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14. ABSTRACT The synthesis of new photo and electrical materials for molecular devices was completed comprising a signaling moiety (fluorophore), a spacer group and a guest-binding site (receptor); useful in electro- and photochromatic, OLED, and photovoltaic materials. Our research effort is concentrated on the development of new organic materials that exhibit unique and useful luminescent and electrochemical properties of scientific interest for DoD applications. In this research project, organic ligand compounds containing p-phenylenevinylene, fluorine,					
15. SUBJECT TERMS fluorene, perylene, fluorescent probes					
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## Report Title

Designing Electronic Components and Devices from Inorganic Molecular Scaffolds

### ABSTRACT

The synthesis of new photo and electrical materials for molecular devices was completed comprising a signaling moiety (fluorophore), a spacer group and a guest-binding site (receptor); useful in electro- and photochromatic, OLED, and photovoltaic materials. Our research effort is concentrated on the development of new organic materials that exhibit unique and useful luminescent and electrochemical properties of scientific interest for DoD applications. In this research project, organic ligand compounds containing p-phenylenevinylene, fluorine, perylenebis(dicarboximide), and ethynyl metal-chelating molecular scaffolds were synthesized and the luminescent properties investigated.

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**Enter List of papers submitted or published that acknowledge ARO support from the start of the project to the date of this printing. List the papers, including journal references, in the following categories:**

**(a) Papers published in peer-reviewed journals (N/A for none)**

Received                  Paper

**TOTAL:**

**Number of Papers published in peer-reviewed journals:**

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**(b) Papers published in non-peer-reviewed journals (N/A for none)**

Received                  Paper

**TOTAL:**

**Number of Papers published in non peer-reviewed journals:**

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**(c) Presentations**

**Number of Presentations:**      2.00

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**Non Peer-Reviewed Conference Proceeding publications (other than abstracts):**

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**Number of Non Peer-Reviewed Conference Proceeding publications (other than abstracts):**

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**Peer-Reviewed Conference Proceeding publications (other than abstracts):**

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**(d) Manuscripts**

Received                  Paper

**TOTAL:**

**Number of Manuscripts:**

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**Books**

Received                  Paper

**TOTAL:**

**Patents Submitted**

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**Patents Awarded**

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**Awards**

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**Graduate Students**

<u>NAME</u>	<u>PERCENT SUPPORTED</u>
<b>FTE Equivalent:</b>	
<b>Total Number:</b>	

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**Names of Post Doctorates**

<u>NAME</u>	<u>PERCENT SUPPORTED</u>
<b>FTE Equivalent:</b>	
<b>Total Number:</b>	

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**Names of Faculty Supported**

<u>NAME</u>	<u>PERCENT SUPPORTED</u>
<b>FTE Equivalent:</b>	
<b>Total Number:</b>	

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**Names of Under Graduate students supported**

<u>NAME</u>	<u>PERCENT SUPPORTED</u>
<b>FTE Equivalent:</b>	
<b>Total Number:</b>	

**Student Metrics**

This section only applies to graduating undergraduates supported by this agreement in this reporting period

- The number of undergraduates funded by this agreement who graduated during this period: ..... 1.00
- The number of undergraduates funded by this agreement who graduated during this period with a degree in science, mathematics, engineering, or technology fields:..... 1.00
- The number of undergraduates funded by your agreement who graduated during this period and will continue to pursue a graduate or Ph.D. degree in science, mathematics, engineering, or technology fields:..... 0.00
- Number of graduating undergraduates who achieved a 3.5 GPA to 4.0 (4.0 max scale):..... 1.00
- Number of graduating undergraduates funded by a DoD funded Center of Excellence grant for Education, Research and Engineering:..... 0.00
- The number of undergraduates funded by your agreement who graduated during this period and intend to work for the Department of Defense ..... 0.00
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**Names of Personnel receiving masters degrees**

<u>NAME</u>
<b>Total Number:</b>

**Names of personnel receiving PHDs**

<u>NAME</u>
<b>Total Number:</b>

**Names of other research staff**

<u>NAME</u>	<u>PERCENT SUPPORTED</u>
<b>FTE Equivalent:</b>	
<b>Total Number:</b>	

**Sub Contractors (DD882)**

## **Inventions (DD882)**

### **Scientific Progress**

The synthesis of new photooptical organic materials was completed comprising of a fluorophore, spacer group and in many instances, a guest-binding site. Our interest was to develop electro- and photochromic materials useful for OLED and photovoltaic applications. Organic compounds containing phenylenevinylene, fluorene, perylenebis(dicarboximide), and ethynyl-bridged scaffold materials were developed.

