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6. AUTHOR(S)
Larry Dalton

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)

University of Washington
Department of Chemistry
Box 351700
Seattle, WA 98195-1700

8. PERFORMING ORGANIZATION REPORT NUMBER

9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES)

Dr. Charles Y-C. Lee
Directorate of Chemistry and Mat. Science
Air Force Office of Scientific Research
4015 Wilson Blvd. Room 713
Arlington, VA 22203-1954

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13. ABSTRACT ***(Maximum 200 Words)***

This research focuses on:: (1) Organic electro-optic materials with the objective of realizing materials characterized by electro-optic coefficients greater than 100 pm/V at telecommunication wavelengths and which pass Telecordia standards. New processing techniques were developed for fabrication 3-D 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 the national resource for state-of-the-art electro-optic materials providing materials to DoD laboratories, DoE labs, NIST researchers, industry, and academic researchers. (2) Metal core dendrimer materials were developed for applications as sensors, organic light emitting diodes, and light harvesting solar cell coatings. Materials were designed for improved emission properties and photochemical stability both by systematic design of the chelated metal and by design of the surrounding dendrimer structure. Materials were provided to DoD and NASA laboratories and to industry. (3) Single wall carbon nanotube actuators were developed and various mechanisms of actuation characterized. These materials were used to fabricate simple optical switches. Materials were provided to industry and to academic researchers.

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Submitted to

DR. CHARLES Y-C. LEE
DIRECTORATE OF CHEMISTRY AND MATERIALS SCIENCE
AIR FORCE OFFICE OF SCIENTIFIC RESEARCH/NL
801 N. RANDOLPH STREET, SUITE 732
FAIRFAX, VA 22203-1977
Tel.: (703) 696-7779; Fax: (703) 696-8449
e-mail: charles.lee@afosr.af.mil

by

PROFESSOR LARRY R. DALTON
DEPARTMENT OF CHEMISTRY
UNIVERSITY OF WASHINGTON
BOX 351700
SEATTLE, WA 98195-1700
Tel.: (206) 543-1686; Fax: (206) 685-8665
e-mail: dalton@chem.washington.edu

Final Technical Report

ORGANIC ELECTRO-OPTIC MATERIALS: Since the late 1990s, the Dalton laboratory has been the sole source of state-of-the-art organic electro-optic materials. Materials from this AFOSR grant effort have gone to Jim Grote at AFRL (references 22,47,54,75,85,88,91,102,109) to support his research on the development of conducting cladding materials for state-of-the-art electro-optic devices, to the Navy Weapons Center at China Lake (Jeff Lindsay) and the Army Redstone Arsenal Laboratory (Paul Ashley) to support development of the optical gyroscope, to University of Texas Austin (Ray Chen) and Radiant Photonics in support of BMDO (MDA) research and a variety of prototype device development projects (references 21,26,37,68,71,96,100), to TACAN/IPITEK (Jim Becthel) in support of BMDO (MDA) research and to produce high bandwidth electro-optical switches (reference 53). Our laboratory has also hosted researchers from NIST (Colorado) in their evaluation of the high frequency response of organic electro-optic materials and in their utilization of our materials to develop high frequency test instrumentation. Materials have been provided to a number of companies (Lockheed Martin, Boeing, Lucent, General Electric, Corning, etc.). Materials and simple prototype devices have been provided to AFRL and DARPA programs to evaluate thermal, photochemical, and radiation stability. The successes of the Dalton research group has contributed significantly to a number of companies re-launching research efforts in the area of organic electro-optics including Lucent (reference 123), Corning (reference 124), IBM, DuPont, Dow Corning, Boeing, etc.

Let us briefly review why materials produced in the Dalton research laboratory have motivated a renewed interest in organic electro-optic materials and let us review newly defined research paradigms that have guided the critical improvements in materials (for more in-depth discussions, please see references 2,8,32,65,97,103). Then we will briefly review prototype devices that we have fabricated and evaluated with various generations of materials (references 14,17,19,26,35,37,39,48,52,57,63,68,69,71,80,100,101,110-114). Stated most simply, organic electro-optic materials are of interest because of their potential for ultrafast electro-optic response (large bandwidth), exceptionally large electro-optic activity that translates to low operational voltages for devices, and processability that translates into the cost efficient production of sophisticated (including 3-D) device structures. Of great concern with organic materials are issues of optical loss, thermal stability, photostability, and radiation hardness. ***Bandwidth***: The easiest characteristic to achieve is fast response to applied voltages (device bandwidth). The fundamental response time of an organic electro-optic material is the phase relaxation time of the π-electron system. This is on the order of femtoseconds and indeed terahertz signal generation and detection (to 15 THz) has been accomplished by Michael Hayden (University of Maryland Baltimore County) working with the Dalton research group. However, bandwidth is normally limited by the resistivity of metal electrode structures. Recently, researchers at Lucent (reference 125) have demonstrated Mach Zehnder modulators, fabricated from organic materials, which exhibit operational 3 dB bandwidths of 200 GHz. Observable modulation was demonstrated by these workers to 1.6 THz. This is consistent with both published (references 1,65,&126) and unpublished observations out of the Dalton/Steier/Fetterman collaboration. Because electrical components typically define bandwidth, considerable effort is now being expended to develop device configurations (heterodyne (reference 53), ring microresonator and

photonic bandgap (references 84,98,99) that permit exploitation of the enormous intrinsic bandwidth of organic electro-optic materials. This will be discussed at somewhat greater length later in this section. ***Electro-Optic Activity/Drive Voltage***: In general electro-optic coefficients in the range 60-200 pm/V are required if organic electro-optic materials are to have significant commercial impact. This applies to both analog and digital information processing applications. For analog applications, signal-to-noise and dynamic range (defined by the noise floor) are both related quadratically to electro-optic activity. For digital signal processing, large electro-optic activity is required to avoid costly and bandwidth-limiting digital amplifiers. For both digital and analog applications, drive voltages on the order of one volt or less are typically required. For electric-to-optic-to-electrical signal transduction (e.g., RF photonics) such voltages lead to "lossless" RF distribution or even "gain" in the transduction (transformation) process if the electro-optic activity is large enough. Also, different device structures will require different levels of electro-optic activity for operation; for example, polarization-insensitive electro-optic modulators using electrically-poled organic materials require three times the electro-optic activity of polarization-sensitive modulators. As demonstrated by both Joe Zyss (reference 127) and ourselves (references 65,110), polarization-insensitive electro-optic modulation can be achieved by either rotating the direction of poling or by rotating the positioning of drive electrodes as one proceeds along a waveguide modulator. Since $r_{33} = 3xr_{13}$, a factor of three greater modulation is required than for a simple Mach Zehnder based utilization of r_{33} alone.

To obtain large marcroscopic electro-optic activity one must typically synthesize chromophores with large molecular first hyperpolarizabilities, β, and then one must organize such chromophores into a noncentrosymmetric (acentric) lattice characterized by a large number density, N, and order parameter, $\langle\cos^3\theta\rangle$. Note electro-optic activity, r, is proportional to $N\beta\langle\cos^3\theta\rangle$. Over the period from 1990 to the present, we and others (Seth Marder, Tobin Marks, Alex Jen, etc.) have achieve approximately a factor of 1000 improvement in $\mu\beta$ (in the absence of intermolecular electro-static interactions, $\langle\cos^3\theta\rangle = \mu F/5kT$ where F is the effective poling field felt by the chromophores, m is the chromophore dipole moment, and kT is the thermal energy at the poling temperature). Indeed, FTC and CLD chromophores (1,65) based on a tricyanovinyl furan acceptor group (exhibiting $\mu\beta$ values of 18,000 and 30,000 x 10^{-48} esu respectively) represented critical breakthroughs in electro-optic activity and stability (references 1,2,8,31,39,58,65,69,97). These chromophores led to the first sub-1V electro-optic modulators (references 31,97). There are four aspects to the design of successful chromophores: (1) Use of quantum mechanics to prepare molecules yielding large molecular hyperpolarizability, (2) use of knowledge of organic chemistry to design chromophores exhibiting good stability and good processability, (3) synthesis of chromophores in high yield by cost effective routes, and (4) efficient processing of chromophores into hardened ordered macroscopic lattices characterized by large N and $\langle\cos^3\theta\rangle$ (Since for real systems with intermolecular electrostatic interactions, N and $\langle\cos^3\theta\rangle$ are not independent, the trick is to maximize the product $N\langle\cos^3\theta\rangle$). The use of quantum mechanics (both by the Dalton group and the Dalton group working with theorists Jean-Luc Bredas (UArizona) and Kim Ferris (Pacific Northwest National Laboratory, PNNL)) to systematically improve molecular hyperpolarizability is illustrated by a consideration of Figure 1.

