semiconductor optical materials, and electronic materials to produce inexpensive, versatile systems. 2) Solitonic device structures based on $\chi^{(3)}$ polymers for ultrafast self-guided switching. 3) Tailor made integrated photonic systems for ultrasensitive chemical/biological analysis making use of responsive character of polymers. 4) Integrated photonic/electronic microsystems for biological data storage.

Future Plans

Our plans for the next award year call for continuing and expanding the activities initiated during the past reporting period. A collaborative effort will be launched with researchers at Northwestern University (led by Professor Tobin Marks) to add Merrifield-type sequential synthesis (exploiting robotic control) to our repertoire of nanoscopic fabrication methodology. In particular, an effort will be made to integrate such methodology with photonic crystal circuitry and ring microresonators being fabricated within the STC.

Thrust Name	Light Emission and Organic Electronics
PI Name	Thrust Leader: Bernard Kippelen

Research Objectives

The thrust is focusing on the central processes of charge transport and light-emission in organic and hybrid materials with tailored morphology. New materials under development include dendrimers, self-assembled mesophases, and semi-crystalline thin films processed by physical vapor deposition. The objectives are to: (i) develop new light-sources for telecommunications and displays; (ii) develop stable high-mobility organic materials for electronics. These materials will be processed at low temperature and inserted into devices on shatterproof plastic flexible substrates using printing and soft lithography techniques. Each task is vertically integrated and incorporates four core competencies: (i) new material synthesis; (ii) theory and modeling; (iii) characterization of the optical and electrical properties in bulk, thin films, and nanostructured forms of the materials and interfaces with metals; (iv) device fabrication, performance testing, and optimization of processing techniques.

The thrust consists of the following three major research areas:

A. Light Sources for Telecommunications

Objectives: Develop amplifiers and fiber lasers based on rare-earth doped dendrimers. Develop conjugated polymers and molecules with infra-red emission.

Approach: Use dendrimer chemistries and site isolation to control absorption, emission, and energy transfer. Develop materials with high concentrations of rare-earth elements such as Er/Yb with long lifetimes. Demonstrate amplifiers with high gain, short length, high spectral bandwidth, and small footprint. Fabricate tunable fiber lasers pumped by inorganic semiconductor lasers. Design new conjugated polymers and molecules with infra-red emission.

Participants and their role: **Frechet, Harper, and McGrath** are synthesizing new lanthanide containing dendrimers. **Kippelen** and **Mathine** will fabricate waveguide structures and measure emission lifetimes and cross-section, optical gain and losses. **Mescher** will incorporate the new materials into optical fibers.

B. Light Sources for Displays

Objectives: Develop organic light emitting diodes with increased stability, performance, and functionality. Develop displays for the near infra-red.

Approach: Develop new materials with higher ionization potential and electron affinity that are less sensitive to oxygen and compatible with stable metal electrodes. Make the material photopatternable and crosslinkable to allow easy fabrication of pixels, multilayer processing from solution, and integration with organic electronic drivers. Lower operating voltage and increase light output by using doping and/or high-mobility materials such as self-assembled mesophases. Use site isolation in dendrimers to optimize color purity of devices. Increase lifetimes by decreasing the operating voltage to reduce Joule heating effects, controlling morphology changes during heating, tailoring interfaces to improve adhesion at organic/metal interface.

Participants and their role: **Marder** is synthesizing oxadiazole and phthalocyanine containing mesophases for electron and hole transport, **Frechet** is synthesizing dendrimers for white-light emission, **Jenekhe** is synthesizing side-chain and main-chain infra-red emitting polymers. **McGrath** is synthesizing light-emitting quinacridone dendrimers. **Kippelen** is fabricating organic light-emitting diodes with these new materials and is testing their optical and electrical properties. **Heeger** is developing light-emitting electrochemical cells and is improving their stability and lifetime by creating frozen junctions using cross-linking approaches. **Armstrong** and **Campbell** are characterizing organic/metal interfaces and frontier orbitals of the newly developed materials using combined adsorption microcalorimetry and photoemission spectroscopy.

C. Organic Electronics

Objectives: Develop an organic material platform to develop low cost, large area electronic circuits on plastic substrates for applications that do not require high speed and high current. Develop thermally stable high-mobility organic materials with mobilities comparable to amorphous silicon ($0.5 - 1 \text{ cm}^2/\text{Vs}$).