### **Technology Transfer**

**Final Report**  
**Grant Period: 09/01/08-03/07/12**  
**Grant Agreement No. W911NF-08-1-0359**  
**Kenneth Yamaguchi (PI) and Alberto Pinkas (CoPI)**  
**New Jersey City University**

The fabrication of molecular electronic devices from inorganic and organic compounds is being actively pursued. This quest is driven by the potential to create photo- and electrooptical materials that are capable of performing logic operations, have favorable light-emitting properties under a voltage load, and can be manufactured cheaper and have a large current density. The design and fabrication of nanostructures can serve as building blocks for molecular switching devices, organic light-emitting diodes (OLEDs), photovoltaic, field-effect transistors (FETs), electrochromic materials and solar cells.

Molecular architectural design and their macroscopic properties will dictate the material properties. Systematic changes in ligands, the guest binding site (dictated by the type and oxidation state of the metal ion) and the medium surrounding these metal-organic complexes can be used to tune the luminescent, electronic and communication properties of inorganic materials with desirable photophysical properties. The essential features of a molecular device capable of performing electronic switching or logic functions are thought to comprise of a signaling moiety (fluorophore), a spacer group and a guest-binding site (receptor); useful in electro- and photochromatic, OLEDs, and photovoltaic and solar cell materials. Efforts to synthesize, functionalize, and use organic light-emitting (OLED, phototransistors, photovoltaic cells, and organic field-effect transistors<sup>1</sup>) in electrical circuitry is driven by the potential to replace inorganic semiconductors with organic counterparts thereby decreasing manufacturing costs and allow fabrication of devices over large areas or on lightweight, flexible substrates. The excellent hole (cation) transport properties of many organic semiconductors make them suitable for photovoltaic devices and for solar cell and OLED devices applications providing less expensive and less power, light weight and flexible alternatives to traditional silicon-based devices.<sup>2</sup>

In this research project, organic ligand compounds were synthesized and characterized containing a signaling moiety (donor group), a molecular switching component, a spacer group and a guest-binding site (acceptor group). Donor, bridging, and acceptor groups (D-B-A) were constructed consist of phenylenevinylene, fluorene, and perylene bis-(dicarboximide), and rhodamine components. A family of these molecular scaffolds were fabricated containing the 8-hydroxyquinolate chelating group which would later be used to chelate metal ions (e.g. – Zn<sup>2+</sup>, Al<sup>3+</sup>, Ga<sup>3+</sup>, Ni<sup>2+</sup>).

