

## 1. Vision Statement

The LMITA Partnership seeks to join two historically important minority-serving institutions, New Mexico Highlands University and Morehouse College, to bring tangible, scientific research-based learning to Hispanic and African-American students of high school and college age. The research basis will reflect competencies of NMHU and MC faculty in light-matter interactions, greatly augmented through partnership with one of the nation's leading Science and Technology Centers, the NSF Center on Materials and Devices for IT Research (CMDITR). This three way partnership will exploit the 7-year experience of CMDITR in education and diversity enhancement by replicating successful programs and building or adapting new programs in New Mexico and Georgia with CMDITR guidance. The broader impacts plan will embrace students, teachers, and researchers at high schools and community colleges in New Mexico and Georgia, NMHU, Morehouse College, CMDITR partner universities, and the Los Alamos and Sandia National Laboratories. The goal is for underrepresented students to view STEM studies as a viable career path and for educators and researchers to gain improved skills in mentoring minority students so as to maximize their chances of reaching the end of the proverbial "pipeline".

## 2. Specific Research and Education Goals

**Research** – The overall goal is to increase our understanding of light-matter interactions in three important state-of-the-art materials, through a multi-disciplinary and multi-institutional approach that emphasizes the role of two minority-serving institutions and their faculty and students. More specifically, we aim to:

1. publish at least 10 peer-reviewed papers each year, starting in year-2, with one or more NMHU or MC co-authors. At least 8 of these papers will have a NMHU or MC student author listed.
2. involve at least 12 BS or MS candidates at NMHU and MC in LMITA research per year, and to have all of these students visit a CMDITR laboratory at least once during their academic tenure
3. send 3 undergraduates each summer from NMHU, MC, or LMITA community college partners to CMDITR's *Hooked-on-Photonics* REU Program
4. send at least 4 NMHU or MC students each summer to LANL or SNL for a research internship
5. host a LMITA Annual Retreat each year, alternating between Las Vegas, NM and Atlanta, GA, with emphasis on student participation in the form of oral and poster presentations and professional development and training activities

**Education** – The overall goal is to impact a broad cross section of students from various minority groups and their teachers in high schools, community colleges, and universities by building education and outreach programs around a contemporary research theme dealing with light-matter interactions. The desired impact is to show our target "underrepresented" communities that science is understandable, relevant, interesting, and a good career choice. Specifically, we aim to:

6. create two courses (1 undergraduate and 1 masters level) at NMHU and one at MC by infusing LMITA/CMDITR curricular material
7. significantly modify other existing courses using tools and modules developed by CMDITR
8. double the NMHU chemistry master's degree program from 6-8 graduates per year to 12-16
9. expose at least 30 undergraduates per year at NMHU and MC combined, to LMITA curricular material developed to address light-matter interactions.
10. annually expose at least 15 community college students to a LMITA lecture/demonstration, preferably combined with a campus visit to a LMITA partner university
11. annually expose at least 30 high schoolers in NM and GA to the same
12. train at least 2 community college or high school teachers per year in a LMITA-sponsored summer workshop or research mini-project
13. host at least two visits per year at NMHU and MC by CMDITR faculty for guest lectures, research interactions, or special seminars
14. have 100% of NMHU and MC PIs participate in education/outreach activities

**Evaluation** – The LMITA evaluation goal is to implement a rigorous assessment program using an

experienced third party, review major programs as they develop, and quantify improvements over time in the quality of our programs as measured by participants' experience and attainment of positive milestones in expanding the STEM education/career pipeline.

### **3. Partner Background Information**

Why New Mexico Highlands University and Morehouse College? First, both institutions have expertise in materials science and a working relationship with CMDITR (but with limited funding). Second, both institutions have extremely rich heritages with respect to educating minority groups, and both are poised to bring more of their students into STEM disciplines and careers. And third, because both institutions have relatively small science programs, their sphere of broader impacts will be greatly expanded by teaming together. At both NMHU and MC, the main locus of LMITA activity will revolve around their respective chemistry departments. Together, Morehouse and NMHU graduate approximately eighteen chemistry majors per year). NMHU also grants 8-10 masters degrees each year in chemistry – a number we intend to double with PREM support by 2012. Several students from Biology and Computer and Mathematical Science Departments may also be involved in the project.

Founded in 1893, NMHU was America's first institution of higher education serving the Hispanic population, and even today, is one of only a few primarily Hispanic institutions (59%) in the country. NMHU maintains the lowest tuition and fees of any four-year college in an 11-state region in the West, thus ensuring access by lower income families. Morehouse College was founded in 1867 as the Augusta Institute, with its original mission to train black men for the ministry and in education. In the past five years, Morehouse has received critical acclaim from the Wall Street Journal, Newsweek, Kaplan, Inc., and Black Enterprise Magazine for its undergraduate liberal arts program and remarkably high rate of graduates entering into the nation's elite post-graduate schools.

CMDITR, one of 17 current NSF Science and Technology Centers, has evolved around three principal partners, the University of Washington (lead institution), Georgia Institute of Technology, and University of Arizona, but also counts six other partners at the present time: CalTech, Norfolk State University, University of Maryland, Baltimore County, Cornell, University of Central Florida, and NMHU. The Center's research is focused on creation of photonic and electronic materials and devices based on molecular (organic) building blocks, in order to serve the information technology, energy, transportation, and defense sectors. The Center provides a highly integrated, interdisciplinary, multi-institutional research infrastructure for scientists and students in chemistry, physics, optical sciences, materials science, electrical engineering, and applied physics. The subset of CMDITR players who will work most closely with the new PREM partnership will come principally from the Georgia Institute of Technology (hereafter GT), but LMITA has the full support of the people and resources of the CMDITR (see letter of support which also describes plans for post-2012 when this STC sunsets). CMDITR has been prolific with respect to research outputs and broader impact programs. For example, it lists nearly 1,000 publications and 229 patents filed in its first six years of existence. CMDITR has been recognized as a leader in the founding of an STC-wide partnership with GEM (Consortium for Graduate Degrees for Minorities in Engineering and Science), in partnering with industry to develop well-funded, collaborative research and internship programs, in sustaining a multi-campus summer REU program that recruits heavily from community and small liberal arts colleges, in developing a model scientific ethics online training course now used by 44 registered groups from around the world, and much more. Clearly, CMDITR has much knowledge and experience to share with LMITA.

### **4. List of Participants**

The skills of the NMHU and MC faculty listed below are highly complementary to those within CMDITR. At NMHU, Dr. Mikhail Antipin is one of the first crystallographers to evaluate results on the basis of precise diffraction experiments that are the same as those predicted from quantum computations. This provides an important window to understanding of materials properties. Dr. David Sammeth has experience in studies of light-matter interactions in biomaterials. Dr. Rudy Martinez, a former scientist at Los Alamos National Laboratory, is a recognized expert in the synthesis of low-cost pure enantiomeric materials and isotopically labeled (e.g. C<sup>13</sup>, deuterated) materials. Dr. Kurt Short came to NMHU from

Participant	Affiliation	Primary Role(s)
Tatiana Timofeeva	Associate Professor, Chemistry - NMHU	Director, PI - Thrust 2
David Sammeth	Professor, Chemistry - NMHU	Co-PI, PI - Thrust 1
Jennifer Hernandez-Gifford	Assistant Professor, Biology - NMHU	Collaborator, Thrust 1
Rudy Martinez	Professor, Chemistry - NMHU	Co-PI, Collaborator, Thrust 1&3
Kurt Short	Research Scientist - NMHU	Collaborator – Thrust 1
Mikhail Antipin	Research Professor, Chemistry - NMHU	Collaborator, PI - Thrust 2
Jennifer Lindline	Professor, Natural Resources - NMHU	Co-PI, Director E&O, Thrust 2
Gil Gallegos	Assistant Prof., Computer Science - NMHU	Collaborator, Web Coordinator
Brian Lawrence	Assistant Professor, Chemistry - MC	Co-PI, PI - Thrust 3
Seth Marder	Professor, Chemistry – GT/CMDITR	CMDITR Liaison, Trusts 2&3
Jean-Luc Bredas	Professor, Chemistry – GT/CMDITR	Collaborator, Thrust 2
Joseph Perry	Professor, Chemistry – GT/CMDITR	Collaborator, Thrust 1
Steve Barlow	Principal Research Scientist – GT/CMDITR	Collaborator, Thrust 2
Veaceslav Coropceanu	Principal Research Scientist – GT/CMDITR	Collaborator, Thrust 2
High school students	Las Vegas School System	Education/Outreach Program
HS and CC faculty	Northern New Mexico Region	Summer Workshops/Research Proj.
Undergraduates	NMHU, MC	Research Experiences
Masters students	NMHU	Research, exchanges, internships
Postgraduates	CMDITR's 9 partner universities	LMITA Postgraduate E&O Fellows

Los Alamos NL where he applied vibrational and fluorescence techniques to biophysical and biomedical imaging and has deep knowledge of cell biology. Dr. Jennifer Hernandez Gifford a microbiologist was recently hired as a NMHU assistant Biology professor after postdoctoral experience at Washington State University, Pullman, WA. Dr. Jennifer Lindline works with powder diffraction techniques that are very useful in many areas of materials science. Dr. Gil Gallegos came to NMHU from Applied Technology Associates (ATA) and the Air Force Research Laboratory (AFRL) in Albuquerque, NM where he worked for the infrared imaging software/hardware development group. And PI Tatiana Timofeeva has extensive experience in the synthesis and crystallography of organic photonic materials, large portions of which have been associated with her collaboration with CMDITR and GT (S. Marder). She also served from the very beginning on CMDITR's Management Team, where she represented the Alliance for Nonlinear Optics (ANLO) and helped recruit minority students from the Alliance into CMDITR-supported programs. Timofeeva's involvement in CMDITR research and educational programs have prepared her well to lead a new PREM collaborative program. At Morehouse College, Dr. Brian Lawrence (Harvard PhD) is a synthetic organic chemist interested in the development of new chemical reaction methods (esp. transition metal catalyzed reactions) that play a critical role in our ability to synthesize complex organic materials from simple feedstocks.