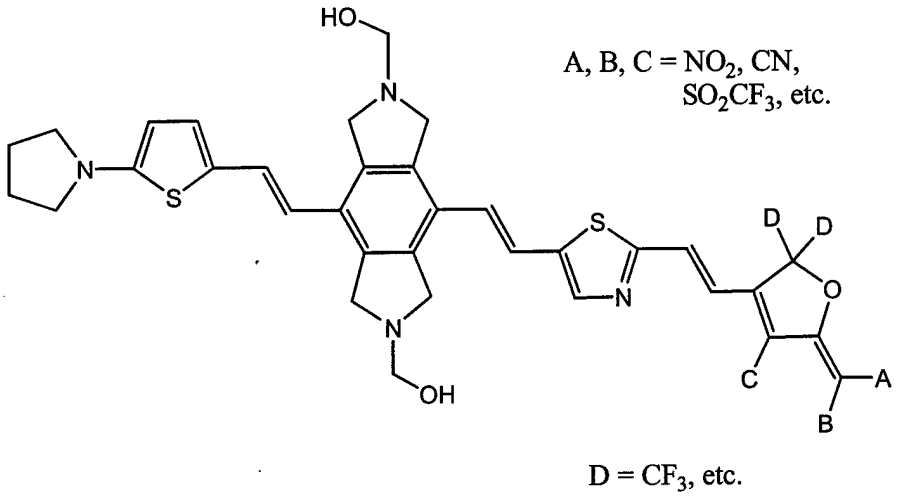
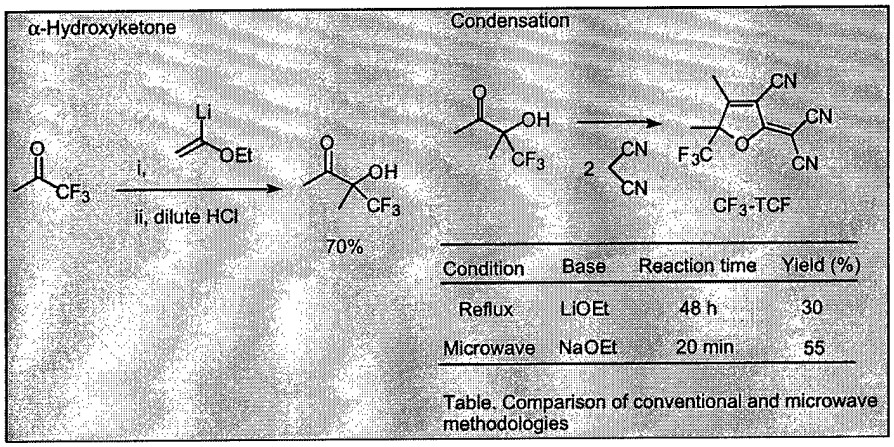


Figure 1. A prototypical high μβ chromophore structure is shown. Theoretical calculations (discussed in the text) suggest how molecular hyperpolarizability can be systematically improved by variation of bridge structure and acceptor ligands. One can think of optimum structures as "gradient bridge" "mixed ligand acceptor" structures.

If A=B=C= CN, then one has the tricyanofuran group already familiar from chromophores such as FTC, CLD, and CWC (reference 97). Theory predicts and experiment confirms that replacing a single CN group with a nitro group doubles the molecular hyperpolarizability. In like manner, a bridge with thiophene and thiazole groups such as shown in Figure 1 exhibits three times the molecular hyperpolarizability of a bridge segment containing two thiophene groups. During much of the preceding grant period we were able to carry of characterizations of μβ and β using EFISH and HyperRayleigh Scattering (HRS) instrumentation located in the laboratory of our collaborators (e.g., references 9,25,41). As that instrumentation became unable (because of investigators moving on to other positions), we have had to construct such capabilities at the University of Washington. Such instrumentation is now available at 1.3, 1.55, and 1.9 micron wavelengths and hyperpolarizability is now routinely being investigated as a function of wavelength. Moreover, we have constructed femtosecond time-resolved spectroscopic capabilities capable of defining other relevant parameters such as two-photon absorption and excited state energy transfer mechanisms (e.g., reference 3).

Thermal and Photochemical Stability. We have also designed molecules for significant stability. Indeed, a chromophore must be capable of withstanding temperatures to 300 C before it is considered for processing into electro-optic materials. Efficient and high yield syntheses are considered important and a number of papers

(references 24,29,72) simply focus on introducing new synthetic routes or optimizing generally known procedures. Recently, we have found microwave synthesis techniques useful for both reducing reaction time and increasing yields. An example is shown in Figure 2.



Condition	Base	Reaction time	Yield (%)
Reflux	LiOEt	48 h	30
Microwave	NaOEt	20 min	55

Table. Comparison of conventional and microwave methodologies

Figure 2. An example of the enhancement of reaction yields and decrease in reaction time using microwave synthesis is shown.

Microwave synthesis has proven relevant to enhancing reaction efficiency for many of the reactions involved in chromophore synthesis including protection/deprotection, coupling, etc. reactions.

Although considerable effort must be expended in the design, synthesis, and characterization of chromophores, identification of a potential candidate chromophore is just the start of the long process of achieving a useful electro-optic material. The central problem is that large intermolecular electrostatic interactions among high dipole moment chromophores oppose the realization of a large $N\langle\cos^3\theta\rangle$ and hence electro-optic activity. The centrosymmetric crystallization driven by such interactions also impacts other aspects of the processing of chromophores into high quality waveguide materials; in particular, chromophore aggregation can lead to light scattering and unacceptably high levels of optical loss. Derivatization has been used for several decades to improve the solubility and processability of "conducting polymers" (e.g., the work of Wudl, students of Stille, and others); however, because of the high dipole of electro-optic chromophores intermolecular electrostatic interactions are both much larger and spatially anisotropic. Indeed, quantitatively understanding the action of such interactions is no simple

theoretical feat and has occupied a significant fraction of our attention during the preceding grant period (references 34,55,65,67,79,89,97,119) and will continue to do so during the period of proposed research. The fundamental statistical mechanics problem is that of defining the potential that a reference chromophore experiences from a large surrounding ensemble of interacting dipolar chromophores. We have pursued two approaches to this problem: (1) Derivation of an analytical expression for such a potential function and (2) definition of such a potential by Monte Carlo methods. The agreement between these two methods is satisfactory and both leads to essentially quantitative prediction of the variation of macroscopic electro-optic activity with chromophore shape and loading in a host polymer matrix (see Figure 3 for the example of CLD in amorphous polycarbonate (APC)).

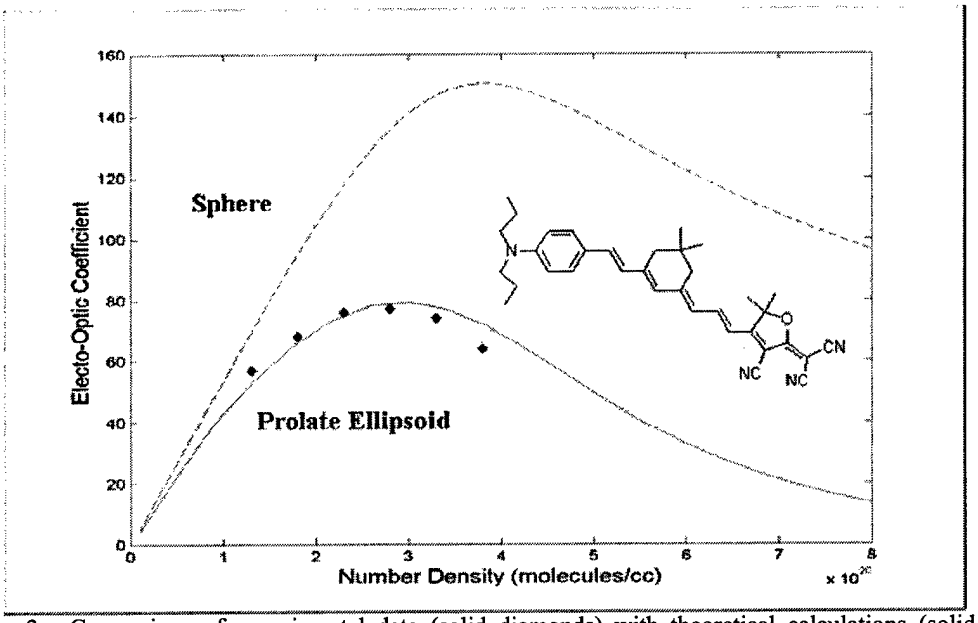


Figure 3. Comparison of experimental data (solid diamonds) with theoretical calculations (solid and dashed lines).

Figure 3 shows the predicted variation of electro-optic activity with chromophore loading (number density, N) calculated using the analytical potential function mentioned above (without adjustable parameters). Although this potential function is not as accurate as that of Monte Carlo methods, it does have the advantage of permitting analytical expressions for the dependence of electro-optic coefficient on N to be derived and of permitting calculations (such as shown in Figure 3) to be run on personal computers. Thus, the effect of varying chromophore shape and dipole moment can be quickly assessed. The analytical potential function calculations readily permit the variation of electro-optic coefficient with chromophore loading to be assessed from the independent particle limit (low concentrations where electro-optic coefficient increases linearly with number density) to the centrosymmetric crystallization limit (where electro-optic activity goes to zero for a pure chromophore lattice). As is evident from Figure 3, simple theory immediately permits identification of the material composition leading to optimum

electro-optic activity and permits prediction of the variation of maximum electro-optic activity with chromophore shape. Simple analytical theory also permits understanding of the weak dependence of N_{max} (the concentration at which maximum electro-optic activity is observed) on the strength of the electric poling field. Simple theory is also capable of providing semi-quantitative understanding of the results obtained by Professor Tobin Marks and coworkers (reference 128) in preparing electro-optic materials by sequential synthesis from a surface utilizing covalent coupling. In this case, theory predicts and experiment shows the tilting of chromophores from the normal to the surface with increasing chromophore dipole moment. This both attenuates macroscopic electro-optic activity and increases the potential for disorder in the assembly process. Again, the take-home observation is that chromophore shape ("footprint") is important for sequential synthesis methods as well as for electric field poling methods.