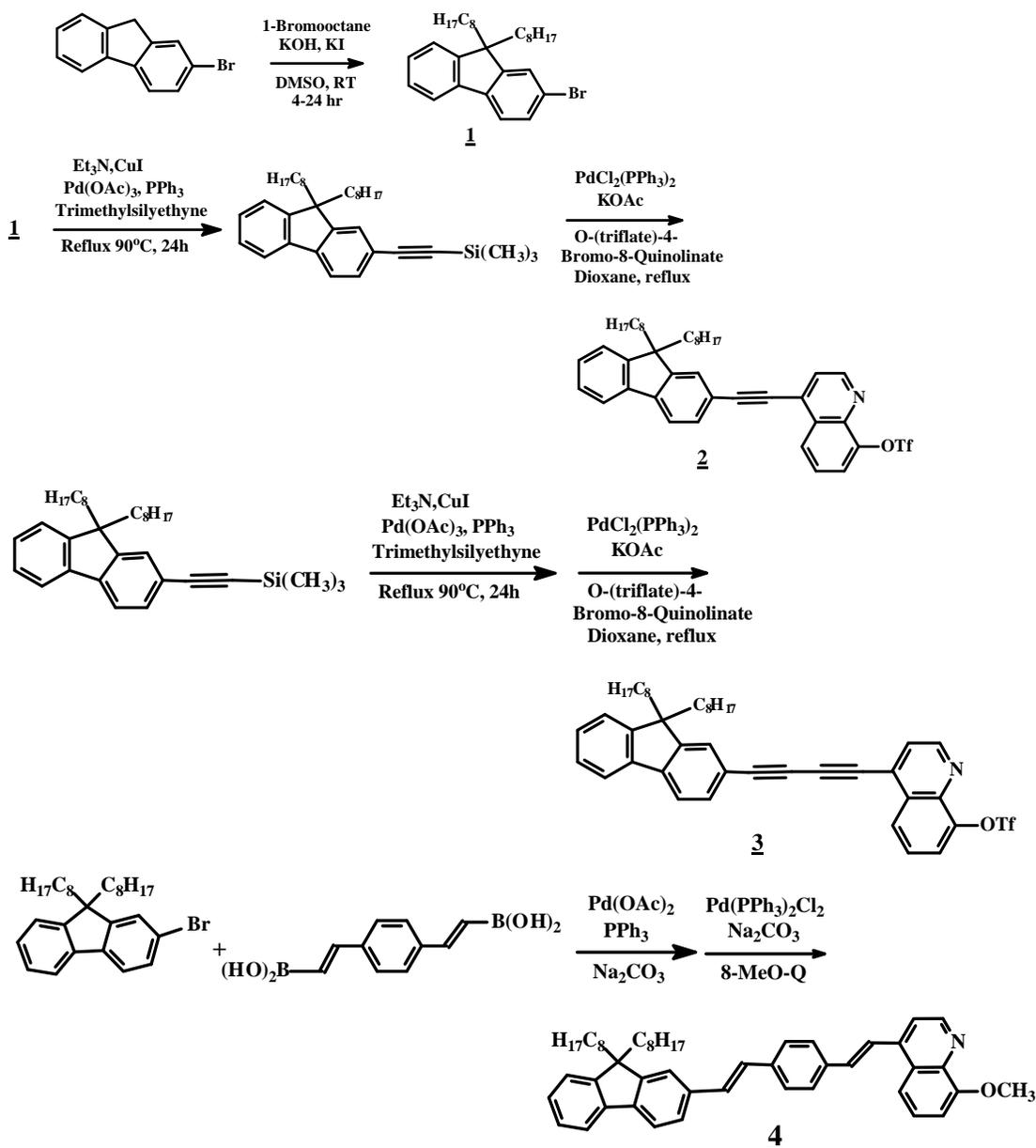
Fluorene adducts have been used from materials with interesting luminescent properties. The emission spectra of organic polymer blends of thiophene and diarylfluorene units were found to be controlled by varying the chain length of thiophene core.<sup>3</sup> Similarly, fluorene units have been appended to emissive platinum compounds<sup>4</sup> and in polymers forming liquid crystal-like behavior.<sup>3</sup> Ethynyl-bridge compounds have also been shown to have desirable luminescence qualities for an efficient photophysical PET process in metal compounds.<sup>5-8</sup> Very recently, Wong<sup>61</sup> reviewed the development of rigid-rod metallopolyyne polymers of the late transition metals and showed that the luminescent and electronic properties can be tuned by proper manipulation of the S<sub>1</sub> (singlet) and T<sub>1</sub> (triplet state) energy gap.

The following report summarizes the work completed to synthesize and characterize a family of these ligand classes (phenylenevinylene, fluorene, and perylene bis-(dicarboximide),

and rhodamine) which will be used to chelate selected metal ions with desirable photophysical and electrooptical properties. Tremendous effort has been devoted to finding appropriate synthetic protocols and the optimization of synthetic conditions.