The partner lineup at CMDITR includes many internationally known researchers with extensive research facilities and personnel. In the interest of conserving space, we'll mention only three of the lead PIs – all from GT. Dr. Seth Marder is the Deputy Director of CMDITR and the Director of GT's own Center for Optical and Photonic Electronics (COPE). Dr. Marder, Professor of Chemistry at GT and expert in the design and synthesis of photonic materials, will be the point person for all CMDITR commitments and obligations. Dr. Jean-Luc Bredas is one of the 100 top most cited chemists in the world over the past ten years and CMDITR's leading materials theoretician. Dr. Joseph Perry is a project leader in CMDITR with expertise in multi-photon absorption and 3D micro and nanofabrication.

## 5. Collaborative Research and Related Activities

LMITA is not a currently funded PREM and this is not a re-competing proposal. Therefore, we will use this space to describe past NSF contributions and collaborative research undertaken at NMHU and MC.

**NMHU** - Research-based education began at NMHU in the area of optical materials about 15 years ago as a result of NASA's Alliance for Nonlinear Optics (1996-2004), a consortium of seven minority-serving universities headquartered at NMHU. From 2003-2008, materials studies at NMHU were supported by NSF's EPSCoR program funded under the New Mexico Nanoscience Initiative (NMHU PI – T. Timofeeva; co-PIs Antipin and Sammeth). These studies on nanoporous materials underpinned steady collaborations with LANL and Sandia NL and led to summer internship opportunities for NMHU students at both labs that we will formalize under the LMITA Partnership. NIH has supported studies of the kinetics and chemistry of retinal damage due to light (PI D. Sammeth). This work examined the photodegradation of the retinal chromophore within the protein bacteriorhodopsin. The US Civilian Research and Development Foundation (CRDF) has supported structural studies of nonlinear optical materials in cooperation with Yerevan University (Armenia), and LANL has supported studies of inorganic luminescent materials (Antipin PI on both of these projects). The above mentioned projects involved nonlinear optical, two-photon absorbing, and light-emitting materials. These investigations formed the basis for collaborative studies with the CMDITR, begun in 2002. Most recently, T. Timofeeva began a collaboration with the University of Central Florida in fall 2008 (Dr. Kevin Belfield), where her role is the structural characterization of multiphoton absorbing materials. This research is complementary to Research Thrust 2 outlined in this proposal. The current UCF collaboration supports two Hispanic students at NMHU and two more are planned to be supported during the summer of 2009.

The research infrastructure of NMHU's Science Departments was significantly improved after 2000 through NSF's Major Research Instrumentation (MRI) program. A cluster of X-ray single crystal and powder diffraction instruments has supported the graduate work of over 15 masters candidates and allowed us to publish about 50 papers in peer-reviewed journals, with students as coauthors on most of these. NMHU has recently acquired instrumentation to measure the magnetic properties of minerals. This same equipment can be used to characterize magnetic properties of organic materials of relevance to this proposal. This instrumentation along with the existing at NMHU laser lab will form a solid basis for a new lab/lecture course on materials characterization.

**MC** – Morehouse College is an independent, fully accredited, predominantly black, liberal arts college for men that graduates approximately 500 students each year and awards more baccalaureate degrees to African-American men than any other institution in the country. Our Department of Chemistry follows the ACS-approved curriculum and has a longstanding tradition of producing young men who successfully pursue graduate degrees in chemistry. Within the Department, there are four active research laboratories, and two instrumentation facilities. Recently, co-PI Lawrence, in collaboration with Clark Atlanta University (CAU) faculty, procured funding to bring new instrumentation to MC/CAU for the solution/solid state determination of polymer structure via nuclear magnetic resonance spectroscopy. This instrument will create a solid foundation for scientific inquiry in this Department for years to come.

## **6. Project Description**

### **6.1 Research Plan**

LMITA's framework for its three research thrusts is presented in Figure 1. The thrusts are illustrated in vertical columns and subdivided into synthesis, characterization, and theory to differentiate PI areas of emphasis and expertise. All research thrusts will be carried out by multidisciplinary, multi-institutional teams that will include undergraduate and graduate students. The schematic shows that NMHU and MC faculty are widely dispersed across all thrust areas. CMDITR collaborators for all reside mainly at GT.

#### **6.1.1 Research Thrust 1. Design and Spectroscopic characterization of Two-Photon Absorbing Materials for Photodynamic Applications (Sammeth, Short, Martinez - NMHU/Chemistry; Hernandez Gifford - NMHU/Biology; Perry, Bredas - GT)**

**Introduction:** There is great interest in agents for photodynamic therapy,<sup>1</sup> for the treatment of cancer with a combination of a photosensitive drug and light exposure of the cancerous tissue. The development of new, efficient photodynamic therapy agents is the subject of this thrust. In photodynamic therapy, light

is used to excite a “sensitizer” molecule which typically transfers energy to triplet oxygen creating singlet oxygen or oxygen radicals, which causes cellular apoptosis. The development of such agents requires a combination of chemistry, physics, and biology and provides an excellent platform for the interdisciplinary research training of students during their formative educational years. This will allow students to truly understand and apply interdisciplinary approaches for transformative solutions to difficult problems. The project described here will allow future scientists receiving their education at NMHU to gain experience in a growing area of interdisciplinary research and to work actively in the laboratory side-by-side with their professors and colleagues.



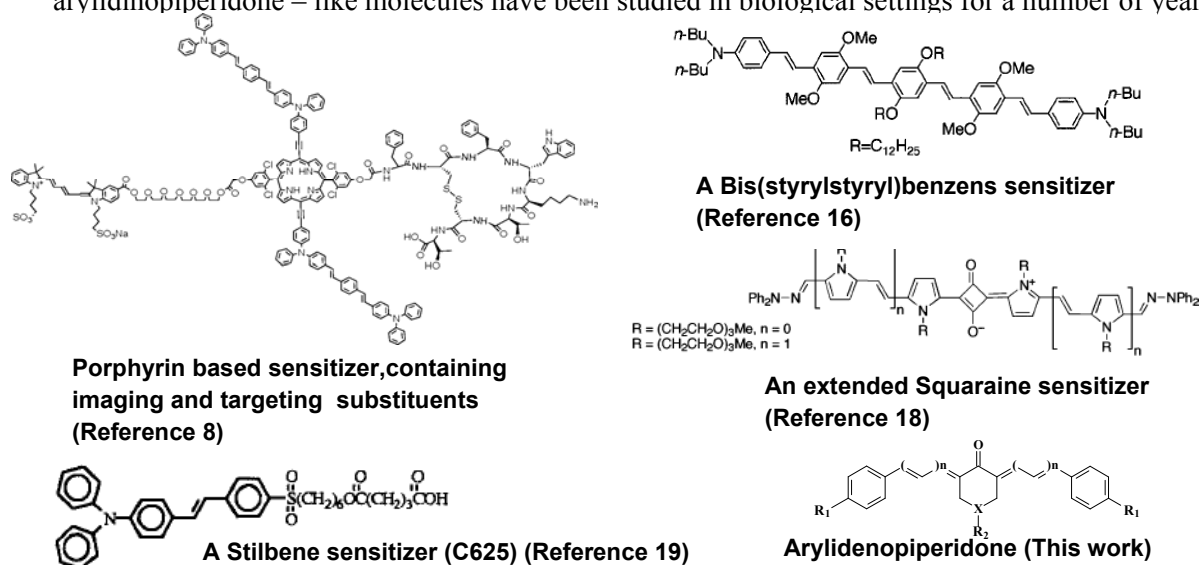
**Figure 1. Proposed Research Framework for LMITA Partnership**

**Goal of the proposed research:** The goal of this research is to prepare and evaluate the optical and photochemical properties of a variety of N-substituted 3,5-bis(arylidene)-4-piperidones<sup>2</sup> (arylideneopiperidones) (Figure 2) that will act both as sensitizers and as fluorescent biomarkers. These materials have a Donor- $\pi$ -Acceptor- $\pi$ -Donor structure. An important potential application of these materials is use as two-photon photodynamic sensitizers for photodynamic therapy. The research will involve interplay between physical studies, synthetic preparation, and cell culture based biological tests. The observed spectroscopic properties and the cyto- and phototoxicity response of the materials will be used to guide the synthetic preparation of additional arylidenopiperdone compounds. Another goal of this project is to provide students with training and experience in chemical synthesis, optical spectroscopy and photo- and cyto-toxicity studies.

**Background:** Sensitizers that simultaneously have both one- and two-photon response are of interest here. Two-photon photodynamic materials have the advantages being active in the biological transparent region near 800 nm allowing for deeper tissue penetration in potential treatments. And, because of the need of a focused laser beam for the two-photon response, the sensitizer affect can be highly localized, avoiding damage to non-target areas. The ideal two-photon sensitizer should have the following characteristics: low cost simple preparation, large two-photon absorption cross sections in the biologically transparent region near 800 nm, significant triplet state production, solubility in an aqueous environment, and sufficient fluorescence signal to allow tracking. Aryldinopiperidones have been chosen because they have most of these characteristics. In addition, our preliminary results have suggested that the photo-toxicity of arylidenopiperidones can be increased without affecting their cyto-toxicity, by increasing the length of the linkage between the donors and the central acceptor group. Some preliminary spectroscopic characterization of a limited number of arylidenopiperidones has been done,<sup>3-6</sup> but it has not clearly defined or thoroughly explored the relationship between their chemical structure and spectroscopic properties. We will physically characterize an expanded set of arylidenopiperidones (see below), while at the same time using photo- and cyto-toxicity results to guide preparation of improved materials that will

be appropriate as two-photon photodynamic sensitizers. These materials will include both arylidenopiperidones that are either readily soluble or mostly insoluble in an aqueous environment. The soluble materials would be more useful in situations where there is a need to have a systemic dispersion of the materials. The insoluble materials would be more useful for localized photodynamic therapy.