It is important to note that the theoretical advances described above have contributed in large part to the realization of the current record electro-optic activity of 130 pm/V (for a Mach Zehnder device operating at 1.3 microns). Theory has provided the critical design paradigm that has permitted systematic improvement in electro-optic activity over the past three years. Kinetic Monte Carlo (KMC) methods have the added advantage of permitting visualization (although at the cost of added computational complexity) of chromophore spatial distributions for different concentration regimes. This can be thought of as defining the phase diagram for homogeneous and inhomogeneous chromophore distributions. KMC calculations indicate that through the region of the maximum in the plot of electro-optic activity versus number density a homogeneous distribution of chromophores applies. The effect of increasing concentration is to tilt the orientation of the "reference chromophore" away from the poling field direction (decrease $<\cos^3\theta>$) much like the tilting of chromophores from the normal to the surface in Tobin Marks' sequential synthesis arrays. However, as the concentration leading to maximum electro-optic activity is significantly exceeded aggregates start to form (these can be considered to represent a Boltzmann distribution of aggregate sizes). Such aggregates will lead to increasing light scattering as chromophore number density is increased. Finally, aggregates will coalesce into centrosymmetric crystals.

A striking observation of the previous research is that electro-optic activity (and auxiliary properties of optical loss and thermal stability) could be significantly improved by synthesizing multi-chromophore containing dendrimer materials (references 40,60,65,82,90,93,111). Factors of two to three improvement in electro-optic activity was observed relative to the same chromophore in a conventional polymer host (references 40,60,65,82,90,93,111). The ordering of multi-chromophore containing dendrimers in an electric poling field is considerably more difficult to understanding (simulate by theoretical methods) than for "rigid" object chromophores existing in a polymer composite. Atomistic KMC calculations, which accurately treat bond rotation potentials, are required to understand the conformations leading to observed electro-optic activity. We have carried out preliminary calculations that rationalize the results observed to date; however, full atomistic KMC calculations are very costly and a more cost effective approximate route to the theoretically-inspired systematic design of multi-chromophore dendrimers is required and will be the subject of proposed research.

Atomistic KMC calculations suggest the following picture of multi-chromophore containing dendrimers. First of all, the dendritic branches do not appear to interpenetrate (from dendrimer to dendrimer). This is likely a steric feature and may relate to increased density near the surface of dendrimers. This theoretically-derived picture appears consistent with experimental data to-date. For example, excellent optical-quality spin cast films are obtained from "uncrosslinked" dendrimers but these films crack on standing indicative of weak dendrimer entanglement. Moreover, the cracks readily anneal on heating. Theory suggests that multi-chromophore dendrimers adopt a partially closed umbrella shape and that the action of the poling field is to further close the dendrimer umbrellas. Crosslinking is critical to stabilizing the poling-induced conformations and plays an important part in the exceptionally large electro-optic activity values observed. Dendrimers lead to excellent solubility in traditional spin casting solvents and the reduced inter-dendrimer interactions lead to excellent homogeneity of the spin cast films. This, together with reduced proton density in partially fluorinated dendrimer structures, leads to very low values of optical loss (tenths of dB/cm—comparable to lithium niobate waveguides at telecommunication wavelengths). Clearly, multi-chromophore containing dendrimers provide a new route to improved organic electro-optic materials and the potential of this approach is only just being to be explored.

Stabilization of electric field poling induced acentric chromophore order by intermolecular crosslinking reactions and control of polymer segmental flexibility has been a continuing theme of our research on organic electro-optic materials (references 2,13,16,46,58-61,65,69,82,90,93,111). Crosslinking enhances photochemical stability as well as thermal stability due to its effect on slowing the diffusion of oxygen through the polymer matrix. The general observation is the higher the crosslink density, the greater the thermal stability. A typical trend would be a thermal stability of about 50°C for a chromophore such as CLD dissolved in PMMA to form a composite material, the thermal stability typically improves to 80-90°C if one end of the chromophore is covalently attached to a PMMA matrix, and the thermal stability improves to 170°C if both ends of the chromophore are attached to a three-dimensional crosslinked matrix. Thermal stability in the preceding sentence is defined as the temperature at which second order nonlinear optical activity (second harmonic generation or electro-optic activity) is first observed to decrease in a thermal ramping experiment (heating at rates of 5 to 10 °C/minute). Of course, the detailed thermal stability depends on the detailed polymer structure (segmental flexibility); this explains the improved thermal stability observed for some dendrimer structures. A significant problem is simultaneously achieving both high electro-optic activity and thermal stability of that activity when thermal crosslinking reactions are employed. This is due to the fact that the kinetics of poling and crosslinking complete with each other. The impact is somewhat reduced by using computer-controlled stepped (temperature, electric field) poling protocols. However, the temperature dependence of the crosslinking reaction must in general be compatible with poling temperatures and this must be keep in mind when identifying new crosslinking chemistry. We have devised (references 60,93,111,119) crosslinking reactions that avoid water sensitivity; this has led to some significant improvements in material properties (reduced optical loss).

Photochemical stability (references 65,69,80,111,113,119,129) is essentially a matter of avoiding singlet oxygen chemistry. We have looked unsuccessfully for secondary decomposition mechanisms in materials that we have produced. Studies include femtoseconds pulse studies employing pulse powers significantly in excess of 10 GW/cm^2. We, and others, have shown that photochemical stability can be dramatically improved by exclusion of oxygen (simple packaging—see accompanying figure), by chromophore design, by crosslinking, and by use of scavengers. The following figure is

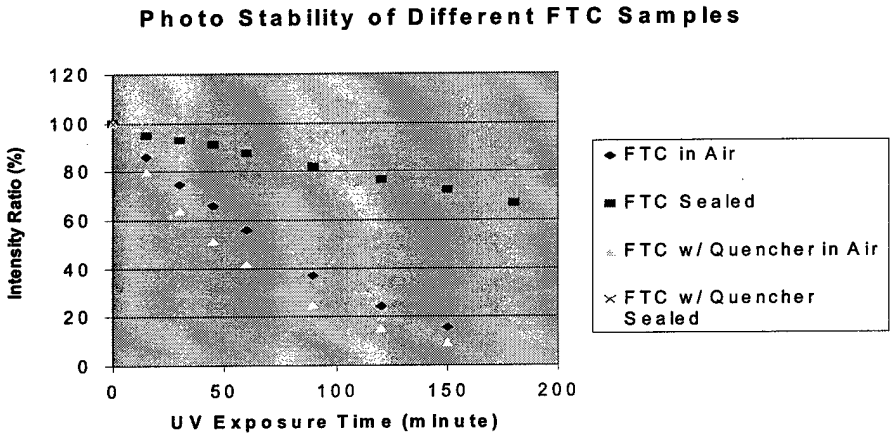


Figure 4. The variation of photostability with the presence of quenchers and partial exclusion of oxygen is shown. Results are discussed in the text.

illustrative of effect of various variables. The most rapid photodegradation is observed in the case of addition of scavengers (which causes plastization of the chromophore/polymer composite) but the sample is always exposed to an excess of oxygen. The singlet oxygen chews up the scavenger and then proceeds to destroy the chromophore. This result illustrates the effect of lattice flexibility on oxygen diffusion rate and photostability. When oxygen is limited, the scavenger results in an improvement in photostability. The problem of photostability encountered with electro-optic materials is analogous to that encountered with organic light emitting diodes and indeed is likely somewhat less problematic that for OLEDs as no current flow occurs. Packaging has been shown to be critical for both classes of materials.

Processability and the Fabrication of Sophisticated Device Structures. In the previous funding period, we have demonstrated a number examples of exploiting the excellent processability that can be achieved with organic electro-optic materials (2,5,7-10,20,65). Three dimensional optical circuitry can be achieved by exploiting novel etching techniques using gray scale, shadow ion, and offset lithographic masking techniques (7); power and polarization splitters have been fabricated as well as stacked electro-optic device structures (e.g., those used for phased array radar). We have also explored the use of 2-photon and multi-color photolithographic techniques to fabricate 3-D structures. New processing techniques have also been used to fabricate low insertion loss electro-optic device structures. Recently, our research collaborator, Bill Steier (USC EE Dept.) has achieved device insertion loss values as low as 3 dB. This is lower than

has been achieved to-date with lithium niobate devices (typical insertion loss values are 5-6 dB). (With lithium niobate, reduction of insertion loss is a matter of index of refraction matching while with organic electro-optic materials reduction of insertion loss depends of mode size matching).

We have also demonstrated the processability of organic electro-optic materials by fabricating a number of prototype device structures with superior performance capability. These include RF photonic phase-shifters for phased array radar applications (14,57), spatial light modulators (laser beam steering devices) (21,68,71,96), an acoustic spectrum analyzer (48), optical switches (26,37,53), and analog-to-digital converters (35,52). One of the most interesting prototype devices fabricated is illustrated in Figure 5 (reference 99).