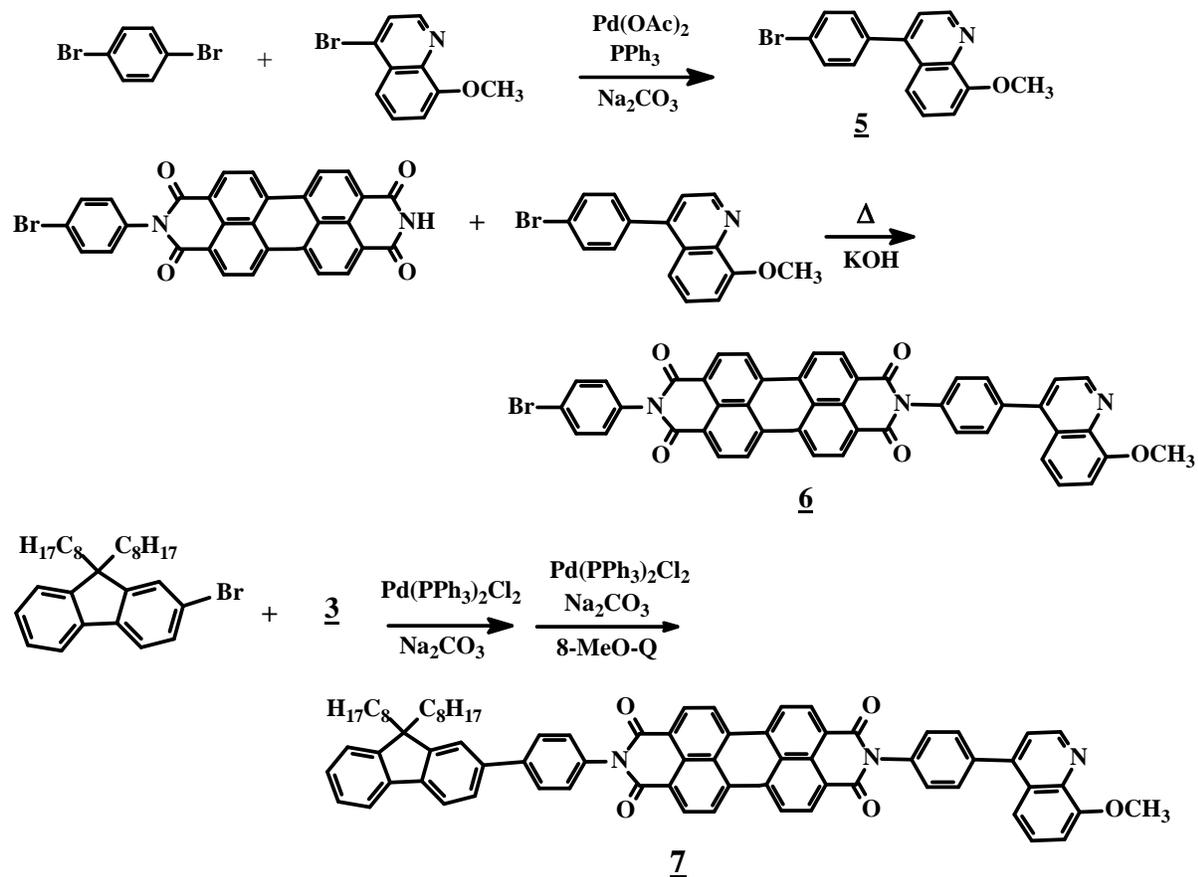
### Synthesis and Characterization of a Series of Fluorene-Based Ligands

The goal of this research project is to synthesize fluorene-based luminescent compounds. Recently, fluorene adducts have been used to form materials with interesting luminescent properties. Fluorene has several inherent qualities that make it a perfect candidate for the synthesis of novel light-emitting compounds. Taking advantage of the luminescent properties of fluorene, longer and more complex luminophores can be made that have longer lifespan and more efficient luminescence compared to current OLED luminophores. A great deal of effort was devoted to optimizing the synthesis of these fluorene-based ligands using modified conditions outlined by others.<sup>9,10</sup>



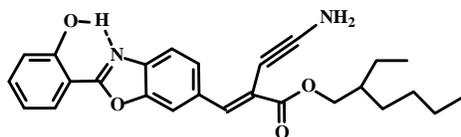
## Synthesis of Functionalized Perylene bis-(dicarboximide) Based Ligands

Perylene bis-(dicarboximides) represent an important class of compounds to investigate due to their fluorescent and electrochemical properties.<sup>11</sup>