Others materials have recently been prepared for potential use as two-photon sensitizers. Examples of these materials include both porphyrin<sup>7-15</sup> and non-porphyrin<sup>16-22</sup> molecules (Figure 2). Non-porphyrin materials include bis-donor diphenylpolyene and bis(styryl)benzene derivatives,<sup>16</sup> amine-terminated cyano-substituted phenylenevinylene oligomers,<sup>17</sup> extended squaraine dyes,<sup>18</sup> stilbene derivatives,<sup>19,21</sup> chromophores based on dithienothiophene,<sup>20</sup> a hexa-peri-hexabenzocoronene core containing chromophore<sup>22</sup> and other compounds. These materials, both porphyrin and non-porphyrin, have drawbacks when compared to arylidenopiperidones in both their preparation and physical properties. Many have comparable or larger two-photon absorption cross sections, but, where reported, their fluorescence quantum yields are an order of magnitude larger than arylidenopiperidones.<sup>13,16,17,20,21</sup> This means that when used as photodynamic sensitizers they will have lower triplet-state production, since most of the excitation energy that could go into triplet state formation is lost by fluorescence. Frequently, these materials have absorption bands too red-shifted for biological applications,<sup>9-11,18</sup> have rapid photo-bleaching rates,<sup>12</sup> or have large two-photon absorption cross sections but no known sensitizer function.<sup>19,22</sup> Many of the synthetic procedures are three or more steps.<sup>7,8,14,15</sup> In contrast, arylidenopiperidones can often be made in a one-step reaction. Some of the other two-photon materials have been attached to drugs, carrier molecules, or labeling molecules.<sup>7,8,19,21</sup> The spectroscopic properties of arylidenopiperidones are relatively insensitive to modification of the substituent at the nitrogen atom on the central ring (Figure 2), which is outside of the electron conjugation chain. So, if in the future there is a desire to attach arylidenopiperidones to a carrier molecule or to a nanoparticle, the synthetic procedure will allow, incorporation of groups onto the central ring that will permit this. Porphyrin based sensitizers have also been modified to be water soluble.<sup>15</sup> However, arylidenopiperidones can be made water soluble by incorporation of phosphorylated piperidones during the synthesis, without need for later modification. Because they fluoresce, the localization of these molecules in cancer cells as sensitizers can be tracked without the addition of a labeling molecule. The non-porphyrin materials referenced above<sup>16-22</sup> have been proposed for potential use as photodynamic sensitizers. However, little or no testing for biological compatibility has been reported. Our data from cyto- and photo-toxicity testing has already shown that some of the arylidenopiperidones may be useful as photosensitizers, as some show a cyto-toxicity/photo-toxicity concentration ratio in cell culture of near 100. In addition, arylidenopiperidone and arylidenopiperidone – like molecules have been studied in biological settings for a number of years.<sup>23-25</sup>



**Figure 2.** Examples of sensitizers proposed for use in photodynamic therapy are shown.

In contrast to the use of the materials as sensitizers and as fluorescent biomarkers that is proposed here, these materials have been studied as cytotoxic and anticancer agents,<sup>23,24</sup> and as antibacterial agents.<sup>23</sup> So, unlike the non-porphyrin materials described above, there is a precedence for using arylidenopiperidones in biological settings. They are potentially useful in a variety of treatments, but appear not to be overly cyto-toxic to the whole individual. For arylidenopiperidones the  $\pi$ -conjugated linkage between the donors and acceptor can vary in length, which will affect the spectroscopic response. A longer linkage causes a red-shift of the spectra. Preliminary results have shown that the two-photon absorption cross section can be affected by the nature of the donor groups. Strong donors  $R_1$ , such as dimethylamine, result in large cross sections, whereas weak  $R_1$  donors, such as fluorine, result in loss of two-photon activity. For two-photon materials, the potential triplet state yield is most directly controlled by the magnitude of the two-photon cross section. So again, this can be controlled by the nature of the donor groups  $R_1$ .

**An Overview of Planned Work:** A small number of arylidenopiperidones have already been prepared and are being spectroscopically characterized. The results thus far, which show enhanced two-photon absorption cross sections and suggest large triplet state production, make it clear that it would be useful to take several approaches to further spectroscopic characterization. First, one-photon properties including absorption, fluorescence, fluorescence lifetime, and fluorescence quantum yield will be determined. Second, these arylidenopiperidones are relatively strong two-photon absorbers,<sup>3, 5, 6</sup> therefore the two-photon absorption cross sections and two-photon emission spectra will be determined for the new compounds. Finally, for use of these materials as photosensitizers in an area such as photodynamic therapy, conversion to the triplet electronic state upon illumination is important. So, measurements of phosphorescence, to first gain evidence for and then to characterize conversion to the triplet state will be made. Additionally evidence for the conversion to the triplet state will be determined by measuring the compound singlet oxygen generation. Plans for these three experimental areas, along with some preliminary results, will be considered in more detail below. During the course of this study, ongoing experimental results will to some extent guide further synthetic preparations. We have also made, and will make additional arylidenopiperidones that are water soluble. This will be an advantage in situations where, when used as sensitizers for photodynamic therapy, they need to be dissolved in an aqueous phase. Finally, depending of results from this study, we plan to also consider arylidenopiperidones with an Acceptor - $\pi$ - Donor - $\pi$ - Acceptor structure. During the course of these studies, for materials that might eventually be used as sensitizers, it will be necessary to perform cell-culture based cyto- and photo-toxicity tests. Results from these tests help guide the design and synthesis of additional sensitizers. We have available complete cell culture facilities in the NMHU Biology Department and experience in handling human cancer cell lines. A number of different cell lines are maintained locally, with additional ones available from collaborators at NM Tech.

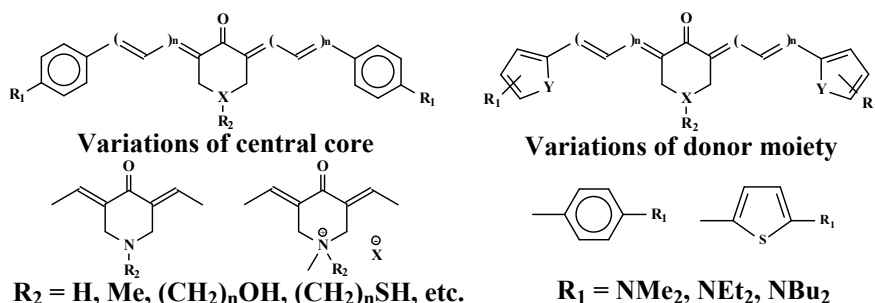
**Overview of Instrumentation and Facilities:** At NMHU, we have a variety of equipment that will be used to carry out this work. For spectroscopy we have available an HP 8453 UV-Visible spectrophotometer for absorption measurements, a Jobin Yvon Horiba Fluorolog Tau 3 Lifetime system for fluorescence and fluorescence lifetime measurements, and, a Spectra Physics Millennia pump laser and a Spectra Physics Tsunami femtosecond Ti-sapphire oscillator for multi-photon experiments. The calibrated detector for this system is set up to measure full emission spectra. Also available in our department is a Spectra Physics Quanta-Ray nanosecond laser system that is tunable from the near UV to the near IR. NMHU has labs that are well equipped for carrying out synthesis and purification, and structural characterization of the materials by NMR and X-ray diffraction.

### **Specific Experimental Plans**

**One-Photon Spectroscopy - Preliminary Results and Plans:** The materials made thus far, have absorption maxima between 456 and 476 nm, and one-photon fluorescence maxima between 567 and 593 nm for compounds with two double bonds in a pi-bridge. For the single compound with three double bonds between the donors and acceptor, measured thus far, the absorption maximum is at 508 nm, and the one-photon fluorescence maximum is at 564 nm. Visually, these compounds have a bright fluorescence when there is one-photon excitation with a bright or focused beam of light, which would make them



attractive for use to track photosensitizer distribution. So, it was expected that they would have significant fluorescent quantum yields. Fluorescence quantum yields and fluorescence lifetimes have not previously been measured for any of these compounds. Surprisingly, our initial results show that the fluorescence quantum yields are 7% or less. The method used to determine quantum yields is based on using 9,10-diphenylanthracene as a standard.<sup>26</sup> These low quantum yields suggest that non-radiative decay and/or conversion to an excited triplet state are occurring at significant levels. Measurement of fluorescence lifetimes (phase-modulation method) also has given unexpected results. The lifetimes have thus far been found to be less than 402 ps. Given the visual strength of the fluorescence signal, they were expected to be an order of magnitude longer. The short lifetimes are further evidence that there is non-radiative decay and/or conversion to the triplet state. Given our preliminary results, the plan is to continue one-photon measurements on an expanded series of compounds some examples of which are presented below.



It will be determined if there are any correlations between the measured parameters and, the type of electron donor groups, the types of groups on the central acceptor ring, and the number of double bonds between the donors and acceptor and molecular protonation.

**Two-Photon Spectroscopy - Preliminary Results and Plans:** Using femtosecond excitation in the near-IR, two-photon characterization of the arylidenopiperidones has started. Two-photon absorption cross sections are being determined. The compounds have been found to have cross sections similar to or larger than that found for Rhodamine B. The maximum two-photon absorption cross sections have been near 800 nm and near 850 nm. This is a biologically transparent region for light, and shows that these compounds may be ideal candidates as two-photon sensitizers. In conjunction with two-photon absorption cross section measurements. When compared to the one-photon fluorescence spectra, an interesting observation is made for this group of materials. The two-photon emission spectra are red-shifted (by up to 120 nm) compared to the one-photon fluorescence spectra -- quite unexpected.<sup>27</sup> Work will be done to investigate the underlying cause of this observation, to determine if it is an intrinsic molecular property or is of an experimental (concentration effect, excimer formation, etc.) origin. Either result would be of interest. If the property is intrinsic, the molecule could be a dual fluorescent marker with the emission wavelength depending on the wavelength of the excitation. A concentration effect would suggest that the two-photon emission might be tuned simply by varying the concentration. Finally, the two-photon experiments will, as in the case of the one-photon experiments, survey an expanded set of compounds to determine if there are correlations between molecular structure and spectroscopic properties. Since some of the compounds are water soluble, the effects of solvent on two-photon properties will also be investigated.

