**Abstract**

This research focused on: (1) Organic electro-optic materials with the objective of realizing materials characterized by electro-optic coefficients greater than 300 pm/V at telecommunication wavelengths and which pass Telecordia standards. New processing techniques were developed for integration of organic EO materials with silicon photonic devices and circuits and for achieving low insertion loss electro-optic devices including active wavelength division multiplexing (WDM) transmitter/receiver systems. During this period of time, the Dalton research group served as

**Subject Terms**
The ultimate objective of our theoretical effort has been and continues to be the "first principles quantitative simulation" of the physical properties of organic electroactive materials and simulation of the performance of devices fabricated from these materials. To relate our statistical mechanical (and finite element) methods to atomic and molecular properties, we needed to develop a reliable quantum mechanical approach to the computation of electron distributions, linear and nonlinear optical properties, etc. We started our development of improved quantum mechanical methods by a comparative evaluation of different methods (Semi-empirical, Hartree-Fock, MPn, CC, DFT, TD-DFT) and basis sets (Gaussian, numerical, pseudo-potential) [10-12,15,28]. Our computations were frequently compared with those of others including Marks and Ratner at Northwestern (particularly as related to novel chromophore structures, e.g., X-shaped chromophores and twisted π-electron bridge [10,81] chromophores) to computations carried out by Bredas at Georgia Tech [28], and to computations executed by theorists at Federal laboratories [28]. While various methods proved effective in predicting trends for the variation of molecular first hyperpolarizability with chromophore molecular structure [28], it became increasingly apparent during cross comparison of various theoretical approaches and comparison of experiment with theory that quantitative simulation of experimentally-measured molecular first hyperpolarizabilities required explicit consideration of time-dependent applied and internal electric fields. This point has also been realized by others, e.g., Marks and Ratner in their computation of molecular first hyperpolarizability for twisted-bridge chromophores [81]. The Real-Time, Time-Dependent Density Functional Theory (RTTDDFT) method [73,82] appeared to be ideally suited for this task. Incorporation of oscillatory fields (e.g., fields of optical frequencies) to the RTTDDFT Hamiltonian has lead to quantitative prediction of the frequency dependence of various molecular hyperpolarizabilities including those relevant to electro-optic activity and second harmonic generation [36,39,58,69-73]. Moreover, time-dependent reaction fields derived from PAMC CMD calculations have been incorporated into RTTDDFT calculations leading to quantitative prediction of the dependence of molecular first hyperpolarizabilities and linear optical spectra on dielectric permittivity [36,58,69-73]. An example of the success in simulating the experimental variation of chromophore molecular first hyperpolarizability with dielectric permittivity (of host solvents) is shown in Fig. 1. For simple chromophore structures, molecular first hyperpolarizability is observed to be an approximately linear function of (ε - 1)/(ε + 2) (see Fig. 2). Coupled RTTDDFT/PAMC CMD theory has also led to a quantitative prediction of the variation of dielectric permittivity with temperature (Fig. 3). Fig. 3 shows the experimentally observed variation of the dielectric constant of a three-chromophore containing dendrimer material (PSLD_33) through its glass transition temperature. Correlated RTTDDFT/PAMC CMD theory provides a quantitative simulation of this behavior including prediction of a saturated value of 27 for the melt state and has led to quantitative simulation of electro-optic activity [36].
In addition to quantitatively understanding the dependence of molecular first hyperpolarizability on frequency and dielectric permittivity, it is crucial to know if excitonic interactions strongly influence linear and nonlinear optical properties at high chromophore number densities. To test the utility of theoretical calculations for such cases, we prepared several model systems corresponding to bundles of chromophores tethered together at their ends [5,9] to define their spatial proximity and relative orientation. Theory and experiment for these model systems [5,9] and for multi-chromophore-containing dendrimers [36] confirm that high chromophore number densities can be achieved without deleterious chromophore-chromophore excitonic effects.