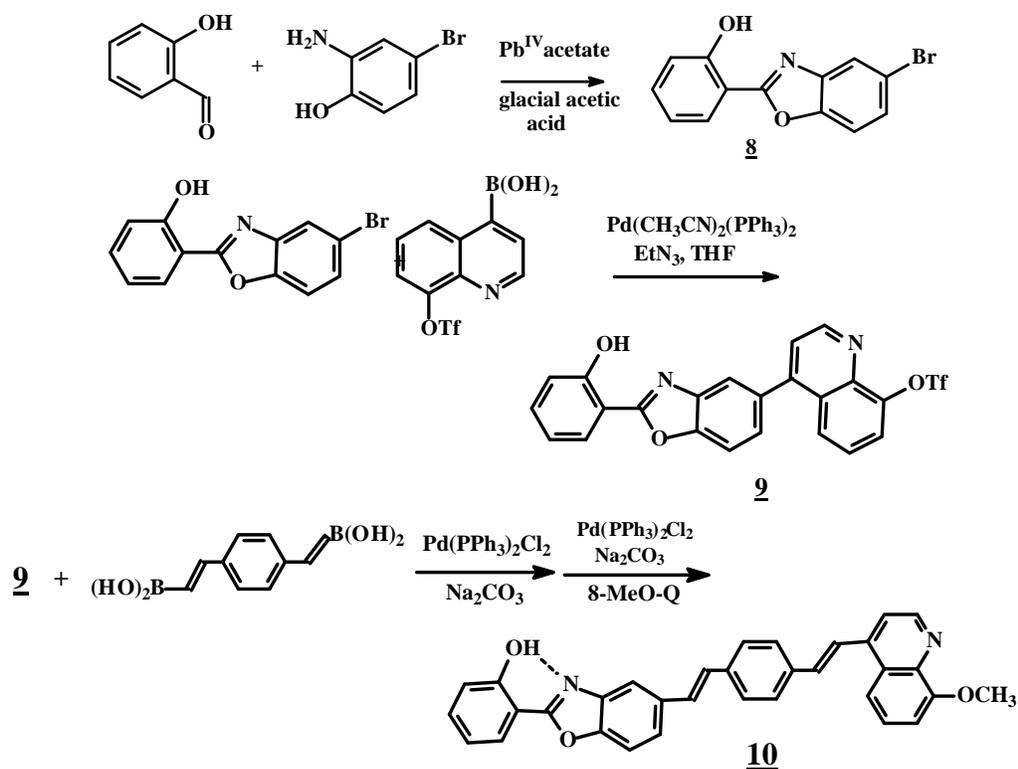
## Synthesis of Substituted Benzoxazole Ligand for Electrooptical Compounds

Recently, Park et. als.,<sup>12</sup> reported that the following substituted benzoxazole undergoes an intramolecular hydrogen bond between the enol and keto form.



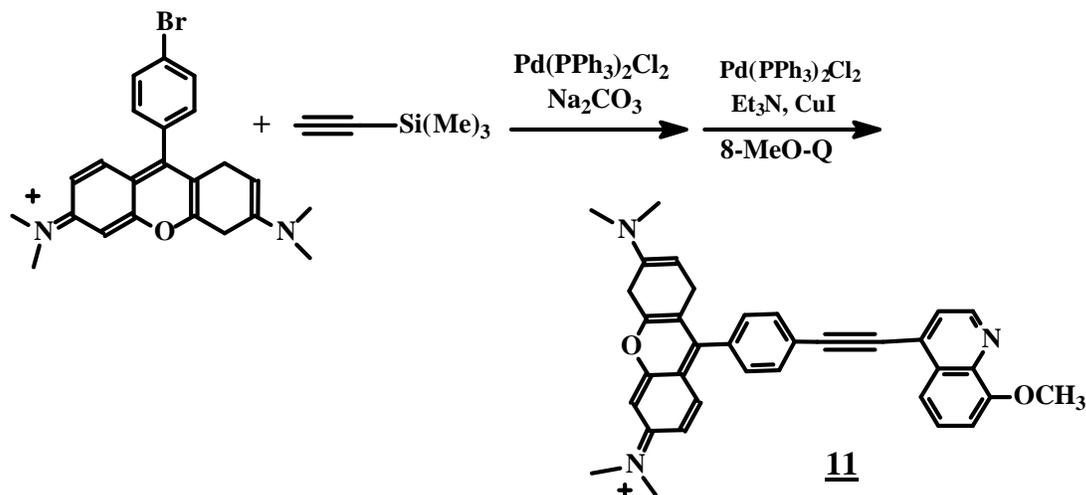
The keto form shows a substantially large red solvatochromic shift in emission spectrum and was thought to be due to enhanced charge transfer interaction with a conjugative electron acceptor in the keto tautomer. A family of molecules will be studied utilizing different bridges and placement of the proposed switch. These families will be fully characterized and their effects on the fluorescence process will be reported.