Approach: Synthesize highly ordered organic materials that can be processed from solution or by physical vapor deposition. Explore the intrinsic limitations to high mobility in organic materials through a combined experimental/theory experiment. Fabricate field-effect transistors with high on/off ratios and low drive voltages. Increase functionality of these devices and develop

phototransistors and light-emitting transistors. Fabricate electrically injected lasers. Integrate organic FETs with OLEDs. Develop a library of key electronic components and derive their corresponding SPICE parameters.

Participants and their role: **Marder** is synthesizing high-mobility mesophases and small molecules that can be processed into thin films using vapor deposition. **Jenekhe** is synthesizing various azaacene derivatives for transistors. **Kippelen** and **Mathine** are fabricating and testing organic field-effect transistors, and are developing organic capacitors. **Kippelen** is measuring the transport properties of the newly developed materials by time-of-flight experiments. **Armstrong** and **Campbell**, with complementary tools, will study interfacial chemistries of organic/metal interfaces. In particular, they will study band-edge misalignment and interfacial chemistries using various photoemission spectroscopies. In the first year they will start with pentacene and NTCDI as models and later expand their studies to the new materials under development in the Center. **Frank** is developing materials that exhibit spin-correlated conductivity for spintronics applications.

Progress in Three Subthrust Areas

During the first year, we have made significant progress in all three research areas of this thrust:

A. Light Sources for Telecommunications

Activities and Results: New lanthanide-containing dendrimers have been synthesized (**Harper**) and their photophysical characterization has been performed. Site-isolation phenomena as well as antenna effects have been quantified in europium-cored dendrimers. The synthesis of erbium-cored dendrimers (**Harper and McGrath**) is in progress and should be completed by the end of the first year. Fluorinated polymers incorporating lanthanide coordination complexes have been prepared (**Harper**) and work has started to incorporate them into micro-ring resonator structures in collaboration with colleagues from the thrust on electro-optics devices (**Steier**). Efficient green light has been generated, through third-harmonic generation using an infra-red laser emitting at 1500 nm, in organic dyes having strong third-order nonlinear optical properties (**Marder, Kippelen**). Real-time imaging through scattering media using third-harmonic generation in these chromophores has been demonstrated. These molecules have been delivered to the University of Washington (**Mescher**) for incorporation into PMMA optical fibers. Osmium dendrimers have been successfully incorporated into PMMA fibers. The fiber absorbs UV and emits red light. Procedures have been optimized for purifying and drying MMA monomer, incorporating the dendrimer, casting the material into a preform rod shape, polymerizing the preform, and finally drawing the preform into a fiber (PMMA host) of any specified diameter from 100 to 1000 microns. At this time, the optimal diameter tolerance that was achieved is +/- 5 microns.

Plan for the next reporting period: Luminescent properties of the newly synthesized erbium-cored dendrimers will be studied in thin film and waveguide geometries (**Kippelen, Mathine**). Most promising materials will be incorporated into plastic optical fibers (**Mescher**) and stimulated emission in these structures will be measured (**Kippelen, Mathine**). New generations of modified materials will be synthesized based on the feedback received from the photophysical experiments conducted on the first generation of materials. Third-order optical parametric amplification experiments will be conducted in single mode plastic fibers doped with the novel third-order nonlinear dopant molecules. Using feedback control system, preforms will

be drawn into fibers with diameter tolerance of +/- 1 micron. Fiber optic lasers incorporating rare-earth dopants will be designed and fabricated.

B. Light Sources for Displays

Activities and Results: Photocrosslinkable hole-transport polymers with various ionization potentials have been synthesized (**Marder**) and incorporated as photodefinable hole-transport layers in organic light-emitting diodes (**Kippelen**). The polymers were obtained by copolymerization of bis(diarylamino)biphenyl-based acrylate monomers with cinnamate-functionalized acrylate moieties. Polymers with a range of redox potentials were obtained by varying the substitution patterns of the bis(diarylamino)biphenyl units. The 2+2 cycloaddition of the cinnamate moieties following UV irradiation allows for patterning of the polymer, and simultaneously enables the fabrication of multilayer structures from solution. Hole mobilities have been measured in these copolymers using the time-of-flight technique. Electroluminescent devices with multiple hole-transport layers having different ionization potentials have been fabricated from solution and the quantum efficiency of these devices could be improved compared with devices based on a single hole-transport layer. Lifetimes of devices fabricated from various hole-transport polymers and small molecules have been measured. Ongoing efforts focus on the control and the understanding of the role of surface energies of these different materials using self-assembling monolayers (**Armstrong, Campbell**).