An important test of the utility of correlated RTTDDFT/PAMCMD calculations was the simulation of electro-optic activity of multi-chromophore-containing dendrimers where covalent bond potentials must be correctly taken into account. The results of such simulations are discussed in detail in reference [36] and the critical summary comparison of theory and experiment is shown in Fig. 4 below:

Figure 4. Comparison of Theory (diamonds with error bars) and Experiment (solid circles) for two multi-chromophore-containing dendrimers and for the PSLD_33 dendrimer dissolved in amorphous polycarbonate (APC) is...
shown. The error bars represent the observed variation in "equilibrium" electro-optic values for different PAMCMD trajectories. $r_3^R$ is the ratio of the principal element of the electro-optic tensor in the electric poling field strength and is experimentally obtained from a linear least squares fit of the variation of $r_3^R$ with poling voltage.

A number of important observations derive from the comparison of experiment and theory including the fact that the covalent bond potentials operative in the dendrimers prevent chromophores from undergoing centrosymmetric aggregation and quenching of electro-optic activity. A linear dependence of electro-optic activity on chromophore number density (loading) is predicted and observed, consistent with chromophores acting as independent particles. Note that very high chromophore concentrations are achieved without attenuation of electro-optic activity.

The high chromophore loading achieved for multi-chromophore-containing dendrimers suggested the investigation of doping of chromophore guests into chromophore-containing host materials, e.g., a new class of materials which we label Binary Chromophore Organic Glasses (BCOGs). Course-grained PAMCMD theoretical calculations have suggested that specific spatially-anisotropic guest chromophore/host chromophore interactions lead to enhanced acentric order and EO activity [51] (see Fig. 5 below).

Several very striking observations are noted for Binary Chromophore Organic Glasses (BCOGs). Not only are high chromophore loadings observed without attenuation of electro-optic activity with increasing chromophore number density but the acentic order (and hence electro-optic activity) of both guest and host are improved as a result of chromophore-chromophore interactions. Also, the spectral line broadening and bathochromic shifts observed in the linear optical spectra of traditional chromophore/polymer composite materials are predicted and observed to be absence in BCOGs. Theory and experiment confirmed the existence of a wide range of BCOG materials leading to improved electro-optic activity and reduced optical loss including chromophore/chromophore-containing-dendrimer.
In summary, RTTDFFT/PAMCIM calculations have permitted quantitative “first principles” simulation of electro-optic activity for a number of complex polymeric, dendritic, and BCOG materials. Theoretical guidance has led to the preparation of BCOG materials consistently exhibiting electro-optic values greater than 300 pm/V and optical loss values of less than 2 dB/cm at telecommunication wavelengths. Moreover, as will be briefly discussed in the Proposed Research Section, this theoretical approach is useful for predicting further improvements.

**Development and Application of New Characterization Tools:** Critical to the development of reliable theoretical guidance and definition of critical structure/function relationships is the ability to accurately measure linear and nonlinear optical properties, thermal and photochemical stability, etc. We have assembled a unique tool set providing the capability for measurement of molecular first hyperpolarizability by wavelength-agile, femtosecond HRS and by EFISH [50,69-72,84-86], electro-optic activity by modified Terg-Mac Ellipsometry and attenuated total reflection (ATR) [50,62,69-72], anisotropy order parameters by variable angle polarized absorption spectroscopy (VAPAS) and by atomic resolution techniques including two photon fluorescence microscopy [1,21,69-72], and measurement of photochemical stability at telecommunication wavelengths by pump-probe methods [4,42,54,60,70,71]. More description of these capabilities is provided in the facilities section but we note that in several cases the only capability for such measurements in the United States resides in our laboratory and in other cases our capabilities provide an important complement to capabilities that exist in AFRL and LPS laboratories.