**Excited Triplet State Characterization - Plans:** Arylidenopiperidones have relative large two-photon absorption cross sections and we have found them to be photo-toxic to a number of human cancer cell lines. Their cyto-toxicity is however much lower, in some cases two orders of magnitude lower. This shows they may be useful as two-photon sensitizers in photodynamic therapy. For photodynamic therapy to kill cells, an excited triplet state of the sensitizer materials must form either oxygen radical species (Type I mechanism) or singlet oxygen species (Type II mechanism) inside a living cell.<sup>28,29</sup> These reactive oxygen species cause the initiation of cellular events leading to apoptosis and cell death. The low fluorescence quantum yields and short fluorescence lifetimes discussed above, along with light induced cell death, are only indirect evidence excited triplet state formation in the arylidenopiperidones. A measurement of singlet oxygen phosphorescence at 1270 nm would provide more direct evidence of



excited triplet state formation. We will make corresponding measurements on these materials, to confirm the formation of an excited triplet state. Initial experiments will be done using a simple Indium-Gallium-Arsenide detector, with appropriate filters, in a non-biological environment. The ability to detect singlet oxygen will be shown using a methylene blue control.<sup>30</sup> It will also be shown that if singlet oxygen emission from the arylidenopiperidone materials is present, it can be quenched using either catechin hydrate or L-ascorbic acid.<sup>30</sup> Singlet oxygen and oxygen radical species will be detected and differentiated by chemical means. DMSO, at concentrations as low as 0.02%, inhibits the formation of oxygen radical species.<sup>31</sup> Triplet emission from the arylidenopiperidones will be monitored as a function of increasing DMSO concentration to determine if there is both singlet oxygen and oxygen radicals formation. If these experiments give evidence of excited triplet state formation, it will be determined if there are differences in the amount of triplet state formation as a function of molecular structure.

**Expected Outcomes and Future Extensions:** We expect to develop materials based on arylidenopiperidone derivatives that can be used as both sensitizers and fluorescent markers, in a variety of situations. These materials will be constructed to be soluble in either aqueous or non-aqueous solvents. A future extension of this work, will be to attach some of these materials to carrier particles, such as antibodies, peptides, and nanoparticles. This will allow for specific targeting in biological situations and will allow for use of arylidenopiperidones that are not soluble in aqueous environments.

**Student Participation:** This is a multidisciplinary project. So, there would be a potential for student participation in many separate overlapping areas, particularly for student populations that are underrepresented in the physical and biological sciences. As one example, a student could carry out synthesis of material (Martinez) and also be involved in toxicity studies (Hernandez Gifford) to see how differences in structure (Antipin, diffraction studies) affect the outcomes of spectroscopic studies (Sammeth, Short). Potentially, depending on experience and ability, students could participate in all aspects of this project.

### **6.1.2 Research Thrust 2 - Design of Crystalline Materials for Nonlinear Optical and Electro-optical Applications (Timofeeva, Antipin, Lindline - NMHU, Brédas, Barlow, Coropceanu, Marder – GT)**

**Introduction:** Organic crystalline materials for nonlinear optical (NLO) and electrooptic (EO) applications dependent on large second-order susceptibilities,  $\chi^{(2)}$ , and large third-order susceptibilities,  $\chi^{(3)}$ , have attracted the attention of researchers for more than three decades. For second-order materials, in spite of the significant progress made in the area of electric-field poled organic chromophore /polymer systems,<sup>32-35</sup> crystalline materials are still eliciting significant interest. This interest is not restricted to second-order applications but extends to third-order applications where acentric alignment is not required but can lead to significant enhancement of the usable nonlinearity. Acentric crystals (and crystalline films) can be thermodynamically stable phases exhibiting good thermal and photochemical stability, while the degree of acentric order in poled polymers can deteriorate, for instance, with increasing temperature and/or time. Moreover, crystals usually contain higher densities of chromophores in comparison to poled chromophore-doped polymer films and, therefore, offer potential for higher nonlinearities if efficient strategies can be developed for acentric crystallization of chromophores with high molecular nonlinearities. While growth of high quality crystals is still challenging, it is worth noting that one of the most active materials for THz generation today is 4-dimethylamino-*N*-methyl-4-stilbazolium tosylate (DAST), which is commercially available through Rainbow Photonics. While a general theory of second harmonic generation (NLO activity) in crystalline materials has been developed,<sup>36-39</sup> there is still insufficient in-depth understanding of the multiple factors that influence the crystallization of polar molecules into centrosymmetric (no NLO activity) or acentric (generating second harmonic radiation with intensity related to molecular orientation) space groups. In addition to NLO, other system properties (spectroscopic, charge and energy transport, etc.) also depend on the molecular packing motif and intermolecular interactions. Therefore, the big-picture goal of this research thrust is to better understand intermolecular interactions in crystals so as to be able to design novel NLO materials.

**Goal of the proposed research:** More specifically, the goal of this thrust is to increase our level of understanding of acentric crystal formation via application of two complementary approaches to evaluate

the intermolecular energy in crystals: (1) experimental diffraction data and (2) quantum-mechanical computations. The results will be applied to design novel NLO materials related to organic salts, Lewis acids adducts, and metal-organic frameworks.

**Approach:** At present, intermolecular interactions in crystals can be quantitatively evaluated either computationally, using *ab initio* or semi-empirical approaches, or experimentally, using precise diffraction studies of electron (charge) density distributions in crystals, from which, in accord with Hohenberg-Kohn theorems, the energy characteristics of the structure can be obtained.<sup>40-42</sup> The suitability of the latter approach has been shown in several examples where values of the crystal structure energy obtained from diffraction data and from thermochemical studies have been compared<sup>43-46</sup> (Table 1).

**Table 1. Comparison of crystal energy from X-ray diffraction, thermochemical, and computational data**

Name, formula and reference if results are published	E <sub>latt</sub> , kcal/mol	ΔH <sup>o</sup> <sub>subl</sub> exp. (quantum), kcal/mol
Dibenzenechromium, (C <sub>6</sub> H <sub>6</sub> ) <sub>2</sub> Cr <sup>43</sup>	16.9	18.7± 1.51 (16.0)
1,2,4,5-tetrazine, C <sub>2</sub> H <sub>2</sub> N <sub>4</sub>	8.3	(8.7)
1,3,5-trinitro-1,3,5-triazacyclohexane, C <sub>3</sub> H <sub>6</sub> N <sub>6</sub> O <sub>6</sub>	23.54	26.9
Glycine, C <sub>2</sub> H <sub>5</sub> NO <sub>2</sub> <sup>46</sup>	31.2	32.53
[2,2]-paracyclophane <sup>44</sup>	21.9	(23.0)
1-phenyl-o-carborane <sup>45</sup>	16.4	(17.0)

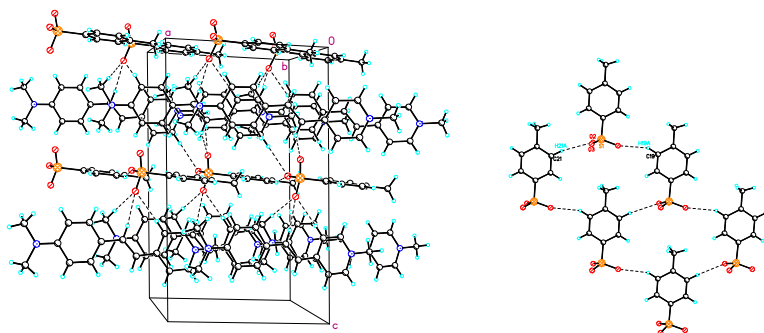
It is especially important that the individual terms (intermolecular pair interaction energies) that impact molecule-molecule or cation-anion interactions be evaluated. It allows to study in the details a participation of different functional groups of molecules (cations and anions) in intermolecular interactions in the crystal. We foresee that such an approach will assist in identifying interactions associated with the desired acentric structures. This type of analysis will be especially significant in cases where we are dealing with specific interactions such as hydrogen bonds,  $\pi$ - $\pi$  stacking, and/or stronger coordination bonds. For instance, such an approach is promising for evaluation of the intermolecular interactions in organic NLO cation-anion structures. Evaluation of atomic charges obtained by integration of the electron density around the corresponding atoms also gives important information and can be used to derive the amount of intermolecular charge transfer, a quantity directly related to the charge transport properties of the material.

Recently it was shown by the NMHU group for a series of glycine salts that the stabilization of the crystal structure is dependent not only on attractive cation-anion interactions but also on cation-cation and anion-anion interactions.<sup>46</sup> It was also demonstrated that the main channels for charge transfer in these structures involve hydrogen bonds. The crystal lattice energy was also characterized from the electron density distribution in the crystal and was found to be in good agreement with the experimental enthalpy of formation.

**Organic Salts.** We plan to apply this approach to DAST and a series of related materials. DAST, due to its adoption of an acentric structure in which the chromophores have a favorable relative orientation, exhibits one of the largest  $\chi^{(2)}$  values of any organic crystal.<sup>47,48</sup> Acentricity of DAST and related compounds was explained *qualitatively* in publications by Marder et al.<sup>49</sup> as due to the formation of alternating cationic and anionic sheets that facilitated the formation of macroscopically polar structures. As mentioned above, an approach based on electron-density distributions and related energy terms will allow a discussion of the reasons for the formation of acentric crystals by members of the DAST series on a *quantitative* level. We also plan to use quantum computational approaches, which will be conducted in collaboration with the Brédas group at GT, to determine the electronic structure of these systems and assess their intermolecular interactions. The combined analysis of diffraction data and quantum-chemical results will allow a better understanding of the factors influencing the stability of centrosymmetric/acentric crystals.