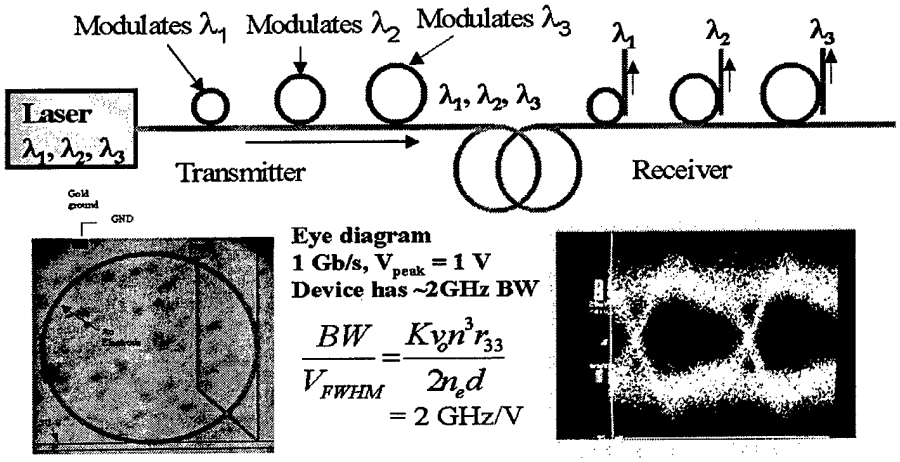


Figure 5. An active polymeric WDM transmitter/receiver is shown.

Transmitter and receiver microresonator devices are fabricated from organic electro-optic materials. For such structures (particularly for minimizing the size of microresonators) it is desirable to have as large an index of refraction contrast between active waveguide and cladding waveguide as possible. The relatively small index of refraction contrast that is achieved with all organic structures limits microresonator dimensions to radius values between 25 and 200 microns. For such resonators, we typically obtain quality factor, Q, values of 10^5 to 10^6. This leads to a wavelength selectivity of 0.01 nm and as shown in Figure 5 we are able to transduce (in our first efforts using CLD/APC materials) data at a rate of 1 Gb/sec employing a 1 volt drive voltage. A bandwidth sensitivity product of 2 GHz/volt was demonstrated. Both digital and analog active wavelength division multiplexing (WDM) has been demonstrated using both 1.3 and 1.55 micron telecommunication wavelengths as the optical carrier.

METAL CORE DENDRIMER MATERIALS: (references 43,78,81,86,92,94,95,98, 104, 105,107,108, 115). Although we are pursuing the study of both dendritic and polymeric matrices incorporating chelated transition and rare earth metal ions, our studies ultimately focus on exploiting the unique control of physical properties afforded by dendrimers; thus, our discussion will focus upon both metal chelation and the design of chelates amenable to serving as the building blocks of dendrimer architectures. To

conserve space, we limit our discussion to selected examples of our work and not to a comprehensive overview.

Luminescent metal complexes have been used widely in applications such as emission sources for displays and organic light emitting devices (reference 130), sensors for temperature and pressure (reference 131) and harvesting materials for energy transfer (reference 132). Part of the usefulness of metal complexes is the fact that the complexes can be designed to be extremely photo-stable and have strong emission quantum yields. The emission may be tunable by changing the ligand field around a metal core, or changing the metal core, or by changing both. Emission that ranges from the ultraviolet to the infrared has been achieved from various metal complexes. Thus, the emission may be tuned for the specific application. Here we pursue a variety of applications for metal complexes, which require new synthetic schemes for the desired result.

When a metal complex, absorbs a quanta of energy and goes to an excited state, there are a variety of ways that the energy may be released to return the system to its lowest energy confirmation, all of which are relevant to the proposed research (reference 133). These include luminescent, non-radiative, chemical decomposition, and the quenching process. Non-radiative (or non-luminescent) and photodecomposition pathways are generally to be avoided. Non-radiative processes reduce the intensity of the emitted light decreasing the usefulness for some applications such as organic light emitting devices (OLEDs). Decomposition is more serious as once the emitter decays the device fails and needs to be replaced. Thus, it is desirable to make the complexes as stable as possible. (However, decomposition could find usefulness as a sensor to determine exposure to UV light.) The last method of deactivation is the quenching process. In this pathway of deactivation, a bimolecular reaction takes place between the excited state entity and another entity, B that collides with it. Energy is transferred to B and it is excited to its excited state. An example of a molecule that acts as a quencher is molecular oxygen. Molecular oxygen exists in a triplet ground state. When molecular oxygen collides with a species in an excited state, singlet oxygen (excited state oxygen) is formed and gives the species in its relaxed ground state.

For transition metals, the emission is from either one of two states. These states are the ligand centered state (LC). This is defined as the π–π^* transition on the ligand. Another state is the metal to ligand charge transfer state (MLCT) which is defined to be the transfer of an electron from the metal core to the ligand π^*. There is an additional state, called the metal centered state (MC), which is a molecular transition (t_{2g} to e_g^* for complexes in O_h symmetry) within the metal core and is antibonding in nature. This state is non-luminescent and leads to increased degradation and loss of emission yield with increasing temperature. Thus, it is preferable to design a molecule with the MC state as high in energy as possible as to avoid population of the state. The position of the states to each other is dependent upon where the metal core is located in the periodic table (reference 133). Divalent iron has the metal centered state lowest in energy. The consequence of this is iron complexes are non-luminescent. Both divalent ruthenium and osmium have the MLCT state lowest in energy; thus, both form luminescent complexes. However, the separation of the MC state from the MLCT state in ruthenium complexes is small while it is large for osmium. The consequence of this is that divalent osmium

complexes are more photo-stable and there is less loss of emission yield with increasing temperature than ruthenium complexes (Table 1). Using this theory in synthetic strategy complexes have been synthesized that have photo degradation of less than 1% under excitation from quartz halogen tungsten lamps, and there has been no observable degradation under direct exposure to sunlight over a period of 20 months.

Table 1: Properties of Ruthenium(II) and Osmium(II) Compounds

Complex	Emission (MLCT) nm	Temperature Dependence %/°C	Photo-degradation %/90min
$Ru(batho)_3$	610	1.2	20
$Ru(batho)_2Cbx$	673	0.48	3
$Os(batho)_2dppene$	619	0.33	1
$Os(diphbpy)_2dpae$	650	0.08	0
Ir(coumarin-6)	575	0.65	1
Ir(btp)	600	0.37	1

Batho = 4,7-diphenyl-1,10-phenanthroline, Cbx = 4,4'-dicarboxybutylester-2,2'-bipyridine, diphbpy = 4,4'-diphenyl-2,2'-bipyridine
Bpy = 2,2'-bipyridine, dppe = diphenylphosphinoethane, dpae = diphenylarsenoethane
Btp = 2-pyridine-2-benzo[b]thiophene
Photo-degradation was carried out at 25 °C, 760 torr pressure, and a photon flux of 1,000 □w/cm^2.

Quantum yields of up to 24% for divalent osmium complexes have been reported. However, these complexes emit at 600 nm (yellow-orange in color) and would require significant tuning to make either a green or red emitter. For successful application in organic light emitting diodes (OLED), the complex would have to either be blue or red shifted significantly. However, there could be significant problems with red shifting. The energy gap law describes the often-observed loss in quantum yield with red shifting emission. This is due to the narrowing of the energy separation between the ground and emitting states. As the energy separation decreases (red-shifting), the non-radiative rate is enhanced leading to a decrease in emission yield. Thus, the energy gap law is an obstacle for successful application of divalent osmium complexes to OLED applications. To over come this obstacle, one must observe what enhances non-radiative decay. It is well known that bond vibrations and stretches, such as C-H, N-H, or O-H bonds, may lead to decreased quantum yields. Also, bond rotations, such as C-C rotations, may lead to decreased quantum yields. Thus, elimination of these example sources of non-radiative decay may lead to an increase in emission yield. It has been shown with divalent ruthenium complexes that the addition of phenyl groups on a polypyridyl structure can result in a violation of the energy gap law. This has been explained in other reports by intramolecular motion. Figure 6 gives a crystal structure of one of the osmium complexes. It can be clearly seen that the phenyl groups in the

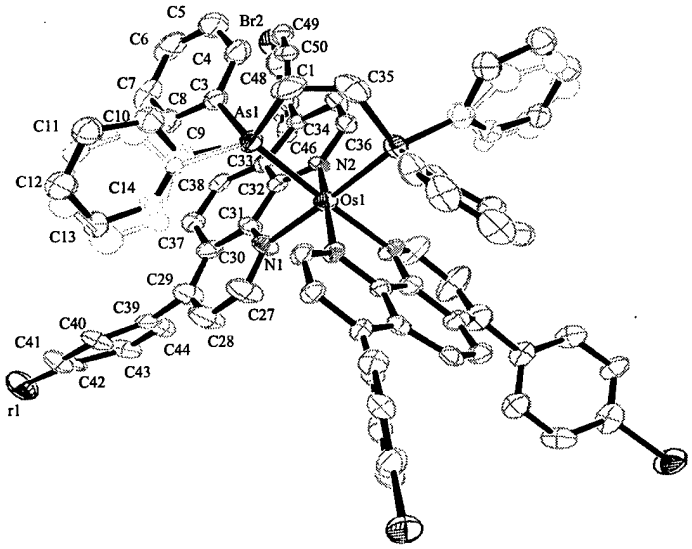


Figure 6. Crystal Structure of [Os(II) (4,7-bis(p-bromophenyl-1,10-phenanthroline)$_2$ cis-1,2-vinylenebis(diphenylarsine)]$^{2+}$. Counter ions and hydrogens removed for clarity; 50% probability spheres

4,7 positions are rotated out of plane of the main 1,10-phenanthroline structure. It has been shown that the phenyl groups rotate to a co-planar position in the excited state. This leads to an extension of the π network and produced a hindrance of C-C bond rotation in the excited state. Also, two C-H bond vibrations are reduced by the addition of phenyl groups. Using these techniques, complexes have been developed which have quantum yields up to 45% while red shifting to 650 nm, which is a violation of the gap law.