Several generations of dendritic quinacridone derivatives for organic light-emitting diodes and lasers have been synthesized at the gram quantity level (**McGrath**). Nearly 100% photoluminescence efficiencies could be achieved in these materials. The electrochemical characterization of these materials has been completed. Molecules have been sent to the University of Washington (**Mescher**) to be incorporated into plastic optical fibers for optically pumped lasers emitting in the visible. Materials sent to Durel Corporation for incorporation into powered thin-film AC electroluminescent devices (collaboration UA, UW, Durel Corp.; **McGrath, Armstrong, Kippelen, Durel Corp., Mescher**).

In the area of light-emitting electrochemical cells, an ampholytic co-monomer (AMPS/METMA) has been synthesized (**Heeger**) and combined with emissive conducting polymers such as MEH-PPV. Devices that consist of a thin film of this mixture sandwiched between two electrodes are being fabricated and evaluated. Current efforts focus on the polymerization of the co-monomer to freeze the junction after the desired charge distribution is achieved.

Plan for the next reporting period: We will incorporate quinacridone containing dendrimers synthesized by **McGrath** into organic light-emitting devices processed from solution to increase device efficiency using Forster energy transfer. Dendrimers will provide site isolation and prevent self-quenching, and simultaneously will enable the processing of these materials from solution. These materials will be combined with the crosslinkable hole transport materials that have been fully characterized (**Marder, Kippelen**). White light sources with good color rendition will be fabricated by combining dendrimers emitting at different colors (**Frechet, Kippelen**).

C. Organic Electronics

Activities and Results: discotic liquid crystals based on oxadiazoles with benzene and triazine cores have been synthesized (**Marder**) and their charge mobility has been measured using time-of-flight experiments (**Kippelen**). The materials were found to form a columnar discotic liquid crystalline mesophase between 38°C and ca. 210°C. The time-of-flight electron mobility at room temperature was as $10^{-3} \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$, which is the highest electron mobility measured at

room temperature in oxadiazole-based compounds. Solution-based fabrication procedures of electrodes on plastic flexible substrates were developed and micro-size features could be fabricated using micro-contact printing and photolithography (**Kippelen**). New dielectrics that can be patterned as gate oxides have been developed and characterized. Films with good dielectric strength could be fabricated. Pin hole densities could be measured with high sensitivity using electrochemical techniques (**Armstrong, Mathine, Kippelen**). Organic field-effect transistors were fabricated on silicon substrates using pentacene as the organic semiconductor. Very low threshold voltages (< 1 V) could be obtained (**Mathine**) by treating the gate oxide with a coupling agent. Several devices have been designed and modeled including a seven stage ring oscillator, an inverter, NAND and NOR gates. Gold surfaces modified with alkanethiols and partially fluorinated alkanethiols were characterized by UV-photoelectron spectroscopy (**Armstrong**). Changes in the effective work function of these surfaces due to the presence of significant interfacial dipoles are observed as alkyl chain length is increased, and as the fraction of fluorinated methylene groups is increased in a constant length alkyl chain. Comparison of the shifts in gold/SAM vacuum level (changes in effective work function) as a function of the apparent dipole moment of the molecule provides an estimate of the band-edge offsets for these molecules on the gold surface and an estimate of the intrinsic dipole moment for the gold-thiolate bond, both relevant to the functioning and efficiency of electrode/organic interfaces in organic electronic devices.

Plan for the next reporting period:

New generations of discotic liquid crystal compounds in which the core is larger and can help impart greater order will be synthesized. In particular, compounds containing phthalocyanine, pyrene and aza aromatic cores will be examined (**Marder**). Charge mobility in these materials will be measured by time-of-flight experiments and in field-effect transistor geometry (**Kippelen**). In addition, the use of metallo-organic compounds such as metal dithiolene compounds will be explored. These materials can also form meso-phases and are readily reduced. Applications of these materials as transport materials in OFETs will be investigated. In the next reporting period we build and test a seven stage ring oscillator, an inverter, and NAND/NOR gates (**Mathine/Kippelen**). We will focus on other modifiers on gold, ITO, silica thin films on Au, etc. and try to extend this work to all of the interfaces of interest in emerging OFET technologies (**Armstrong**). During the second reporting period, we will also develop organic photodetectors (**Marder/Kippelen**).