The experimental portion of the subproject will also include crystal engineering of acentric NLO materials. Our preliminary data on the electron density distribution in DAST crystals have shown that

there are significant attractive interactions between cations and anions in this structure (Figure 3, left). Charge transfer between cation and anion was found to be equal to 0.49 e. In addition, the anion layers are stabilized by attractive interactions between anions (Figure 3, right). This conclusion is based on topological analysis of experimental electron density in term of “Atoms in molecules” theory by R.Bader.<sup>40</sup> Bond critical points which indicate an attractive interaction of two atoms are found for (C-) H...O(-SO<sub>2</sub>) intermolecular contact. At this stage, we can speculate that the nature of anions is an important factor defining DAST structure, since attractive interactions between cations were not found.



**Figure 3.** Left: Layers of cations and anions in DAST; the total energy of cation...anion interactions is equal to -11.674 kcal/mol. Right: attractive interactions in anion layers between CH and SO<sub>3</sub> groups; the total energy of O...H contacts per molecule is -1.24 kcal/mol.

**Lewis Acid Adducts.** There are several ways to manipulate supramolecular organization to produce acentric structures. First, the most successful approach to date for creating organic NLO materials has been based on mixed crystals built from polar organic cations and organic anions, such as the DAST-type materials discussed above and other organic salts.<sup>47-57</sup> The second approach is based on specific supramolecular architectures of hydrogen bonds that result in acentricity of a final product. In this case, both single compounds and mixed crystals (co-crystals) with different ratios of components can be used for crystal design.<sup>58-61</sup> The most obvious pathway to acentricity is a co-crystallization of polar molecules with enantiomerically pure components, such as amino acids.<sup>62,63</sup> This approach always results in obtaining non-centrosymmetric crystals. However, in many cases, attempts to orient polar molecules in a parallel fashion fails, since highly polar molecules tend to pack in a quasi-centrosymmetric manner (i.e., with the polar axes of adjacent molecules anti-parallel to one another). Some other approaches including crystallization of polar guest molecules in the channels of a host crystal<sup>64</sup> or the use of columnar mixed octupolar crystals<sup>65</sup> have also been discussed in literature.

Recently, we co-crystallized 1,2-bis(chloromercurio)tetrafluorobenzene – a Lewis acid with strong adduct formation abilities – with nitrobenzene and three nitrotoluene isomers as a model system to examine the possibility of obtaining acentric crystals.<sup>66,67</sup> X-ray studies revealed supramolecular organization in 1:1 complexes showing that they are built of molecular layers where the central section of the layers is stabilized by non-bonded interactions between Cl and Hg atoms, while the surface of the layers is formed by the aryl rings of both co-crystal components. Two types of layer superposition in these complexes were found: parallel, producing an acentric structure, and antiparallel, leading to crystallization in a centrosymmetric space group. This observation indicates that supramolecular organization involving Hg non-bonded interactions can be helpful in producing acentric structures of polar molecules. We plan to develop this approach and apply it to chromophores with higher molecular nonlinearities (e.g. nitroaryl groups as acceptors in dipolar push-pull chromophores), some of which will be provided by our collaborators at GT.

**Metal-Organic Frameworks.** Metal-organic frameworks (MOFs) are materials in which organic ligands are coordinated to metal ions, metal oxide clusters, or metal clusters to form 2D or 3D organic-inorganic polymer networks.<sup>68</sup> Recently, it was found that MOFs containing polar organic linkers can be utilized to assemble supramolecular networks with desired topologies. Because a single strong interaction (coordination bonds) dominates in such systems, other weak intermolecular interactions play a less important role in the crystal packing.<sup>69</sup> It was demonstrated that 3D diamond-like networks with particular metals and relatively short non-flexible linkers are very likely to form acentric structures. For 2D

networks, the probability of obtained acentricity is lower, but in this case non-centrosymmetric arrangement can be engineered by specific ( $\pi$ - $\pi$  stacking and other) interactions. In comparison with traditional dipolar chromophores, NLO-MOFs can have significantly improved transparency-optical nonlinearity tradeoff. It is encouraging that several engineered MOFs already have demonstrated second harmonic generation efficiencies similar to or higher than that of  $\text{LiNbO}_3$ .<sup>69</sup>

Our groups have experience with MOFs for different applications, for example, porous MOFs specific for gas adsorption.<sup>70-72</sup> We plan to transfer our expertise in this area to crystal engineering of MOFs with NLO properties. Usually ligands that can be used to form acentric MOF structures are rigid unsymmetrical linking groups that also introduce electronic asymmetry, and their rigidity assures good conjugation between electron donor and acceptor groups. In addition to standard linker groups, we plan to design NLO-MOFs based on V-shaped chromospheres with dual NLO and two-photon absorbing action to form 3D diamond-like acentric networks.

At present, most MOFs are synthesized using a hydrothermal synthesis that usually takes several days to several weeks. Recently researchers started to explore the possibility of faster, higher-yielding syntheses, such as microwave assisted solvothermal synthesis (the use of microwaves in rapid synthesis of organic materials has been widely used for more than 20 years<sup>73</sup> with promising results. Such microwave-assisted methods for the synthesis of MOFs allow one to synthesize materials rapidly (sometimes in minutes) and to grow relatively large crystals, which is a critical requirement for obtaining detailed information on their structures.<sup>74-76</sup> However, general guidelines for identifying conditions for obtaining the best yield and crystal quality of MOFs are not well-developed yet; accordingly, optimization of time/temperature/concentration/solvent conditions will be important tasks for student research projects. To evaluate crystallinity and unit cell parameters we plan to use powder diffraction techniques and the STEM facilities at UNM.

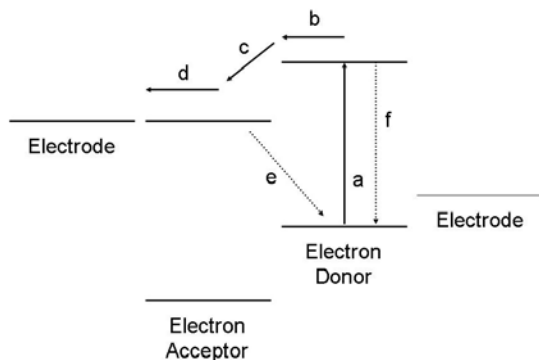
**Student Activities and Collaborations.** For students, it will be very important to obtain an understanding of the interconnections between molecular structure and crystal structure and of how the properties of crystalline materials can be related to internal molecular orientations within the crystals. We also believe that student-researchers will gain significant skills in organic synthesis, crystal growth, and X-ray structural analysis at NMHU and our partner organizations.

**NMHU-GT Coordination.** The three NMHU researchers identified in this thrust have collaborated with the Marder and Brédas groups at GT for roughly 7 years. Their effort has primarily been devoted to structural analysis of organic NLO and optoelectronic materials designed and synthesized at GT, and to revealing and understanding geometrical peculiarities and molecular properties based on results of diffraction analysis.<sup>77-81</sup> In the framework of this project, we plan to achieve a higher level of understanding and interpretation of material properties via consideration of molecular environment and interactions in the crystals. Such issues have always been an area of interest for the GT groups,<sup>48,49,82,83</sup> however, only recently have tools for the extraction of energetic information from diffraction data been developed and new approaches to crystal engineering emerged. In particular, the Marder group will provide the NMHU group with chromophores for co-crystallization investigations and key compounds (DAST derivatives) for precise diffraction studies. Results of high-level diffraction analysis will be discussed along with results of quantum-chemical computations in the Brédas group to improve theory/experiment connections and bring a heightened level of understanding into the design of new materials.

### **6.1.3 Research Thrust 3. New functional materials for organic photovoltaic devices (Lawrence - MC; Marder, Bredas, Coropceanu – GT; Martinez, Antipov - NMHU)**

Since the first publications describing bulk heterojunction photodiodes incorporating conjugated thiophene-based polymers and methanofullerenes,<sup>84</sup> much progress has been made towards improved device performance as it relates to the organic p-type semiconductor polymers (i.e. poly-3-hexylthiophene)<sup>85-90</sup> that these devices incorporate. While the scope of materials research in this arena has certainly broadened, significant challenges still remain. For example, there is still room for

improvement in materials with long exciton diffusion length to facilitate their migrations from their site of origin upon photoexcitation to the donor/acceptor interface where they dissociate, and materials that have high charge carrier mobilities for electrons and holes towards their respective electrodes (Figure 4).<sup>91,92</sup> To address this need, the goal of this research thrust is the development of synthetic methodologies that enable the preparation of highly electron deficient conjugated polymers (n-type semiconductors) as *new functional materials*. It is our hope that these materials will then be employed in the fabrication of the first generation of low cost, highly efficient, and mass produced organic photovoltaic (OPV) cells in collaboration with CMIDTR.