**Development and Application of New Synthesis and Processing Methodologies:** We have pioneered microwave-assisted synthesis as applied to the production of organic electroactive materials and have been a leader in developing new lattice hardening chemistries, particularly Diels-Alder/Retro-Diels-Alder cycloaddition reactions, which have yielded organic electro-optic materials with glass transition temperatures exceeding 200 °C [34,38,47,70,71,87,88]. Our laboratory has pioneered the fabrication of complex device structures, such as coupled multi-ring microcavatators by soft and nanoimprint lithography [70,71,89] and we have been actively involved in the fabrication of conformal and flexible devices by lift-off techniques [17,26,70,71]. Recently, we have introduced laser-assisted electric field poling [55] as a means of improving electro-optic activity while maintaining low optical loss and even more recently we have demonstrated that nanoscopic metal oxide surface coatings and surface functionalization with an oriented chromophore monolayer can lead to improved optical nonlinearity [79,71] (see Fig. 6). Our observations have recently been repeated and verified by Paul Ashley at US Army RDECOM, Redstone Arsenal, AL and Warren Herman at the Laboratory for Physical Sciences (LPS), College Park, MD [90,91]. We have also pioneered the incorporation of organic nonlinear optical materials into silicon photonic waveguide and nano-slot waveguide device structures [3,16,37,53,59,70,71]. This integration has included utilization of doped silicon as poling and drive electrodes. The integration of organic NLO materials with silicon photonic structures has been extended to the demonstration of Reconfigurable Optical Add/Drop Multiplexer (ROADM) devices (for chip-scale information routing) carried out in collaboration with Boeing [59]. Examples of device structures and performance are shown in Fig. 7. A significant accomplishment of our theoretical simulations of device performance is the prediction of concentration of light in nanoscopic slots etched into silicon photonic waveguides. These slots permit nearly lossless transition of light from high index of refraction silicon into lower index of refraction organic nonlinear optical materials for active control of light.

![Figure 6. The behavior of poling current in the presence and absence of a nanoscopic titanium dioxide buffer layer is shown (upper left). The presence of the TiO2 buffer resulted in a 30% increase in poling-induced electro-optic activity (upper right). In a BCOG material (not shown), the EO activity increases from 280 pm/V to 250 pm/V.](image-url)
Figure 7. Micrographs of slotted silicon photonic waveguide ring microresonator devices are shown. The theoretically computed optical mode profile is shown (center) and electro-optic modulation is shown (right). Such device structures permit significant concentration (amplification) of optical and electric fields. A ROADM is shown in the lower center.

Photostability Studies: In a collaborative study with Professor Peter Gunter of the ETH, Zurich, we have analyzed the photochemical kinetics (employing optical pump powers in the range 400mW-1W for accelerated testing) of dozens of organic electro-optic materials. Improved analysis and measurement protocols have been developed [42]. Singlet oxygen chemistry is found to define the dominant photodegradation mechanisms and packaging of hardened materials has yielded photostability figure-of-merit values (B/ρ) or the number of absorbed photons required to produce a damage event) as large as 5000 x 10\(^{-19}\)m\(^2\) (which would yield more than 100 years of operation for normal telecommunication power levels). Our studies have been particularly useful in demonstrating the dependence of photostability on chromophore structure. Here we have space to illustrate only one example (Fig. 8) but photostability can be typically varied by up to two orders of magnitude with simple variation of chromophore structure. Note that chromophores in dendrimers are usually more stable than the same chromophore in polymer composites consistent with reduced oxygen accessibility in the dendrimer material lattice. The results shown in Fig. 8 are for oxygen saturated samples (worst case scenario).

Figure 8. The variation of photostability with structure is shown for representative chromophore/polymer composite, multi-chromophore-containing dendrimer, and binary chromophore organic glass materials.

Lattice hardening (crosslinking) and use of singlet oxygen quenchers lead to further multiple orders of magnitude improvements of photostability. As with researchers at Corning [26], we observe up to 4-5 orders of magnitude variation in photostability for the same parent chromophore ± electron structure as a function of derivatization of that core structure, lattice hardening, use of quenchers, and packaging to
exclude oxygen. While photostability issues are not as serious for organic electro-optic materials as for organic light-emitting devices and photovoltaic materials (because the operational light is off resonance and current flow is minimum in EO applications), packaging will still likely be required to achieve 10 year operational lifetimes, particularly if optical power levels exceed typical telecommunication powers.