The emission from the lanthanide metals is unlike that for the transition metals described previously. The emission is not molecular in nature and arises from electronic transitions within the metal core itself. Due to a prominent sharp narrow band at approximately 615 nm, chelates of trivalent europium have found applications in organic light emitting devices and display technology. The emission spectrum of europium is due to the transitions between the excited states and the ground (D_0) state. The assignment of the emission bands can be made as follows: 584 nm ($^5D_0 \rightarrow {}^7F_0$); 596 nm ($^5D_0 \rightarrow {}^7F_1$); 617 nm ($^5D_0 \rightarrow {}^7F_2$); 661 nm ($^5D_0 \rightarrow {}^7F_3$); 716 nm ($^5D_0 \rightarrow {}^7F_4$)[6] . For the transitions of $^5D_0 \rightarrow {}^7F_1$, $^5D_0 \rightarrow {}^7F_2$, and $^5D_0 \rightarrow {}^7F_4$, splitting is presented due to the manifold of the corresponding ^7F_x energy levels. Since the transitions are electronic in nature, emission band are extremely narrow and emission with a FWHM of 5 nm with up to 45% quantum yield have been achieved (reference 98).

Some challenges to the widespread use of lanthanide have been the lack of intensity of the emission, the self-quenching of emission as the metal cores come in close proximity to each other, and to increase the absorption coefficient of the various electronic transitions, which are generally weak. A synthetic strategy has been to build energy transfer ligands based upon the β-diketone structure. The binding constant of β-diketones is larger than that of other types of ligands such as ligands based upon a carboxylate functionality. The ligands are formed by Clasian condensation of an ester

with a ketone. This makes for a large number of possibilities for ligand combination and tuning triplet energy levels for optimal overlap with the lanthanide metal core. Thus far research has focused upon building large aromatic or dendritic systems into the β-diketone structure. The purpose of this is twofold. One is to prevent the metal cores from coming in close proximity to each other; thus, preventing self quenching and the other is to act as energy transfer agents to increase quantum yield of the metal centered luminescence. The process of energy transfer takes place by Förester energy transfer. The ligand absorbs light through the π–π^* transition. From the heavy atom effect, intersystem crossing takes place to the triplet state. The triplet energy of the ligand is then transferred to the triplet of the lanthanide metal core where emission takes place. Thus, for efficient energy transfer to take place, the triplet energy of ligand must be tuned to the specific lanthanide being used, not the singlet π–π^* transition. A way that has been employed to test the triplet energy levels of the β-diketone ligands is to complex them with gadolinium. Due to its half filled shell, the metal electronic transitions are very high in energy, thus, no emission is seen from the gadolinium core itself. Emission from gadolinium complexes is observed from the ligands themselves. Because of the heavy atom effect of the gadolinium, the emission is phosphorescence from the triplet energy levels of the ligand. By complexing the ligand to gadolinium, the triplet energy levels can be determined and the appropriate steps can be taken to ensure efficient energy transfer to europium, terbium or any other lanthanide core.

Rapid growth in the use of organic light emitting devices (OLED) is expected in the coming years due to their potential application in large screen flat panel displays (reference 134). For full-color displays, efficient LEDs emitting three primary colors, *i.e.*, blue, green and red, are required. However, obtaining strong red emission from conjugated polymers or small molecules is generally difficult because of the difficulty in obtaining sufficient conjugation length, and the band gap law. Recently there has been some focus on the use of triplet emitting compounds. Some published work in this area has focused on trivalent iridium complexes, various platinum porphyrin derivatives, and divalent ruthenium (Ru) complexes such as Ru(II) tris(4,7-diphenyl-1,10-penanthroline)(reference 135). However, osmium (Os) complexes have largely been ignored for applications in OLEDs (reference 136). There could be various reasons for this. One perception is that Os complexes in general have low quantum yields when compared to its Ru counterparts. We have reported the successful use of various novel Os(II) complexes, which feature strong red emission and high quantum yields, for OLED purposes, and propose new synthetic routes to make higher performing complexes of divalent osmium The lanthanide metals are known for their narrow emission bands and long lifetimes making them ideal choices for use in OLEDs. Progress is still needed in improving the intensity of emission as well as the overall efficiency of device performance.

1. Osmium as emission source

Complexes of divalent osmium have been shown to exhibit properties that make them promising candidates for use as an emission source in OLEDs. Because of the high energy MC state, the complexes of Os(II) would be expected to show very little photo decomposition and very little temperature dependence to their luminescence. Due to the very strong back bonding and large spin orbit coupling parameter of osmium and to the

MLCT origin of emission, excited state triplet lifetimes of complexes made from divalent osmium would be expected to be very fast. The short excited state lifetime could lead to increased OLED efficiency since it would be very difficult to saturate the excited state due the rapid decay.

In novel, preliminary work, several OLED's have been fabricated, and have affirmed that the luminescent properties of divalent osmium make for a promising class of OLED technology. The first double layer devices were made from [Os(II) (4,4'-diphenyl-2,2-bipyridine)$_2$ 1,2-(diphenylarseno)ethane] (**1**) in a poly(vinylcarbazole) PVK:PBD mixture with 3% by weight osmium complex. Double layer devices were chosen since the fabrication of such devices is much cheaper and commercializable than corresponding triple or quadruple layer devices. This first device based upon **1** gave performance of over 300 cd/m^2 in brightness and efficiency of 0.64%. As a reference, a CRT monitor gives about 300 cd/m^2 at its maximum brightness. This result was encouraging and work continued. Using synthetic schemes illustrated in Figures 7 and 8, non-radiative pathways were reduced and quantum yields were enhanced to over 45%. The devices based upon [Os(II) (4,7-bis(p-methoxyphenyl)-1,10-phenanthroline)$_2$ cis-1,2-bis(diphenphosphino)ethane](**10**) gave over 1400 cd/m^2 and efficiencies up to 0.78%.

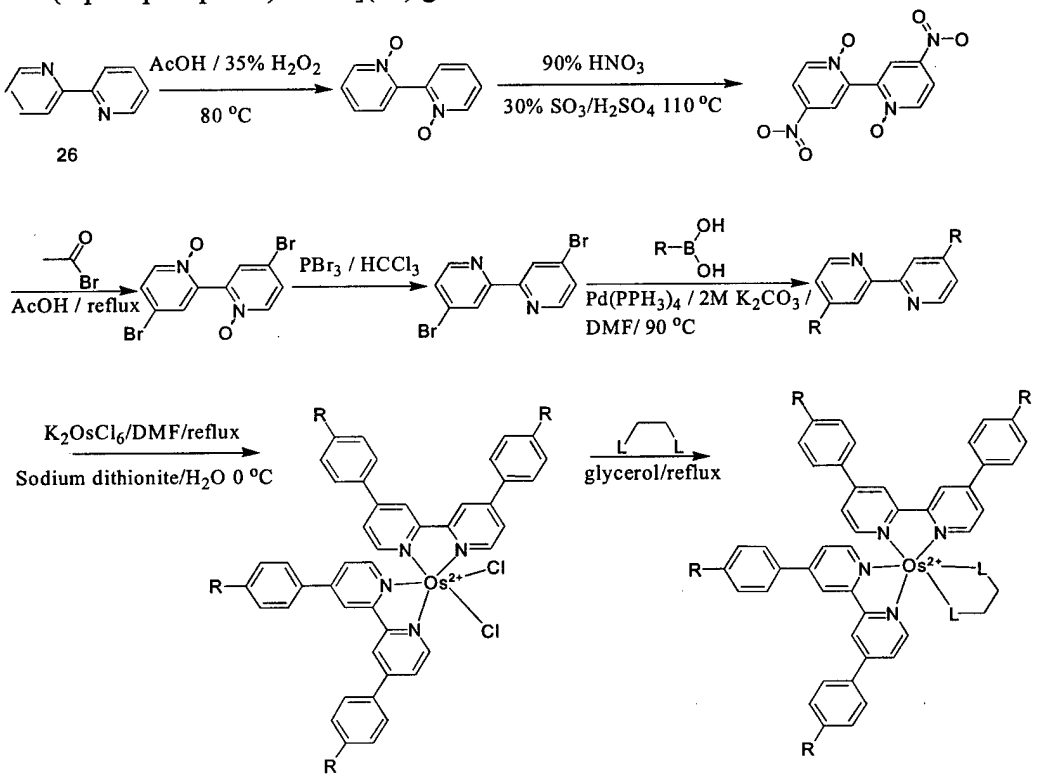


Figure 7. Synthesis of derivatives of 2,2'-bipyridine and osmium complexes is shown.

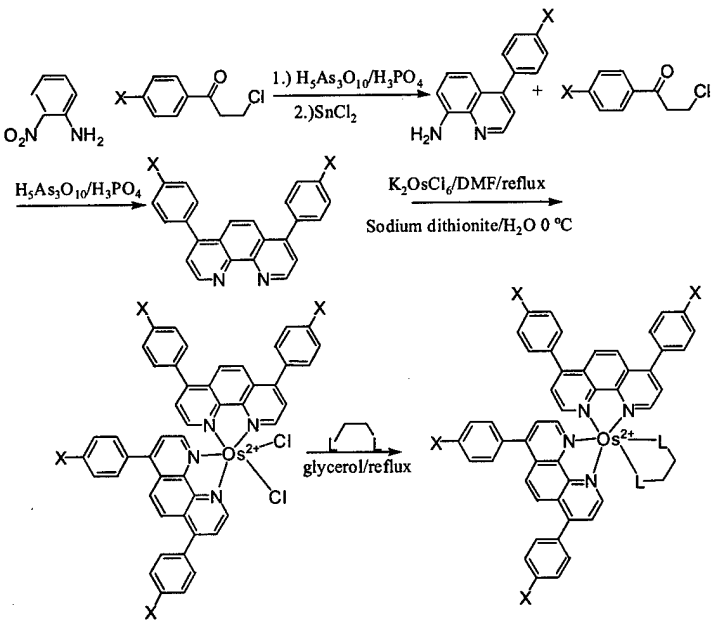


Figure 8. Synthesis of 1,10-phenanthroline derivatives and osmium complexes is shown.