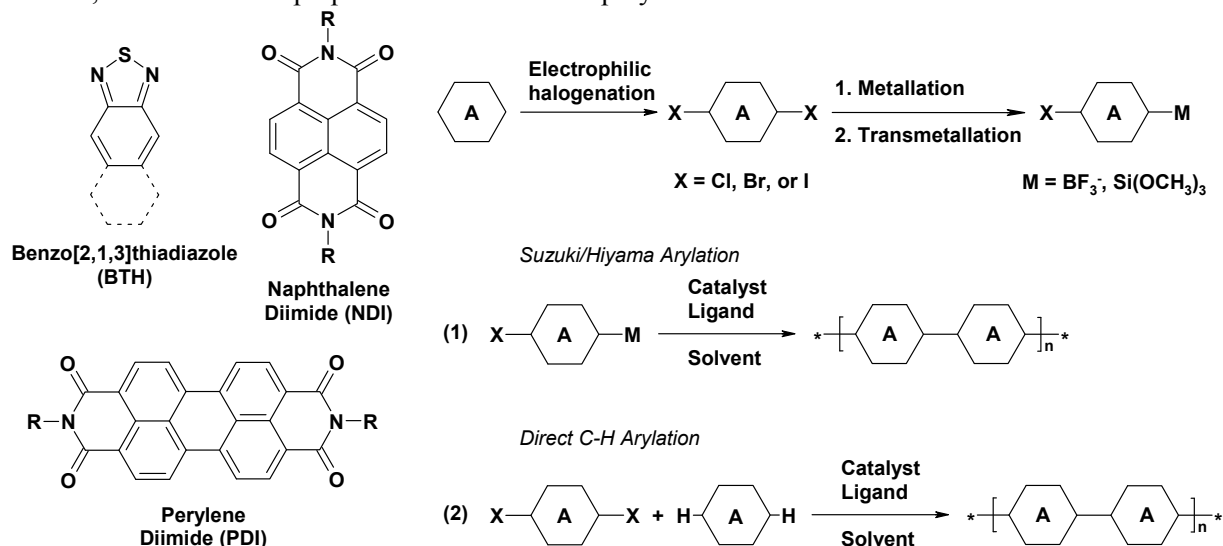


**Figure 4.** Schematic representation of a bulk heterojunction photovoltaic device. Upon photoexcitation of the donor species, (a) an electron is promoted to the donor HOMO to create an exciton, (b) the exciton migrates to the interfacial junction, (c) dissociated by injecting an electron to LUMO of the acceptor, and that electron migrates forward to the electrode (d). At the same time, the corresponding hole moves in the opposite direction. Also illustrated here are two undesirable events: (e) geminate recombination and (f) back electron transfer, both which need to be minimized in a successful applications.

**Synthesis of the proposed materials:** We aim to approach a solution to the problem illustrated above (**Lawrence, Marder, Martinez**) through the application and/or development of new, novel methods for carbon-carbon bond formation (i.e. Hiyama,<sup>93-97</sup> modified Suzuki-Miyaura,<sup>98-104</sup> or direct C-H arylation<sup>105,106</sup> reactions; Scheme 1). To complement this approach, we will take full advantage of an array modern methods of purification (esp. HPLC) to improve both the purity (>99.9%) and polydispersity indexes (PDI  $\rightarrow$  1) for all polymeric materials produced (**Lawrence, Marder**) so as to meet the requirements of material homogeneity necessitated by the product OPV devices. By developing/implementing such reaction methodology, not only would we be able to access a variety of new organic polymers that heretofore were unachievable (eg. the coupling of electron-deficient acceptor monomers) but new, generalized tools for the acceleration of both the synthesis and purification of new organic conductor and semiconductor materials would result.

**Methodological development**—A brief inspection of the relevant literature indicates a continued reliance on specific transition metal-catalyzed cross-coupling chemistries (Suzuki, Stille) for the preparation of conductive organic polymers.<sup>107-114</sup> In spite of this fact, it has been clearly shown that these methods are unsuitable for reactions between electron-deficient coupling partners, owing in large part, to the electron attracting abilities of the compounds themselves. Within this class of coupling partners, there emerges a subset of acceptor molecules including benzothiadiazole (BTH; and its annulated homologs)<sup>115-117</sup> and the structurally interrelated perylene and naphthalene diimides (PDI and NDI, respectively)<sup>115-117</sup> for which this strategy cannot be utilized. Consequently, homopolymers of these materials are practically inaccessible. Relying on the knowledge base of members in this collaboration (**Lawrence, Marder**) with these and related monomeric building blocks, our approach to the construction of high molecular weight polymeric materials will then rely on an ability to control the coupling reaction between monomers of BTH, PDI, and NDI (Scheme 1). We will initiate a study (**Lawrence**) of this coupling strategy utilizing the previously described electron deficient acceptor monomers (BTH, PDI, and NDI) and their corresponding dihalogenated analogs. Their cross-coupling reactivities with regards to scope and effectiveness of the transition-metal partner will be explored (Pd, Pt, Ni, or Rh) in consideration of many variables as ideally, the robustness and scalability of these processes must be of foremost concern. To explore new coupling strategies, metal/metalloid partners including perfluoroborates<sup>98,101-104</sup> and organosilanes<sup>93-97</sup> will be prepared (**Lawrence, Martinez**) using standard procedures. As well, we will explore one especially attractive alternative to organometallic/halogen coupling reactions that has yet to be demonstrated in the context of conductive polymer synthesis, namely the *direct C-H arylation*

reaction.<sup>105,106</sup> This methodology, when successfully applied, would remove the requirement for an additional chemical *and* purification step in route to the desired coupling products, making overall for an efficient, atom economic preparation of the desired polymeric materials.



Scheme 1. (a) Representative acceptor species for use in the construction of and (b) proposed reactivity pathways to be explored toward the production of new functional materials.

**Characterization of the material properties:** Owing to the change in morphology resulting from the incorporation of polymeric n-type materials into OPV devices (esp. when compared to methanofullerenes), we expect there to be changes in the packing of these molecules in said organic semiconductors that effect their ability to carry charge (which, in turn, will detract from the likelihood of electron/hole recombination). Therefore, careful analysis and optimization of each new material developed for bulk heterojunction OPV cells will be carried out. Utilizing the full resources of the members of this collaboration (NMHU, MC, CMDITR), standard physical characterizations of all new monomeric materials (incl. FT-NMR, FT-IR, MS, UV/Vis) and their corresponding polymer products [incl. PDI,  $\mu$  (charge mobility), solubility] will be performed utilizing equipment already available at each member institution.

**Expected Outcomes and Future Extensions:** We expect to develop materials based on electron deficient derivatives of NDI, PDI, and BTH that can be used as electron acceptor charge carriers (n-type semiconductors) in OPVs. A future extension of this work will logically become the incorporation of these materials into devices to test their efficacies in real-life situations.

**Student Participation:** Undergraduate students at Morehouse College will directly participate in this project by engaging in academic year and summer term research relating to the development of new chemical methods as described above (Lawrence) as well as both the synthesis and characterization of new polymeric materials. In consideration of the fact that many undergraduates at Morehouse College are externally funded to participate in faculty-mentored research, we anticipate that four (4) or more undergraduates/calendar year will be able to participate in this project at Morehouse and additionally, through participation in the CMDITR's multi-site summer research program "Hooked on Photonics".

**MC-NMHU-GT Coordination:** The MC researcher (Lawrence) identified in this thrust began collaboration with the CMDITR (Marder) at GT in 2008. Their efforts thus far have primarily been devoted to the optimization of processes involved in the synthesis of organic materials designed at GT. As well, work towards the elucidation of the inherent challenges posed by purification of said materials using advanced methods [i.e. solid phase extraction (SPE), HPLC, gel permeation chromatography (GPC), etc.)] has begun. It is within this context that the proposed research thrust developed, as the realization of a need for such methodology was obviated. Research towards the completion of this project will

incorporate expertise in monomer synthesis at all three member institutions (**Lawrence, Marder, Martinez**). The development of both polymerization and purification protocols will utilize both personnel and instrumentation at MC and GT (**Lawrence, Marder**), respectively. To ensure complete transparency, Dr. Lawrence will serve as the key contact for all personnel engaged.

## **6.2 Education and Outreach**

The goal of the education and outreach aspect of the LMITA program is to enhance the interest and feasibility of students to pursue undergraduate and graduate degrees in materials science and engineering and related disciplines (e.g. chemistry, physics, electrical engineering, biomedical engineering). Our education and outreach plan contains many components that go beyond standard but essential “hands-on” research experiences for undergraduates and graduate students. Our target populations embrace students as well as faculty from high school through graduate school.

Leading this effort will be Jennifer Lindline, Professor of Natural Resources at NMHU and Keith Oden of GT. Professor Lindline has played an important role in NMHU’s “First Year Experience Program” for new college freshmen and as a result, she has become very experienced in working with first generation college students. Her focus has been to create a learning community expressly for students interested in pursuing scientific careers. Lindline will be responsible for a new lecture/lab course, a materials science workshop for high school, undergraduates and science teachers, and the teachers’ summer program at NMHU. Keith Oden is the current Diversity Director for the CMDITR. Dr. Oden holds a Ph.D. in Educational Policy Studies and has spent much of his professional career strategically designing and implementing programs to prepare and recruit students from underrepresented groups for undergraduate and graduate programs in STEM disciplines. Dr. Oden will work with Professor Brian Lawrence of Morehouse College to establish strong linkages with education and outreach programs at this HBCU. Dr. Lawrence has been an active proponent of integrating research into the undergraduate curriculum and bridging the STEM fields of biology, chemistry, and physics since his arrival at MC three years ago.

Here we breakdown our proposed programs by target audience, moving from high schools to community colleges and NMHU and MC.

### **6.2.1 High School Programs**

Dual Credit Program - Las Vegas, NM, site of NMHU’s main campus, has two school districts, each with a high school a short walk from the university. NMHU’s Dual Credit program allows high school student to enroll in college courses prior to high school graduation; dual credit students receive both high school and college credit simultaneously. As a collaborator with a LMITA initiative, the University’s Credit Coordinator, Elizabeth Ratzlaff, will visit each of the local high schools during course registration periods to recruit members of underrepresented groups to enroll in science courses at NMHU. LMITA faculty will hold a workshop at the beginning of each semester for all high school students who have enrolled in a STEM course to assist them to successfully make the transition to college level work. The faculty will also introduce LMITA programs and opportunities to these students and arrange for group tutoring using designated TAs and volunteer LMITA undergraduate and graduate students. Dual Credit students will also be invited to visit the material science research laboratories on campus, attend seminars, and be recruited to enroll at NMHU after graduation to participate in LMITA.