In summary, we have established the world’s leading facility for the characterization and analysis of the photostability of organic electro-optic materials, in both thin films and devices, for a wide range of operational optical wavelengths including both telecommunication bands [42,70,71,86]. We have carried out definition of mechanisms of photodegradation for a wide range of materials including chromophores, polymer composites, chromophore-containing dendrimers, polymers, and dendronized polymers; and for binary chromophore organic glasses. We have also investigated a wide range of processing conditions including examining the effects of lattice hardening, the addition of singlet oxygen quenchers, material packaging, etc. We have all the necessary facilities and expertise to carry out photostability measurements and improvements to meet metrics proposed in the following sections of this proposal.

REFERENCES (AFOSR-FA9550-06-1-0042 relevant publications)


REFERENCES (Other publications)


Nanostructured Materials Annual Report (period 03/01/06 - 06/31/09) Statistics:

Personnel Supported:
Number of PI(s) and Co-PI(s) Involved: 2
Number of Post Docs Supported: 3
Number of Graduate Students Support: 12
Other Researchers Supported: 1

Postdoctoral Fellows Supported (Partial Support)
Yi Liao
Guan Wen
Philip Sullivan

Graduate Students Supported (Partial Support)
Denise H. Bale
Joshua A. Davies
Eric Formo
Anna Pyayt
Brent H. Siemssen

Haishan Sun
Jocelyn Y. Takayasu
Kimberly A. Firestone
Scott R. Hammond
Stephanie J. Benight
Philip Sullivan
Benjamin Olbricht

Other Researchers Support:
Bruce Eichinger

Publications:
Number of Publications in Refereed Journals: 92
Number of Publications which Acknowledge AFOSR Support: 55

Consultative/Advisory Functions:
- Member, Nanotechnology Technical Advisory Group (nTAG) of the President’s Council of Advisors on Science and Technology (PCAST) (2007-2008)
- Consultant, University of Florida (2008)
- Member, Scientific Advisory Committee, University of Alabama (2009)
- Special Government Employee (2006-present)
- Member, Department of Energy INCITE Chemistry Panel; Reviewer for Condensed Matter Physics Panel (2008)
- Member, NSF Partnerships for International Research and Education (PIRE) Program NANO Panel (2007)
- Member, Committee of Visitors, Chemistry Division, National Science Foundation (2007)
- Member, NSF MPSAC Subcommittee on the American Competitiveness Initiative (2007)
- Member, NSF MPSAC Subcommittee on Major Facilities (2007, 2008)
- Member, Organizing Committee for the NSF Workshop on Excellence Empowered by a Diverse Academic Workforce: Achieving Racial and Ethnic Equity in Chemistry (2006, 2007)

- National Science Foundation Materials Education Workshop, September 11-12, 2008, Arlington, VA
- Member, Engineering and Physical Sciences Research Council (EPSRC), England (2005- )
Guest Editor, Special Issue of the *IEEE Journal of Selected Topics in Quantum Electronics* (2007-2008)

Chairman/Member of the External Advisory Committee, NSF PRIEM Center on Metamaterials, Norfolk State University (2007-present)

Chairman/Member of the External Advisory Committee, NSF CREST Center Norfolk State University (2007-present)

Member, Advisory Committee, Mathematical and Physical Science Directorate, National Science Foundation (2005-2008)

Member, ACGPA (Advisory Committee for the Government Performance and Results Act (GPRA), National Science Foundation (2008-2009)

Member, Advisory Group on Electron Devices (AGED), Office of the Undersecretary of Defense (2006-present)

Member, Committee of Visitors, Division of Materials Research, National Science Foundation (2005, 2008)

Member, Committee of Visitors, Chemistry Division, National Science Foundation (2007)

Member, MPS/EHR Subcommittee on Broadening Participation, National Science Foundation (2005)

Member, Engineering and Physical Sciences Research Council (EPSRC), England

Chairman, Arizona Biomedical Research Commission (formerly, Arizona Disease Control Research Commission) Review Panel for Biomedical Engineering, Imaging, and Sensing (2005-)

Member, National Science Foundation Panel on the Technological Challenges of Organic Electronic and Photonic Materials (2004)

Member, National Science Foundation Panel on Sensors and Sensor Systems (2003)

Member, National Science Foundation Workshop on Chemical Bonding Centers (2003)

Member, National Science Foundation "Grand Challenges Workshops" for the National Nanotechnology Initiative (2009)