Different polymer host materials were also used with the osmium complexes. Devices based upon a mixture of poly(2-vinylnapthalene) and PBD (PVN:PBD) (Figure 8) were attempted and the results were encouraging. A double layer device made with PVN:PBD and [Os(II)-(4,7-Bis-(4-naphthalen-2-yl-phenyl)-[1,10]phenanthroline)$_2$ cis-1,2-vinylenebis(diphenylarsine)] (**14**)gave a brightness of 870 cd/m^2 and an efficiency of 2.2%. The same complex in PVK:PBD gave 1,100 cd/m2 with an efficiency of 0.4%. PVN is not as conductive as PVK so a drop in brightness was expected; however, the results exhibit great promise that derivatives of PVN could be used to enhance both the brightness and efficiency of devices based upon osmium complexes. OLED performance is summarized in Table 2.

Table 2. Performance of Os complex doped LEDs: ITO/BTPD -PFCB/Os complex: PVK:PBD (~45 nm)/Ca (Type I) or ITO/BTPD -PFCB/Os complex:PVN:PBD(~45nm)/Ca (Type II).

Os complex	X^-	Device	V_1 (V) [a]	B_{max} (cd/m^2) [b]	η_{max} [c]
1	HFB	I	9.3	310	0.64%
2	HFB	I	7.5	260	0.27%
2	Ts	I	8.7	970	0.27%
3	HFB	I	7.6	410	0.60%
3	Ts	I	7.5	725	0.42%
4	Tf	I	8.4	600	0.32%
6	Tf	I	6.7	799	0.28%
7	Tf	I	6.9	750	0.20%
8	Tf	I	6.4	1030	0.31%
9	Ts	I	9.4	460	0.39%
10	Ts	I	7.6	1430	0.48%
11	Ts	I	8.0	1210	0.78%
12	Ts	I	7.5	760	0.29%
12	PF_6	I	6.0	710	0.19%
12	PF_6	II	12.2	470	0.79%
13	Ts	I	8.2	780	0.31%
14	Ts	I	7.8	960	0.45%
14	PF_6	I	7.0	1090	0.48%
14	PF_6	II	14.2	870	2.2%

[a] Voltage needed for brightness of 1 cd/m^2. [b] Maximum brightness. [c] Maximum external quantum efficiency.

2. Europium as emission source

The use of lanthanides in OLED technology allows for the incorporation of luminescent materials that have very narrow emission (FWHM = 5 nm). There are many factors that must be considered when addressing the issue of optimization of the electroluminescence of these europium complexes including; isolation of the metal ion to allow for luminescence, maximizing the brightness of the resulting emission, and improving the processibility of the complexes.

One way to optimize the emission from the lanthanide centers is to design ligands that will act as a site isolation moiety as well as a source of excitation energy to the metal center. A promising synthetic route has been the use of a partially fluorinated diketone as a chelator to a lanthanide metal. The reaction between 3 acetyl phenanthrene and ethyl heptafluorobutyrate has produced 4,4,5,5,6,6,6-Heptafluoro-1-phenanthren-3-yl-hexane-1,3-dione in yields in excess of 95%. The use of the fluorine allowed for a vast improvement in processibility in the resulting diketone (as well as the lanthanide complexes based on this structure) in terms of it's general solubility. We are currently investigating the polymer processibility of these systems by looking at the physical properties of these materials in commonly used polymer guest host systems such as poly(vinylcarbazole). The resulting europium complexes were incorporated into OLED devices and the results are summarized in Table 3. The materials showed a major emission at approximately 615 nm with a FWHM 5 nm. With our preliminary results we have been able to achieve brightness values of over 300 cd/m^2 and an efficiency of 0.8%.

Table 3. Summary of OLED device data for Europium complexes.

Material	Host Material	B_{max}	η_{max}
$Eu(G1\text{-}3)_3$	PVK	65	0.040
$Eu(G1\text{-}9)_3$	PVK	152	0.048
$Eu(G1\text{-}9)_3$	PVK:PBD	245	0.21
$Eu(G1\text{-}9)_3$	PVKPVO	62	0.80
$Eu(9\text{-}9\text{-}DP)_3P$	PVK	136	0.032
$Eu(3\text{-}9\text{-}DP)_3P$	PVK	66	0.013
$Eu(3\text{-}EHF)_3B$	PVK:PBD	101	0.022
$Eu(3\text{-}EHF)_3B$	PVN:PBD	178	0.45
$Eu(3\text{-}EHF)_3P$	PVK:PBD	116	0.035
$Eu(3\text{-}EHF)_3P$	PVN:PBD	161	0.45

Another technique to improve the properties of the lanthanide complexes is to design and incorporate a second ligand structure into the complex. Europium is able to coordinate up to 8 or 9 chelates to itself in the formation of luminescent materials. Typically, three diketonates are used to fill six of these positions. The final two positions can be filled by the incorporation of a neutral species such as a phenanthroline or bipyridine type structure. These types of structures typically will add a certain amount of rigidity to the complex as well as helping to prevent quenching moieties such as hydroxide or water molecules from attaching to the metal center and leading to a decrease in overall radiative emission. We propose that the careful design of this ligand will allow for even greater increase in device efficiency, brightness, and site isolation of the metal ion.

3. Use of gadolinium complexes to improve efficiency

In the study of our lanthanide complexes, it is possible to create an analogous complex to the photo and electroluminescent europium compounds that do not show metal centered emission, such as gadolinium (Gd). As the reactivity of Gd is similar to that of Eu, it produces similar types of organo-lanthanide complexes, but does not show metal centered photoluminescence. Instead, its phosphorescence is ligand centered due to the energy levels of the Gd. This allows us to match the triplet energy levels of the diketone, phenanthroline, or bipyridine ligand to the energy levels of the emissive lanthanide metal core.

Another application of these Gd complexes was their use as a way to improve the efficiency of the OLED device. The Gd complexes designed such that the ligands that were used on the Gd are of sufficiently different (higher) energy than that of the ligands on the emissive lanthanide (Eu) ensuring additional energy will be transferred to the emissive center.

We have created OLED's that are based on our partially fluorinated diketone 4,4,5,5,6,6,6-Heptafluoro-1-phenanthren-3-yl-hexane-1,3-dione. The device data is summarized in Table 4. A second series of devices were created that contain various ratios of Gd tris-dibenzoylmethane 4,7-diphenyl-1-10-phenantholine in the polymer matrix. The devices that incorporate the Gd derivatives show higher brightness, lower turn on voltage as well as a nearly thirty-fold improvement in the external quantum efficiency relative to devices that contain traditional host materials such as PBD. Future work in this are will be to better understand the energy transfer process.

Table 4. Summary of improved device efficiency using gadolinium cored complexes in polymeric host materials.

Host material	Eu complex	V_1 [a] (V)	B_{max} [b] (cd/m^2)	η_{max} [c] (%)
PVK:PBD [a]	$Eu(DPP)_3B$	10.0	101	0.022
PVN:PBD [a]	$Eu(DPP)_3B$	12.5	178	0.45
PVK:$Gd(DBM)_3B$ [a]	$Eu(DPP)_3B$	5.6	131	0.61
PVK:PBD [a]	$Eu(DPP)_3P$	9.8	116	0.035
PVN:PBD [a]	$Eu(DPP)_3P$	12.0	161	0.45
PVK:$Gd(DBM)_3B$ [a]	$Eu(DPP)_3P$	5.6	201	0.77
PVK:$Gd(DBM)_3B$ [b]	$Eu(DPP)_3P$	7.6	129	0.56
PVK:$Gd(DBM)_3B$ [c]	$Eu(DPP)_3P$	14.0	13.1	0.012

4. **Erbium as emission source**

OLEDs based upon erbium has become of great interest. This is not for display purposes as the emission is far more red than the eye can detect; rather, Er is of interest due to its emission at 1,300 and 1,550 nm, which are the telecommunications wavelengths. However, there has been some difficulty with erbium complexes as C-H vibrational overtones of the ligands and host materials will absorb the emitted light and weaken overall quantum yield of the complexes. Another source of difficulty is the design of the HOMO-LUMO energy levels of the ligand cage around the erbium core to coincide with the energy levels of erbium to ensure efficient energy transfer and thereby create more efficient emitting complexes and OLED's. Also, the ligand cage must ensure solubility and compatibility with host materials being used. In research being done at the University of Washington, porphyrin complexes of gadolinium have been synthesized and used in a variety of host materials as pressure sensors. In these pressure sensors the host material has been poly(dimethylsiloxane), poly(styrene), acrylics, and fluorinated polymers such as FIB7 and the Gd(porphyrin) and it has shown great compatibility with them all.