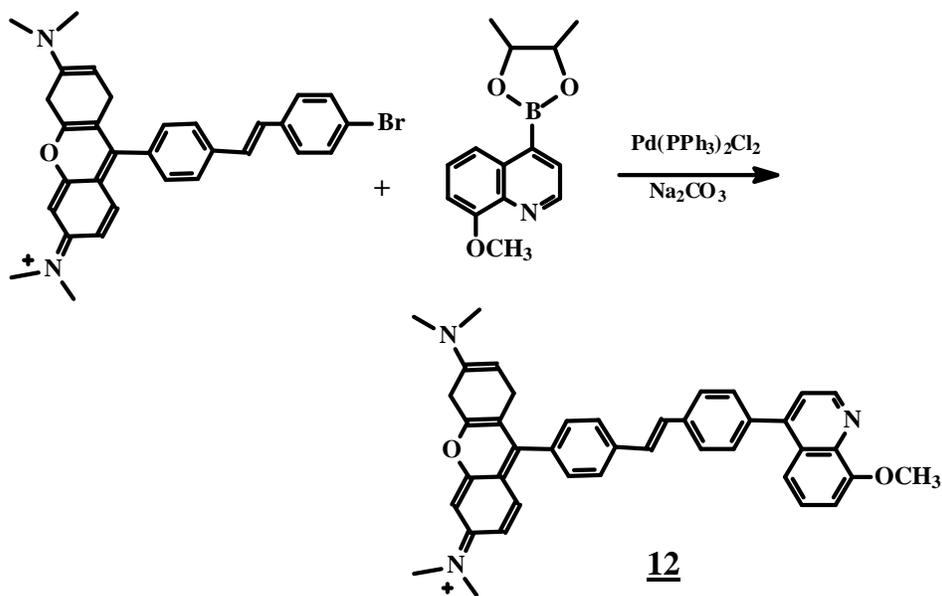
We have synthesized the 2-(2'-hydroxyphenyl)benzoxazole moiety (**8**) and appended this fluorescent moiety to the 8-Q ligand (**9**). Similarly, 1,4-divinylbenzene moiety was used to connect the substituted-benzoxazole adduct to the 8-quinolinolate ligand (**10**). The synthesis of these ligand-based fluorophoric compounds are shown below.



### Synthesis of 8-Q Bridged-Rhodamine Ligands

Following the synthetic protocol outlined by Burgess et. als.,<sup>13</sup> a convenient method was described and used to create a bromo-substituted rhodamine derivatives. Although, the purification of this compound proved to be difficult, we were able to obtain <sup>1</sup>H NMR and LC-MS data to support it's structure. This compound was recently coupled to a bridging (divinylbenzene and ethynyl) and to our target ligand. In this project, we will use these results and synthesize a family of these compounds that also incorporate photooptical and electrooptical switch components (azobenzene, bisthiénylene and spiropyran) into these molecular scaffold components. Synthetic work that has been accomplished is outlined below.