Member, Air Force Scientific Advisory Board, Review of the AFRL Materials and Manufacturing Directorate (2003)

Member, Pacific Northwest National laboratory Peer Review Panel for the Energy Science and Technology Directorate (2003-2006)

Oversight Reviewer of the National Research Council Report on Implications of Emerging Micro- and Nanotechnologies


Chaired/Member, External Advisory Committee, Center for Research and Education on Advanced Materials, Norfolk State University, (2002-)

Member, External Advisory Committee, NSF RISE Center, Alabama A&M University (2005-)

Member, Scientific American 50 Awards Advisory Committee

Board of Visitors, Chemistry Department, University of Alabama

Guest Editor, Special Issue of the *Journal of Physical Chemistry*

Academic Technology Advisory Committee, University of Washington (2003-)

Member, Board of Directors, Loker Hydrocarbon Research Institute, University of Southern California, Los Angeles, CA (2003-)

**Participation/Presentations:** (From March 1, 2006 to May 31, 2006)

**Seminar—March 8, 2006** —Intel Corporation (Corporate-wide by video conferencing) Portland, OR—Invited Presentation: "Exploiting the Best of Electronics and Photonics: Concepts and Applications to Telecommunications, Computing, Embedded Network Sensing and Defense Technologies"

**Seminar—March 13, 2006** —Corning Corporation, Corning, NY—Invited Presentation: "Defining all structure/function relationships required for optimizing electro-optic activity, optical loss, and stability of organic EO materials"

polymer materials"

Conference—August 17-17, 2006—SPIE Optics and Photonics Conference 6320: Complex Photonic Media, San Diego, CA—Invited Presentation: "Theoretically-Inspired Nanoengineering of Complex Photonic Media"


Lecture—September 6, 2006—CIBA Technical Seminar, CIBA, Basel, Switzerland—Invited Presentation: "Nano-engineering of organic electro-optic materials"


Conference—September 24-26, 2007—NSF Workshop on Excellence Empowered by a Diverse Academic Workforce, Arlington, VA—Invited Presentation: "Best Practice Diversity Plans"

Lecture—October 1, 2007—Physics Department Colloquium, University of Washington, Seattle, WA—Invited Presentation: "Understanding Intermolecular (and Intramolecular) electrostatic Interactions in condensed matter: Effects on order and nonlinear optical properties"
**Conference** — October 3-5, 2007 — 2007 IEEE International Topical Meeting on Microwave Photonics, Victoria, BC, Canada—Invited Keynote Talk: “Advances in organic materials for optical modulation”

**Lecture** — October 24, 2007 — Frontiers in Science Lecture, University of Utah, Salt Lake City, UT—Endowed Lectureship: “Nano-engineering a Technology Revolution (in Information Technology)”

**Lecture** — October 25, 2007 — Department of Chemistry Colloquium, University of Utah, Salt Lake City, UT—Invited Presentation: “The Key to Nanotechnology: Understanding Intermolecular Interactions”


**Conference** — December 3-7, 2007 — 10th Pacific Polymer Conference (PPC 10), Kobe, Japan—Invited Keynote Presentation: “Theoretically-inspired nano-engineering of photonic and electronic polymers for exceptional performance”

**Lecture** — April 2, 2008 — Nanophotonics for Breakfast Series sponsored by the Seattle Technology Alliance, Rainer Club, Seattle, WA—Invited Presentation: “Nanophotonics in telecommunications”


**Conference** — May 18-23, 2008 — 10th International Conference on Organic Nonlinear Optics (ICONO 10) and International Conference on Organic Photonics and Electronics 2008 (ICOPF:2008), Santa Fe, NM—Invited Presentation: “Systematic Optimization of Organic Electro-Optic Materials and Integration into Silicon Photonics”


**Conference** — December 7-10, 2008 — MACROMEX, Los Cabos, Mexico—Invited Presentation: “Organic Macromolecular Optoelectronics”


**Interactions/Transitions:**

Transition 1

a. Dalton, UW, b. Data for organic electro-optic materials, c. William Knapp/Boeing Phantom Works, 253-657-8019 d. For a development of a research program for handling both digital and analog data exploiting WDM techniques and explicitly wavelength selective filter and beam steering concepts. tx××1
ROADM device delivered to NAVAIR (2006)—results published in *IEEE Journal of Lightwave Technology*.