Derivatives of porphyrins called porphyrolactones feature very strong absorption bands at 420 nm (ε >300,000). This would ensure good energy overlap with a variety of OLED host materials such as PVK. This would increase Förster energy transfer and make for efficient OLED devices. In our work, gadolinium meso-tetra(pentafluoro phenyl)porphyrin has been shown to have an emission band at 711 nm. This is very close to

the energy levels of erbium. Also in research conducted in our facilities, molecules based upon the meso-tetra(pentafluorophenyl)porphrolactone have shown red-shifts of 100 nm. For example PtTFPP emits at 650 nm while PtTFPL emits at 750 nm. It would be expected that GdTFPL would experience a similar red shift in emission. Thus, we believe that 800 nm emission is possible from gadolinium complexes of porphrolactone. This is important for erbium research. The porphyrins emit from the ligand-centered π–π^*, thus the emission of the complexes show the energy of the triplet state. Thus the energy from the triplet state of the porphrolactone can be tuned to coincide with that of the erbium energy levels at either 650 nm or 800 nm; thus, we believe that we can create a ligand based upon the porphrolactone structure that will transfer energy to the erbium core efficiently. A significant feature of the pophrolactone structure is in its design. The structure consists of only 6 C-H bond vibrations, and these are aromatic. The rest of the structure is made of C-F bonds, which do not have significant overtones at 1,300 and 1,550 nm. Thus, the prophrolactone structure would be expected to be optically clear at the telecommunications wavelengths.

The porphyrin structure has a –2 charge takes up 4 of a possible 8 coordination sites around the erbium core. Thus an ErTFPL would have an overall + charge and 4 coordination sites. In our work with GdTFPL, one of sites has been shown to be taken up with a hydroxyl. Since O-H bond vibrations are notorious for quenching luminescence, the 4 coordination sites need to by taken up with other entities that will not quench luminescence. These ligands could serve other roles as well: providing site isolation to prevent self-quenching of erbium cores and to provide additional source of energy to the erbium core. In our work with other lanthanide metals, the β-diketone structure has proved to be very useful for either or both of these applications. The β-diketone may be modified in many ways. To act as a site isolation moiety, the structure can be functionalized with large dendritic groups, or other large structures. These groups can be designed to include fluorination, which would reduce optical loss by reducing C-H bond vibrations. Large aromatic systems could be used to provide energy transfer to erbium core. The β-diketone is an anion when it coordinates, so this in combination with a porphyrin or porphrolactone would provide charge balance creating an overall neutral molecule. The last two sites on the erbium core could be occupied using a 1,10-phenanthroline or derivatives of phenanthroline; thus, excluding possible quenchers from coming in contact with the metal core and increase quantum yields.

SINGLE WALL CARBON NANOTUBE ACTUATORS: We have demonstrated mechanisms of actuation appropriate for both high and low voltage operation, we have elucidated structural changes associated with the processing of nanotubes, and we have fabricated prototype optical switches (references 64,76,106,116-118). As this work has been described at both conferences and in the print literature, we will not review it here.

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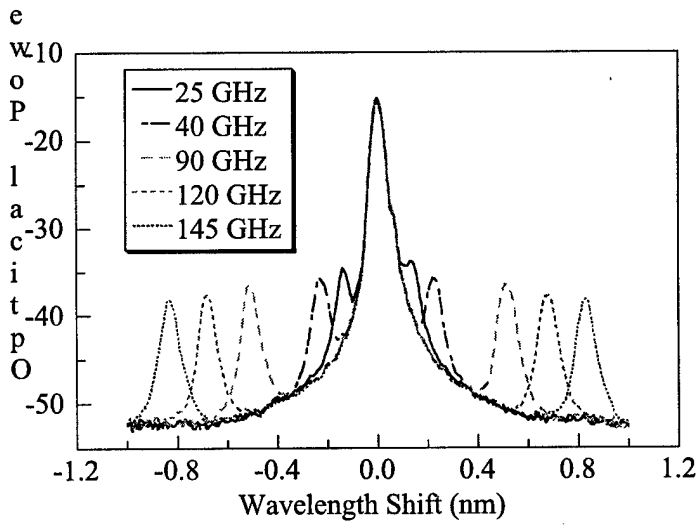

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137. The following email from General Dynamics is indicative of the need for a research program that can provide custom electro-optic materials:

From: "Patterson, David B" <David.Patterson@gd-ais.com>
To: "'dalton@chem.washington.edu'" <dalton@chem.washington.edu>
Subject: Polymer development interest
Date: Mon, 7 Oct 2002 16:56:16 -0400
X-Mailer: Internet Mail Service (5.5.2656.59)

Professor Dalton:

I've been conducting some product searches for electro-optic polymers, and

all roads seem to lead to your work, so I'm hoping that you might be willing to provide me some assistance.

I am an optical device physicist at General Dynamics, and I have a need for a high-speed, low V-pi, low-index polymer. Your polymers appear to meet two of the three requirements, but the index is a bit high - we are looking for refractive indices near that of silica (1.444 at 1.55 microns). I have attempted to contact Lumera and Pacific Wave with little success as of yet, and I thought that it might be more fruitful to discuss direct support of a development effort with your group at Washington, or funding via a subcontract with Lumera, to try putting your E-O chromophores into a lower-index polymer.

If you are interested in discussing this opportunity with me, please contact me via reply to this e-mail, or via telephone at (973) 463 - 4676. I can supply more details on our requirements at that time. Thank you.

Best regards,

Dave Patterson
Senior Lead Engineer
General Dynamics Advanced Information Systems
Whippany, New Jersey

Nanostructured Materials Final Report (period 9/01/01 – 2/28/03) Statistics:

Personnel Supported:

Number of PI(s) and Co-PI(s) Involved: 1
Number of Post Docs Supported: 1
Number of Graduate Students Support: 9
Other Researchers Supported: 1

Postdoctoral Fellows Supported (Partial Support)
Dr. Kaori Kamata

Graduate Students Supported (Partial Support)
Walter Duncan
Wayne Shinoki
Dan Casmier
Denise Bale
Nicholas Buker
Leonard Fifield
Jessica Schendel
Philip Sullivan
Andrew Akelaitis

Other Researchers Support:
William Steier

Publications:
Number of Publications in Refereed Journals: 96
Number of Publications Which Acknowledge AFOSR Support: 76

Publications Which Acknowledge AFOSR Support

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76. P. Rabiei, W. H. Steier, C. Zhang, and L. R. Dalton, "Polymer Micro-Ring Filters and Modulators," J. Lightwave Technology, 20, 1968-75 (2002).

Participation/Presentations: (From March 1, 2002 to end of grant period)

March 1, 2002—Dinner meeting and presentation with Seattle Mayor Greg Nichols ,community leaders, and UW President McCormick.

March 4-5, 2002--NSF Review Panel: Nanoscale Science and Engineering (NSE), Nanoscale Interdisciplinary Research Team (NIRT), NSF Headquarters, Arlington, VA

March 6-7, 2002--DARPA/MTO Molecular Photonics Workshop--Invited presentation."Organic Electro-Optics: Past, Present, and Future".

***Conference*--March 11-15, 2002**-- Government Microcircuit Applications & Critical Technology (GOMAC)-02 Conference, "The Rational Design and Production of Organic Electro-Optic Materials and Devices".

***Conference*--April 17, 2002**--Invited Lecture for New Horizons in Polymer Chemistry Conference, Los Angeles, CA. "Realization of the Promise of Electro-Optic Polymers."

April 29, 2002—Invited Seminar, Washington State University, Pullman, WA. "Electro Optic Materials and Devices".

June 10, 2002--3 presentations in the Palo Alto, CA area

Presentation 1. **Invited presentation before the Select Committee on Science & Technology of the British House of Lords.** Published in "Chips for Everything: Britain's Opportunities in a Key Global Market", Session 2002-02, 2nd Report, The Stationery Office Limited, London.

Presentation 2. EE Seminar Stanford University.

Presentation 3. Seminar at Agilent (Both American and British Agilent researchers attending).

***Conference*--June 20, 2002**--Invited presentation at the IBM Workshop on Organic Electronic and Photonic Materials (T. J. Watson Research Center, Yorktown Heights, NY)

June 28, 2002--Lumera Corporation Board of Directors Meeting. Invited Presentation.

***Conference*--July 10, 2002**—SPIE Seattle National Meeting, Conference 4798: Linear and Nonlinear Optics and Organic Materials II. Invited Lecture: Organic Electro Optics: From Molecules to Devices".

***Conference*--July 11, 2002**—SPIE Seattle National Meeting, SPIE Workshop on the Nanotechnology of Polymeric Smart Materials. Invited Lecture: "Electro-Optic Polymers".

***Conference*--July 12, 2002**—Semiconductor Research Corporation-IFC Topical Workshop on Optical Interconnects, Seattle, WA. Invited Presentation: "Modulators".

August 12-13, 2002--PNNL Nanoscience and Technology Advisory Committee Meeting, Richland, WA.

August 14-16, 2002--Defense Advanced Research Projects Agency (DARPA) Microsystems Technology Office (MTO) CS-WDM Program Kickoff, Whitefish, MT.

August 19-29, 2002—STC Director's Meeting, Atlanta, GA. Overview of UW STC.

August 26, 2002—Invited presentation to U.S. Congressman (D-7th, Washington State) James McDermott, Seattle. The STC and electro-optic materials research.

September 13, 2002—Technology Alliance Presentation, Seattle, WA. Invited Lecture: "Information Technology in the 21st Century: Exploiting the Best of Electronics and Photonics".

September 17, 2002--Washington Roundtable Invited Presentation, Washington Athletic Club. "The New Information Technology Age: Exploiting the Best of Photonics and Electronics".