GEAR UP - The NMHU/Rural Northern New Mexico GEAR UP program is designed to increase the number of low-income students who will be prepared to enter and succeed in college. GEAR UP serves an entire cohort of students beginning no later than eighth grade and follows the cohort through high school graduation. The partnership program includes twenty-three school districts throughout northern New Mexico. LMITA will work with the GEAR UP program to ensure that the graduating class is aware of the exciting opportunities in materials science research that exist at Highlands University. Students participating in GEAR UP have a decided advantage in that a major component of GEAR UP is to assist students facing deficiencies in reading skills, math skills, as well as general academic skills before they matriculate. The director of GEAR UP, Jose C'de Baca, will help to identify strong candidates for the LMITA program early on, thus creating a pool of high school students with a professed interest in science and the potential to excel.



Outreach to High School School Teachers. Every year, two science teachers from Northern NM will be invited to participate in a 10-week summer internship at NMHU. Schools in northern NM will be notified by mailings and the LMITA website, and teachers chosen on a competitive basis. Participants will be paid 2/9 of their regular salary and part of their summer goal will be to produce a light-matter interaction demonstration project or experiment to take back to the classroom in “kit” form. Local CC chemistry/physics instructors will also be invited to participate in this program. The internships will consist of participation in an ongoing research project as well as immersion into the most up-to-date pedagogy for science educators. One of the aims of the program is to expose regional educators to research themes of contemporary importance. This experience will allow science teachers to return to their schools and share current research areas and ideas with their students, while informing them of current expectations and requirements for undergraduate science majors. Experience with chemical synthesis, spectroscopic material characterization, diffraction analysis and molecular modeling research will allow them to share first-hand with their students, a broad array of research areas. A second goal will be to work the teachers to expand and update the experiments that are conducted in their high school science classes. The overall theme is to help them become current with modern trends in light – matter interactions. Examples are using solar energy to produce hydrogen for a toy/model vehicle, light driven chemical reactions, and spectroscopic investigations of chemical phenomena.

### **6.2.2 Community College Programs**

Bridging Careers for Success and LMITA: NMHU was recently awarded a Bridging Careers for Success (BCS) grant from the US Department of Education in collaboration with Luna Community College (LCC) titled “*A Collaborative Hispanic Science, Technology, Engineering, and Mathematics Improvement Program between NMHU and LCC.*” The goal is to support innovative approaches that improve access of educational services to students in the STEM disciplines. The Project Director, Edward Martinez has pledged to integrate his BCS Program with LMITA activities. Among the BCS components in preparation by an experienced staff with a deep understanding of working with a diversity of students in STEM are: (1) a summer or short-term semester internship program, (2) an online and face-to-face mentoring program, (3) on campus science presentations by leading experts, (4) networking opportunities with career professionals, and (5) tutoring and other student development activities.

Outreach to Community College Faculty – This program is described in 6.2.1.

### **6.2.3 Undergraduate Programs at NMHU and MC**

LMITA Research Participation – Undergraduates at NMHU, Morehouse College, and local CC colleges will have two means of participating in hands-on LMITA research. The first is to seek out a faculty advisor, possibly using the LMITA Mentoring Program, to engage in term-time or summer research in light-matter interactions either for pay or credit. The second route is to apply for a position in the CMDITR’s Hooked-on-Photonics NSF Summer REU Program. This well known and highly competitive program bases approximately 10 undergraduates each summer at UW, GT, and UA. All expenses are paid and the programs include weekly lectures, area outings, career and skills development training (e.g. scientific writing, poster preparation, data analysis, etc.), and an end-of-summer symposium. CMDITR has pledged to set aside 3 positions each year for LMITA undergraduates.

LMITA Mentoring Program – Once in full swing, LMITA will join a substantial complement of high school, community college, and university faculty in the Las Vegas and Atlanta areas. These individuals, and in some cases, CMDITR and NMHU graduate students as well, are potential mentors to students at all target age groups interested in LMITA programs. CMDITR has created a model mentoring program aimed primarily at graduate students and postdocs. The CMDITR’s faculty leads will assist Drs. Lindline and Oden with implementing mentoring programs in Las Vegas and Atlanta-Morehouse that include mentoring of high school and community college students. Dr. Oden will connect LMITA undergraduates to the financial and social support resources of the GEM Consortium that enable hundreds of underrepresented students each year to pursue internships in industry and eventually graduate degrees in science and engineering. A very effective dissemination vehicle has been the STC-sponsored FutureTech Meeting held annually for high school students and college freshmen. The last such meeting was

coordinated by Dr. Oden in October 2008 in Albuquerque NM, where 14 NMHU students received valuable information about sources of graduate fellowships.

New Materials Science Course Content Development at NMHU - An undergraduate, three credit hour course, "Material Science Techniques" will be developed and offered as an interdepartmental selected topics course. The course will be coordinated by Prof. Jennifer Lindline and will cover laser spectroscopy, single-crystal and powdered X-ray diffraction, NMR, GC-MS, FT-IR, fluorescence, HPLC, capillary electrophoresis (CE), magnetometry and electrochemical techniques to quantitatively describe materials. The course will be designed to provide students with the rudimentary and generalized laboratory skills that is required before learning the advanced methodologies that will be employed in the research laboratories. The course will be team-taught and offered by NMHU faculty. NMHU educators will improve existing undergraduate (and graduate) courses by using course modules developed by the CMDITR in subject areas including (1) the basics of light; (2) luminescence and color; (3) molecular orbitals; (4) electronic band structure; (5) absorption and emission; (6) liquid crystals; (7) organic light emitting diodes; and (8) solar cells. NMHU faculty will also be trained in the preparation of new course modules using Tegrity 2.0 software and "bridge" lectures to introduce lower level students to advanced subject coverage. LMITA will also invite CMDITR faculty to present condensed one-week courses in chemistry (mainly polymer and liquid crystalline chemistry), physics (especially optics), and materials science (materials fabrication and testing). The goal is to offer one course, suitable to both undergraduates and masters degree candidates, each fall and spring term.

Special Seminars by Leading Experts – Regular visits by LMITA faculty from CMDITR universities will provide opportunities to expose a wide range of LMITA students to general audience level seminars on what future technologies based on light-matter interactions will bring to our lives. LMITA will stage such events at large auditoriums at times when our diverse student and faculty from area high schools and community colleges can attend. Pre- or post-seminar receptions will serve as "mixers" where students of various ages can interact with each other and with faculty from different educational institutions.

#### **6.2.4 Graduate Program at NMHU**

Each year, NMHU graduates about 15 masters degree candidates from its College of Science and Mathematics. LMITA programs aimed at the graduate level will be even more extensive than those directed toward undergraduates. Students will be notified about opportunities to serve as research assistants on LMITA funded projects via the NMHU and CMDITR websites and via websites of universities in NM and neighboring states (TX, AZ, CO, and other). Students will be hired into projects on a competitive basis. All RAs will be required to participate in biweekly seminars and give at least one presentation on their progress per semester. They will also be strongly encouraged to provide mentorship and research assistance to one undergraduate PREM student.

New Course Content – In 6.2.3, we mentioned the CMDITR's rich portfolio of photonics and organic electronics based course content, most of which is directed at students at the graduate level. This resource will be extremely valuable in creating a new graduate course entitled "Organic Materials for Optics, Photonics and Optoelectronics" to be coordinated and taught by Prof. Timofeeva. CMDITR modules will also be adapted and inserted into existing courses at NMHU to expand subject coverage and improve relevancy to contemporary technologies.

Graduate Mentoring – The general approach to building a comprehensive LMITA mentoring program is described in 6.2.3. NMHU graduate students, however, will have the added benefit of being able to participate directly in the CMDITR Mentoring Program and perhaps choosing a mentor based in Seattle, Pasadena, Atlanta, or other STC partner locations. Mentors will encourage and advise mentees to pursue graduate studies in materials science and related fields at CMDITR universities and elsewhere. Dr. Oden will play a key role in match-making students and CMDITR mentors.

Student Exchange Program – As evident from Figure 1 in the Research Plan, NMHU's role in most of the proposed research thrusts emphasizes materials characterization. To expose our student researchers to chemical synthesis, theoretical modeling, and characterization methods not available at NMHU, we will send them to GT or other CMDITR Research-1 facilities for specific purposes related to their work. The

CMDITR has learned that students travel best in pairs and we will follow this strategy. Every graduate student will visit a CMDITR partner site at least once in his or her academic tenure, and we will make special allowance for exceptional undergraduates to participate in the Exchange Program as well. Additionally, NMHU and MC will welcome visits by CMDITR students should they have research needs we can help them address (e.g. to conduct X-ray diffraction experiments). When such students do visit, they will be asked to give a research seminar to set examples for our masters degree candidates. It is impossible to overestimate the usefulness of personal contacts that will help students from a small rural university perhaps find a future advisor, graduate school, or employment opportunity. Our students will also encounter different approaches to research and social networking – an important step in appreciating the globalized nature of science.

CMDITR Annual Retreat - This event is an extravaganza of some 130 participants who gather annually either in Seattle, Tucson, or Atlanta. LMITA's graduate students and exceptional undergraduate students will be sponsored to partake of the science, poster, and career sessions, and to interact with STC counterparts to build bridges into the future.

#### **6.2.5 LMITA Postgraduate Education Fellowship Program**

LMITA will continuously sponsor one CMDITR graduate (masters or PhD) fellowship in STEM education and outreach. This program will meet two needs: (1) to train STC graduates in physical sciences and engineering who have a passion for education and (2) to staff the LMITA education/outreach program with individuals with technical expertise in light-matter interactions and an understanding of the importance of diversity. The Fellowship will be a one-year award with an option to continue for a second year, contingent on performance. Awardees may be based at NMHU or Morehouse College, or they may choose to spend one year at both LMITA host locations.

#### **6.2.6 Los Alamos and Sandia National Laboratory Internship Program**

NMHU enjoys the luxury of long term connections with two national laboratories located in northern New Mexico: Los Alamos and Sandia National Labs. Traditionally, collaborative projects were based on grants from these National Labs to NMHU and support of internships that placed NMHU students in these facilities. As a result of such past collaborations, many papers have been published, for example by Timofeeva's group<sup>76-80</sup>. Our colleagues at LANL and SNL welcome a formal program under the auspices of NSF's PREM Program (see letters of support from each laboratory). Funding at LANL and SNL available for this purpose is uncertain at the current time, however, we are confident that some combination of laboratory money, LMITA funds, and earning of course credit will enable us to send two NMHU or MC students to each facility each summer.