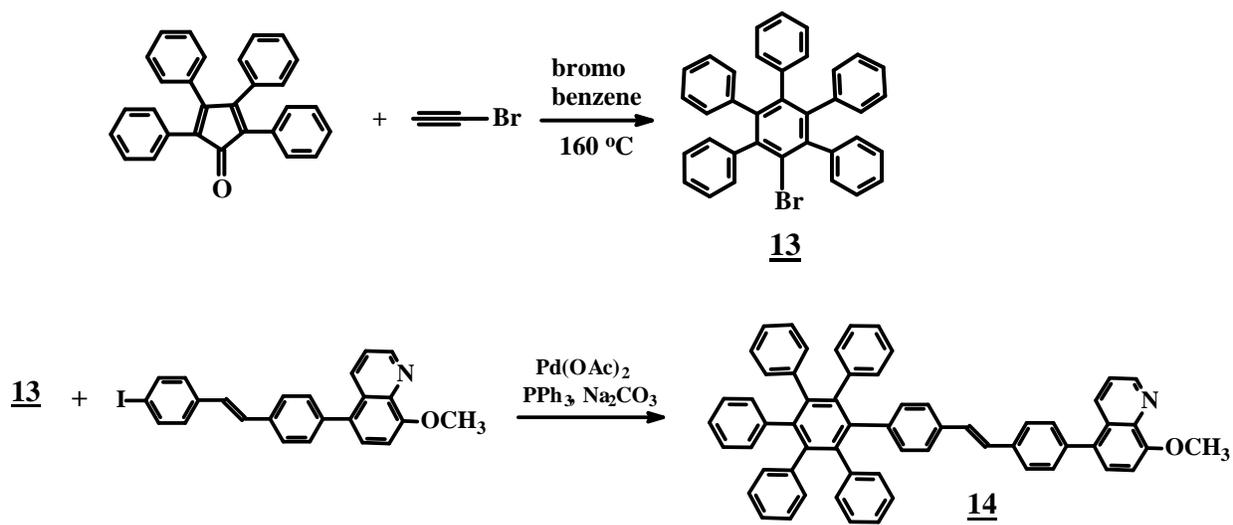


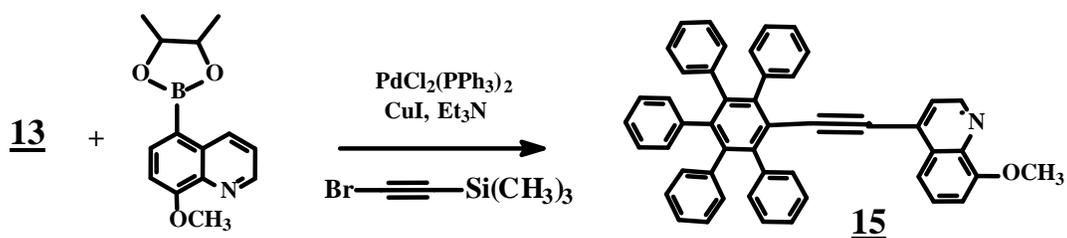


Results from the above synthetic work will be published in peer-reviewed journals after deprotection of the methoxy group, chelation to metal ions (i.e.-  $\text{Al}^{3+}$ ,  $\text{Ga}^{3+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Zn}^{2+}$ ) and the metal chelates are characterized (NMR, IR, UV-visible, fluorescence). We also plan to investigate the electrochemical luminescent properties of these inorganic compounds by spin-coating these onto indium tin oxide (ITO) substrates in an EL cell arrangement and analyze the luminescence and voltage response characteristics of our molecular devices.

### Synthesis of a Polyphenyl Cyclopentadiene Bridged Ligand

Recently, Eisenburg<sup>5</sup> and Chen<sup>14</sup> independently synthesized a tunable fluorophore appended to a organic scaffold molecules grafted to a terpyridyl ligand chelated to a Pt(II) metal center. We have attempted to synthesize a related fluorophore that can be appended to our ligand system. The pentaphenyl-benzene fluorophore core (shown below) is an attractive alternative to the naphthalene fluorophore that red shifts the emission spectrum.





After repeated attempts to optimize the synthetic procedures, product yields and to characterize these compounds (products **14** and **15**) were obtained in very low yields and proved to be difficult to purify. Attempts to continue the fabrication of this ligand were abandoned.

### Student Participation

This project secured the necessary funding for students to work on research projects on materials that are pertinent to a variety of military applications (i.e., Department of Defense). The goal of undergraduate research experience at our institution is to improve the academic preparedness of students and to instill in them the knowledge and skills needed to succeed in advance graduate programs and in the workplace. Over the course of three years, undergraduate students in chemistry and physics designed and studied new and unique materials that have desirable electronic and optical properties. These new materials were constructed from molecular building blocks with unique electrooptical properties for advance devices, electrochromatic materials, light-emitting diodes (LEDs), and photovoltaic and solar cells applications.

This project will secure funding to establish research pertinent to areas of scientific interest to a variety of military applications (i.e., Department of Defense and the Army Research Office). The research conducted in this project was accomplished by undergraduate students since the chemistry and physics departments at New Jersey City University offer only B.S. and B.A. degrees in chemistry and physics. The goal of undergraduate research experience at New Jersey City University (NJCU) is to improve the academic preparedness of students and to instill in them the knowledge and skills needed to succeed in advance graduate programs. This research project gave students the opportunity to work closely with faculty mentors, assured the integration of research and education in the science curriculum and the cultivation of essential and advanced laboratory skills.