September 30, 2002--National Science Foundation Distinguished Lecturer, Inaugural Lecture 2002-2003 NSF Distinguished Lecture Series, NSF Headquarters, Arlington, VA, "The New Information Age: Exploiting the Best of Electronics and Photonics."

October 3, 2002—Invited Seminary, California Institute of Technology. "Organic Electro-Optics".

October 9, 2002—Seminar, Norfolk State University, Norfolk Virginia. "Implementing the New Information Technology Age: Exploiting the Best of Photonics and Electronics".

***Conference*--October 10-13, 2002**--10th Annual Foresight Conference on Molecular Nanotechnology Two invited presentations (one Scientific Tutorial and one Invited Conference Presentation) Bethesda, Maryland. Title of invited lecture:"Breaking the Bandwidth Bottleneck in Telecommunications & Information Processing: New Electro-Optic Materials."

October 23, 2002—Presentation before National Reconnaissance Office Site Visit to the University of Washington. "Organic Electro-Optic Materials: Past, Present, and Future".

November 11-13, 2002—DoD DDR&E Nanophotonics & Nanoelectronics Review, University of Buffalo, Buffalo, NY. Invited Presentation: "Nanophotonic Electro-Optic and Opto-Electronic Materials".

November 26, 2002—Seminar, Department of Electrical Engineering, University of Washington. "Preparation and Utilization of Organic Electro-Optic Materials".

December 5, 2002—Seminar, Applied Physics Laboratory, University of Washington. "Materials for Next Generation Telecommunications".

December 6, 2002—UW Science Forum Lecture, University of Washington. "Implementing the New Information Technology Age: Exploiting the Best of Photonics & Electronics".

***Conference*--December 11-13, 2002**--NSF Nanoscale Science and Engineering, NSF Grantees Conference, Arlington, VA, Invited Presentation: "Nanostructured Optoelectronic Materials: New Concepts in Theoretical Design, Synthesis, and Processing."

***Conference*--January 16-17, 2003**--NSF Workshop on Technological Challenges for Flexible, Light-weight, Low-cost and Scalable Organic Electronics and Photonics. Arlington Hilton Hotel & Towers, Arlington, VA--Invited Presentation: Organic Electro-Optic Materials: Present and Future.

January 24, 2003—DoD DDR&E Review of Polymeric Smart Skin Materials, Seattle, WA. Presentation: "An Overview of Polymeric Smart Skins Materials Research".

***Conference*--January 30, 2003**—Photonics West Symposium on Organic Photonic Materials and Devices VI, San Jose, CA. Invited Lecture: "Organic Electro Optics: Exploiting the Best of Electronics and Photonics".

February 13, 2003—Florida International University, Miami, FL. Invited Seminar:"Technology for the 21st Century: Exploiting the Best of Photonics and Electronics".

February 14, 2004—University of Miami, Miami, FL. Invited Seminar: "Technology for the 21st Century: Exploiting the Best of Photonics and Electronics".

Consultative/Advisory Functions:

•Member, Editorial Board, Materials Today (2002-)
•Board of Visitors, Chemistry Department, University of Alabama (98-)
•Member, Advisory Board, Center for Research and Education on Advanced Materials, Norfolk State University, (2002-)
•Member, Advisory Boards of various designated minority institutions participating in the Alliance for Nonlinear Optics (2002-)
•Oversight Reviewer of the National Research Council Report on Implications of Emerging Micro- and Nanotechnologies (2002)
•Member, PNNL Peer Review Panel for the Nanotechnology Initiative (2002)
•Member, National Science Foundation NIRT Review Panel (2002)
•Member, National Science Foundation Panel on Information Technology Research (ITR) (2000)
•Member, National Science Foundation SBIR/STTR Peer Review Panel (2001)
•Member, National Science Foundation IGERT Review Panel (2001)
•Member, National Science Foundation Nanotechnology Review Panel (2001)
•NSF Panel for the Review of Proposals on Nanoscale Modeling & Simulation (2000)
•NSF Nanotechnology Review (2002)
•DARPA Workshop on Molecular Photonics/Engineering (2002)
•DARPA/Semiconductor Research Corporation Workshop on Optical Interconnects (2002) URL address: http://www.src.org/member/sa/nis/E002117_Opto_wksp.asp
•IBM Corporate Workshop on Organic Electronic and Photonic Materials (2002)
•Corning Corporate Wide Workshop on Organic Electro-Optic Materials (2001)
•British House of Lords Workshop on Next Generation Computing (2002)

Interactions/Transitions:

Transition 1
a. Dalton, UW, b. Data for organic electro-optic materials, c. William Krug/Boeing Phantom Works., 253-657-8018 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.

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
a. Dalton, UW, b. Polymeric electro-optic materials and processing protocols, c. Abraham Gross/Microvision, 425-415-6642 d. For prototyping electro-optic modulator devices for telecommunication and display applications.

Transition 4
a. Dalton, UW, b. Polymeric electro-optic materials and processing protocols, c. Todd McIntyre/Lumera 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. Grote/AFRL/MLPO, 937-255-4474 ext 3263 d. For use with conducting cladding materials developed by AFRL.

Transition 7
a. Dalton, UW, b. Polymeric electro-optic materials and processing protocols, c. James Bechtel/TACAN Corporation, 760-438-1010 ext 3278 d. Polymeric electro-optic materials for device fabrication.

Transition 8
a. Dalton, UW, b. Polymeric electro-optic materials and processing protocols, c. G. A. Lindsey/ NAWCWD, 760-939-1396 d. Polymeric electro-optic materials for optical gyro development.

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
a. Dalton, UW, b. Polymeric electro-optic materials and processing protocols, c. Howard Katz/Bell Labs Lucent Technologies, 908-582-6968 d. Polymeric electro-optic materials for evaluation and to repeat syntheses.

Transition 11
a. Dalton, UW, b. Light harvesting solar cell coatings, c. Paul Hausgen/Kirtland AFB, paul.hausgen@kirtland.af.mil d. Improved solar cell technology.

Transition 12
a. Dalton, UW, b. Pressure sensitive paints, c. Rush Queen/Boeing, 206-655-7761;Tim Rieger/Boeing, 206-655-7769; Doug McLean/Boeing, 206-234-1106; John Harris/Boeing, 206-655-7794 d. Pressure sensitive paints for wind tunnel evaluation of airframes.

New Discoveries, inventions, or patent disclosures:
Significant improvements have been made in organic electro-optic and light emitting materials and a new paradigm for developing materials with further improvement in properties has been validated.

•OTL Ref #:	2636-3380
Inventor(s):	Larry R. Dalton
Title of Work:	Hyperpolarizable Organic Chromophores and Electro-optic Materials
Patent Title:	Hyperpolarizable Organic Chromophores
Patent App. Filed:	7/24/2001

Provisional Filed: 7/24/2000
PCT Application Filed: 7/24/2001
Elect title: Yes
License to the Gov: 8/24/2001

•OTL Ref#: 2727-3487
Inventor(s): Larry R. Dalton, W. Brenden Carlson, Gamal-Eddin, Khalil, Martin Gouterman
Title of Work: Fouorinated Acrylic Polymer based upon 2-[ethyl(heptadecafluorooctyl)-sulfonyl}amino]ethyl methyacrylate (FAB)
Date Disclosed: 5/1/2001

• OTL Ref: 2765-3533
Inventor(s): Larry R. Dalton, W. Brenden Carlson, Gamal-Eddin Khalil, Gregor D. Phelan
Title of Work: Temperature sensing europium chelates
Date Disclosed: 8/13/2001

• OTL Ref: 2766-3534
Inventor(s): Larry R. Dalton, W. Brenden Carlson, Gamal-Eddin Khalil, Martin Gouterman
Title of Work: Novel iridium luminophores for use as oxygen sensors and pressure sensing paint based upon FAB, FTB, acrylic polymers, acrylic/silicone polymers, polydimethylsiloxane, and trimethylsiliyl-1-propyne
Date Disclosed: 8/13/2001

• OTL Ref: 2790-3581
Inventor(s): Larry R. Dalton, W. Brenden Carlson, Alex Kwan-yue Jen, Xuezhong Jiang
Title of Work: Osmium based Organic Light Emitting Diodes (OLEDs). New ligands for osmium based OELDs.
Date Disclosed: 6/11/2002

• OTL Ref: 2636-3701
Inventor(s): Larry R. Dalton, Hong Ma, Alex Kwan-yue Jen, Sen Liu
Title of Work: Focused microwave irradiation assisted synthesis of diversified 2, 5-dihydro five-member heterocyclic compounds as tunable electron acceptors in nonlinear optical chromophores
Date Disclosed: 5/27/2002

Honors/Awards: (Lifetime)
•2003 Chemistry of Materials Award of the American Chemical Society
•2002 Lecturer, Distinguished Lecture Series of the National Science Foundation
•2000 Distinguished Alumni Award of Michigan State University
•1996 Richard C. Tolman Medal of the American Chemical Society
•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, 76-81)
•Camille and Henry Dreyfus Teacher-Scholar Award (75-77)
•Alfred P. Sloan Fellowship (74-77)

Awards Received by Graduate Students Working on This Project:
•Leonard Fifield, Pacific Northwest National Laboratory Fellowship
•Daniel Casmier, SPIE-International Society for Optical Engineering Fellowship
•Undergraduate Student Bjorn Miillard received a Mary Gates Endowment for Students Research Training Grant