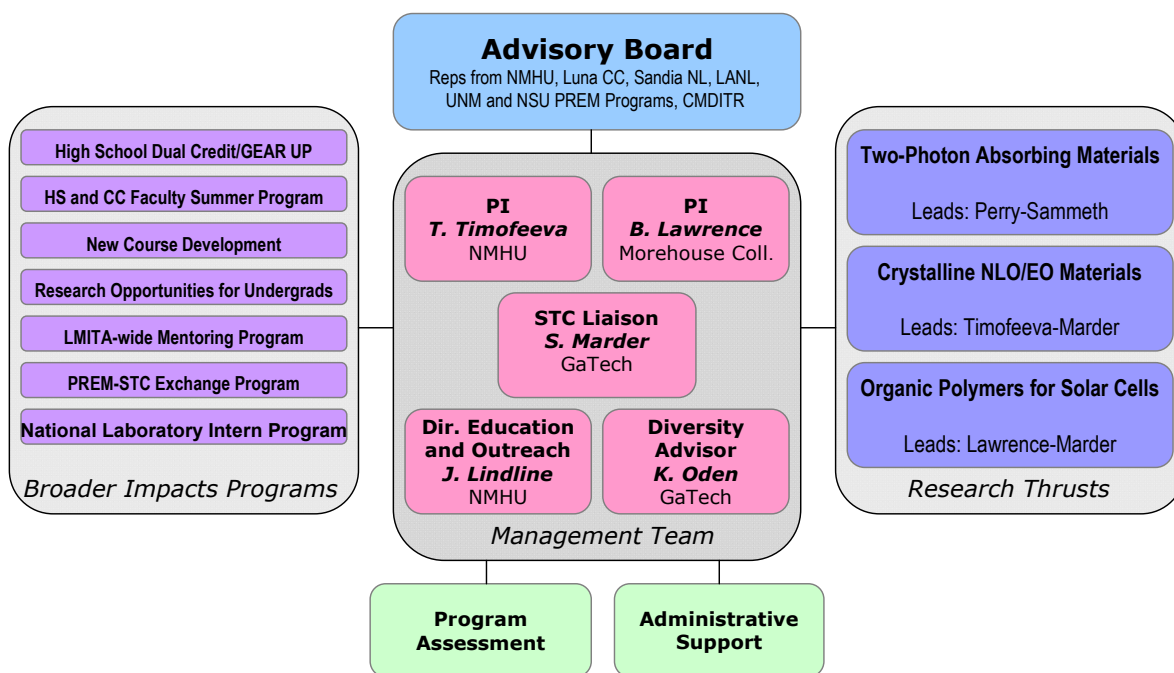
### **7. Management Plan**

At steady-state, LMITA projects a core membership of 10-12 faculty, 10-12 NMHU and MC students conducting research, and another 10-12 close collaborators from local high schools and community colleges, LANL, and the CMDITR. This group of three dozen key participants will impact a much larger population through exposure to LMITA education and outreach programs, but it is small enough that the Partnership's management approach need not be overly complex. The management goal, in its simplest terms, is for LMITA to function as a vibrant community of peers with a common research and education mission. To achieve this, the Partnership's leaders will articulate a clear and visionary work plan and emphasize integration and inclusion. Our ultimate success will be measured by achievements in research and education that will leave lasting positive impacts on society. Shorter term, LMITA will help itself by establishing simple metrics by which to assess its effectiveness – akin to the goals described in section 2.

LMITA's management plan will (1) select and coordinate research activities; (2) allocate funds to research projects; (3) recommend the best use of shared equipment and facilities; (3) manage relationships among all participants including our sponsor, NSF, and the public; and (4) plan, develop, and evaluate education and outreach programs. Our plan calls for an Advisory Board constituted mainly with representatives from our partner schools, community colleges, and national labs, but also with leaders from two other PREM programs who are known to us (i.e. Dr. Suely Black of the Norfolk State-Cornell PREM and Dr. Gabriel Lopez of the UNM-Harvard PREM) and the NM EPSCoR program. Existing

DMR Centers (like CMDITR) and PREM Programs are among the richest resources available for advice and ideas and we will not be hesitant to tap into these programs to avoid reinventing the wheel.

As can be seen from Figure 5, the Management Team will consist of six individuals – the two PIs of this proposal (Timofeeva and Lawrence), the CMDITR Liaison (Marder), the Director of Education and Outreach (Lindline), and a Diversity Advisor (Oden). The PIs and Education/Outreach leaders have been described elsewhere in the proposal. Dr. Keith Oden of GT has been a force over the past four years in increasing the diversity of not only two materials-based Centers (CMDITR and COPE), but of our nation's leading STEM research universities. We have invited Dr. Oden to serve on the LMITA Management Team for his unique perspectives on mobilizing the rich minority student populations at NMHU and MC toward careers in the sciences and engineering.



**Figure 5. Proposed LMITA organizational structure**

The LMITA Management Team will meet monthly via video and internet conferencing. The Team will also meet with the Advisory Board at least twice per year. Meetings to coordinate research thrust and education/outreach program subcomponents will be held as needed and led by respective thrust and program leaders as indicated in Figure 2. Coordination and dissemination of information and opportunities to participate will be facilitated through the creation of a LMITA website (Dr. Gil Gallegos, Computer Science/Engineering, website coordinator). Each year of operation will culminate in an Annual Retreat to be held alternately in Las Vegas, NM and Atlanta, GA. Emphasis at the Retreat will be placed on student research and internship presentations but will also feature talks by faculty and industry/national laboratory representatives and sessions on admissions to graduate school and career planning. LMITA will set aside significant travel funds to assure participation by core Partnership personnel.

## 8. Evaluation

Evaluation of the PREM program will be conducted by Dr. Kayt C. Peck, a local education assessment expert known to the NMHU community (particularly NIH-funded researchers) for over five years. Dr. Peck will work closely with LMITA PIs to design a plan to (1) assess in detail, the quantity and quality of outputs and outcomes of the various E&O programs and (2) synthesize these results into an overall assessment of how well LMITA is meeting its overarching goal to attract minority students into science education and technical career paths. Evaluation methods will rely heavily on judicious use of interviews,

questionnaires, focus groups, document reviews, and live and taped observations. A chronic weakness of broader impact assessment programs has been the inability to longitudinally track students after their initial encounter with the NSF program at hand. CMDITR has developed clever tools and techniques to bypass this obstacle (e.g. signed “contracts” with REU students and interns to report back online for up to 5 years into the future; a tracking database built into the Center website for all graduate students; solicitation of newsletter or website articles from past students now in careers). LMITA will adopt similar techniques to gauge the Partnership’s impact for at least the 5-year life cycle of the program.

## **9. Broader Impacts**

***The setting*** - We have emphasized the large proportion of Hispanic students enrolled at NMHU (59%), but it is also important to note that women outnumber men 3:2, that American Indian and Pacific Islanders account for 10%, and African American students another 6% of the university’s population. NMHU President Jim Fries and leaders from 23 Native American tribes in NM and TX signed an agreement on Feb. 19, 2009 to promote higher education opportunities for Native American students at Highlands. Morehouse College is an exclusively male, African-American undergraduate college. It would be difficult to find more compelling demographics than these in the form of potential host institutions for a new PREM program.

***Diverse Leadership*** - It has been a challenge for many NSF Centers to populate their leadership with women and people of color – particularly among faculty. The presence of underrepresented groups in a center’s leadership sends a powerful message to students and places role models where they can be most effective. LMITA’s proposed leadership roster includes three women, two African-Americans, and four Hispanic faculty. As a result, students recruited into LMITA will see science and education experts who look very much like themselves.

***NSF Goals*** – NSF articulates five broader impact areas in which it demands attention from every proposal. The current proposal squarely addresses the first two: (1) to advance discovery and understanding while promoting teaching, training, and learning; and (2) broadening participation of underrepresented groups. On the former, DMR Director Zakya Kafafi asks that proposers “go beyond their normal teaching duties and commitments...” to “involve undergraduate and high school students...” and “participate in the development of K-12 teachers...”. LMITA will penetrate deeply into area high schools and community colleges to inspire students and teachers with subject matter they would otherwise not likely see. These interactions will enable us to forge even stronger linkages back to NMHU and Morehouse College than currently exist on the strength of Dual Credit and GEAR-UP programs. For the second impact area, we are inspired by the successes of GT, LMITA’s dominant Center partner. We have witnessed that two ingredients are key to attracting large numbers of minority students into science and engineering. The first is to have excellent outreach and recruitment programs in place managed by outstanding and committed people. The second is to be immersed in a region of the country where minority groups feel at home. The task can be incredibly difficult in places like the Midwest, Pacific Northwest, and areas of the Northeast. In northern New Mexico and Atlanta, however, with experienced and dedicated partners from GT, alongside, we know we can succeed.

***Career Opportunities*** - New Mexico is a unique state in several regards that are particularly relevant to the PREM Program and this proposal. It is the first state in the US to reach a minority Hispanic population of 45%. It has a remarkably high density of high-tech infrastructure in the form of Sandia and Los Alamos National Laboratories, Kirtland Air Force Base, Air Force Research Laboratory, Intel, the University of New Mexico, and others. New Mexico is poised above most all other states as a test bed for large-scale solar energy demonstration projects owing to its favorable climate. This collection of facts suggests that it is deeply in New Mexico’s and the nation’s interest to train young residents of the state to qualify for home-grown jobs that require expertise in various fields of technology. LMITA will provide coverage away from UNM and Albuquerque and open the door to young people interested in gaining a toehold in study areas that are directly relevant to the research interests and needs of the state.