There is no better way to infuse these desirable departmental objectives than to create a vibrant undergraduate research environment. Students designed and studied new and unique materials on the atomic scale that have desirable electronic and optical properties. These new materials were constructed from molecular building blocks with unique electrooptical properties for advance devices used in molecular switches, electrochromatic materials, light-emitting diodes (LEDs), and photovoltaic and solar cells. Emphasis was placed on the design and fabrication of new materials with relevance and applications to the DOD mission.

Over the course of three years, students from NJCU and two area high schools (Union Hill and Dickinson High Schools) were supported and conducted research for this research project. Funds allocated for supporting student salaries were distributed amongst seven of the eleven NJCU students with the remaining four students contributing to a lesser extent through enrollment in a research course offered by the chemistry department.

## New Jersey City University Research Students

Akim Abdullahi, Katterin Colon, Adrienne Conklin, Luisa Martinez-Troncoso, Luis Rodriguez, Adolfo Pertuz, Tom Comey, Shirley Iglesias, Irene Ng, Anne Lezama, Faraz Siddique, Ankita Patel, Alexis Dennis

These students presented their research work at numerous national, regional and area conferences and meetings. In addition, Kenneth Yamaguchi (P.I.) has presented research based on this research project at three national American Chemical Society meetings and conferences and much of this work is currently being prepared and written up for publication.

Pertuz, A.R. and Yamaguchi, K., 2010. "Synthesis of a Pentaphenyl Benzene Bridging Ligand." 41<sup>st</sup> MARM Meeting, Wilmington, DE.

Comey, T.J., Lezama, A., and Yamaguchi, K., 2010. "Synthesis and Characterization of Molecular Switch-Containing Organic Bridging Compounds and Their Effects on the Fluorescence Process." 41<sup>st</sup> MARM Meeting, Wilmington, DE.

Martinez, L., Iglesias, S. and Yamaguchi, K. 2010, Synthesis and Characterization of a Series of Fluorene-Based Ligands. National Amer. Chemical Society Conference, San Francisco, CA.

Conklin, A., Ng, I., and Yamaguchi, K. 2010, Synthesis of Halogen-Substituted Diazonium Moieties as Electron Transfer Bridging Units. National Amer. Chemical Society Conference, San Francisco, CA.

Comey, T., Lezama, A., and Yamaguchi, K. 2010, Synthesis and Characterization of Bridged Ligand Systems and Their Effect on the Fluorescence Process. National Amer. Chemical Society Conference, San Francisco, CA.

Rodriguez, L., Dennis, A. and Yamaguchi, K, Synthesis of a Fluorophore-bridged Polyphenyl Ligand. 2009 NANO-DDS Conference, Ft. Lauderdale, FL

Troncoso, L., Iglesias, S., and Yamaguchi, K. Synthesis of Fluorene-bridged Ligands, 2009 NANO-DDS Conference, Ft. Lauderdale, FL

Rodriguez, L Dennis, A., and Yamaguchi, K, 2009, Synthesis of a Fluorophore-bridged Polyphenyl Ligand. Intercollegiate Student Chemists Convention, Elizabethtown, PA.

Conklin, A., Ng, I., and Yamaguchi, K., 2009, Synthesis of a Series of Fluorophoric 2-substituted Rhodamine Ligands. Intercollegiate Student Chemists Convention, Elizabethtown, PA.

Rodriguez, L., and Yamaguchi, K, 2009, Synthesis of a Fluorophore-bridged Polyphenyl Ligand. National Amer. Chemical Society Conference, Washington, DC

Conklin, A. and Yamaguchi, K., 2009, Synthesis of a Series of Fluorophoric 2-substituted Rhodamine Ligands. National Amer. Chemical Society Conference, Washington, DC

Although the four high school students list below were not monetarily supported from this research project they were supported from other funding made available through the Project SEED program and the Liberty Science Center (Jersey City). These high school students completed work on this project and presented their work at regional competitions and national conferences.

Union Hill High School (Union City, NJ)

Rebeca Saborit, Stephanie Cornejo, Caroline Tajeda,

Dickinson High School (Jersey City, NJ)

Vipin Tyagi, Beth Sheil and Joseph Katigbak

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