Transition 2

a. Dalton, UW, b. Data relating to polymeric electro-optic materials and processing protocols, c. Susan Ermer/Lockheed Martin Corporation, 650-424-3131 d. For prototyping high frequency, low drive voltage modulators.

Transition 3


Transition 4

a. Dalton, UW, b. Polymeric electro-optic materials and processing protocols, c. Tom Minn, Jamma Corporation, 425-415-6616 d. For electro-optic device fabrication and consideration for establishing an electro-optic materials production facility.

Transition 5

a. Dalton, UW, b. Polymeric electro-optic materials and processing protocols, c. Ray Chen/UT-Austin Microelectronics Center and Radiant Photonics, 512-338-4942 d. For electro-optic device fabrication and evaluation.

Transition 6

a. Dalton, UW, b. Polymeric electro-optic materials and processing protocols, c. James G. Groeze/AFRL/MLPO, 937-255-4474 ext 3263 d. For use with conducting cladding materials developed by AFRL.

Transition 7


Transition 8


Transition 9

a. Dalton, UW, b. Polymeric electro-optic materials and processing protocols, c. Paul Ashley/Army Missile Command, Redstone Arsenal, 205-876-7484 d. Polymeric electro-optic materials for gyro development.

Transition 10


Transition 11

a. Dalton, UW, b. Light emitting materials and devices, c. Christopher Somogyi, 425-503-3658 d. Light emitting devices for display applications.

New discoveries, inventions, or patent disclosures:

Significant improvements have been made in organic electro-optic and sensor materials and a new paradigm for developing materials with further improvement in properties has been validated. Integration of organic optoelectronic materials with silicon photonics has been demonstrated. Two patents have been reported.

Honors/Awards: (Lifetime)

- Elected Fellow (Inaugural Class), American Chemical Society (2009)
- Awarded Lifetime Achievement Award by SPIE (2008)
• Elected Fellow, Optical Society of America (2008)
• Elected Fellow, SPIE-International Society of Optics and Photonics (2008)
• University of Utah, College of Science, Frontiers of Science Lectures, Davern/Gardner Laureateship (2007)
• IEEE/LEOS William Streifer Scientific Achievement Award (2006)
• Elected Fellow, American Association for the Advancement of Science (2006)

• QEM (Quality Education for Minorities)/MSE (Mathematics, Science, and Engineering) Network 2005 Giants in Science Award
• Elected Senior Member, IEEE (2005)
• Dow/Karakatsanos Lecture Series and the Alumni Distinguished Lectureship, Michigan State University, 2005
• AFRL Materials, Manufacturing & Enabling Technologies Lecture Series, Dayton, 2004
• 2003 Chemistry of Materials Award of the American Chemical Society
• 2003 Eastman Lecturer, University of Akron
• 2002 Inaugural Lecturer of the National Science Foundation Distinguished Lecture Series
• Distinguished Alumni Award of Michigan State University (2000)
• 1996 Richard C. Tolman Medal of the American Chemical Society, Southern California Section
• Paul C. Cross Lectureship, University of Washington, Seattle, WA (1996)
• NASA Lecturer, Fifty-Fourth Frontiers in Chemistry Lecture Series (1995), Case Western Reserve University
• The 1990 University of Southern California Associates Award for Creativity in Research and Scholarship
• 1986 Burlington Northern Foundation Faculty Achievement Award
• NIH Research Career Development Awards (Two Awards, one at Stony Brook, one at Vanderbilt, 75-81)
• Camille and Henry Dreyfus Teacher-Scholar Award (75-77)
• Alfred P. Sloan Fellowship (74-77)

**Awards Received by Graduate Students Working on This Project:**

• Stephanie Benight, SPIE-International Society for Optics and Photonics Educational Scholarship; Invited Participant at the 2009 Meeting of Nobel Laureates in Lindau, Germany
• Philip Sullivan, Intelligence Community Fellowship (2009)