





## Report Title

Final Report: The Development and Study of Molecular Electronic Switches and their Field-Effect Transistor (FET) Device Properties

### ABSTRACT

The fabrication of molecular electronic devices from inorganic and organic compounds is being actively pursued. In this research project, inorganic compounds will be synthesized 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) will consist of fluorene, and perylene and naphthalene bis(dicarboximide) components. Photochromic switching compounds comprising bisthiénylene, azobenzene, fulgimide, and spirocyan will also be used to fabricate materials that have interesting properties as photovoltaic or materials suitable in field-effect transistor (FET).

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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)**

<u>Received</u>	<u>Paper</u>
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**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)**

<u>Received</u>	<u>Paper</u>
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**TOTAL:**

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

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**(c) Presentations**

Number of Presentations: 3.00

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

Received      Paper

**TOTAL:**

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

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

Received      Paper

**TOTAL:**

Number of 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      Book

**TOTAL:**

Received      Book Chapter

**TOTAL:**

**Patents Submitted**

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**Patents Awarded**

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**Awards**

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**Graduate Students**

NAME

PERCENT SUPPORTED

**FTE Equivalent:**

**Total Number:**

**Names of Post Doctorates**

NAME

PERCENT SUPPORTED

**FTE Equivalent:**

**Total Number:**

### Names of Faculty Supported

<u>NAME</u>	<u>PERCENT SUPPORTED</u>	National Academy Member
Kenneth Yamaguchi	0.00	
Bumjung Kim	0.00	
<b>FTE Equivalent:</b>	<b>0.00</b>	
<b>Total Number:</b>	<b>2</b>	

### Names of Under Graduate students supported

<u>NAME</u>	<u>PERCENT SUPPORTED</u>	Discipline
Kamran Namjouyan	0.00	
Efrain Orleans	0.00	
Joseph Bruno	0.00	
Shahzeen Javeed	0.00	
Victoria Tumminia	0.00	
<b>FTE Equivalent:</b>	<b>0.00</b>	
<b>Total Number:</b>	<b>5</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: ..... 0.00

The number of undergraduates funded by this agreement who graduated during this period with a degree in science, mathematics, engineering, or technology fields:..... 0.00

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:..... 3.00

Number of graduating undergraduates who achieved a 3.5 GPA to 4.0 (4.0 max scale):..... 0.00

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

The number of undergraduates funded by your agreement who graduated during this period and will receive scholarships or fellowships for further studies in science, mathematics, engineering or technology fields:..... 0.00

### 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>	

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**Sub Contractors (DD882)**

**Inventions (DD882)**

**Scientific Progress**

**Technology Transfer**

See attachement

**Final Report**  
**Grant Period: 02/01/14-01/31/15**  
**Proposal Number: 64732-EL-REP**  
**Agreement Number: W911NF-14-1-0033**  
**Kenneth Yamaguchi (PI) and Bumjung Kim (CoPI)**  
**New Jersey City University**

In this research project, emphasis is placed on the synthesis of the organic ligands used in this project. Work was done on constructing ligand sets containing a signaling moiety (donor group), a molecular switching component, a spacer group and guest-binding site (acceptor group) was done. The bridging and switch components in this electronic device have been synthesized consisting of fluorene, and perylene bis(dicarboximide) components. Some of these have been coupled to a benzoxazole- and bithienylethene-bridged units. These photochromic switching compounds will be used to fabricate materials that function as photovoltaic or materials.

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 than 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.

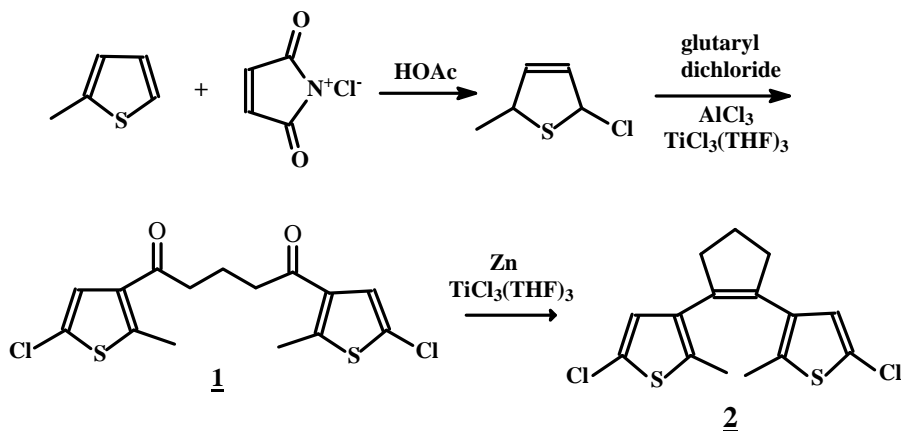
The goal of this research project is to synthesize fluorene- and perylene-based luminescent compounds. Recently, fluorene and perylene adducts have been used to form materials with interesting luminescent properties. Both fluorene and perylene systems have several inherent qualities that make it perfect candidates for the synthesis of novel light-emitting compounds. Taking advantage of the luminescent properties of both the fluorene and perylene systems, 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.

## **Fabrication of Switching Compounds**

### **Synthesis of Bithienylethene Switching Compound**

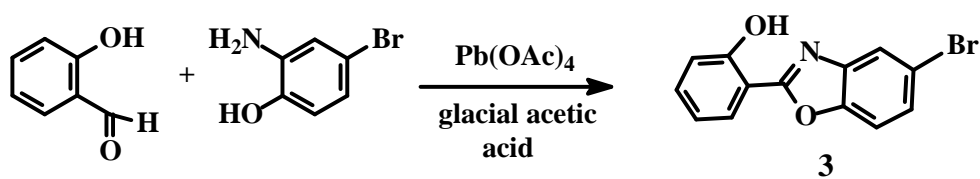
The design and fabrication of nanostructures can serve as building blocks for nano-optical systems, particularly novel electro-optical materials and devices that are of immense interest to the technology sectors. An area that is currently under intensive investigation focuses on the development of molecular systems capable of performing logic operations and consisting of multi-component light-emitting organic and metal-organic compounds.

The synthesis of the following compound is currently being attempted using standard synthetic protocols.<sup>1</sup>

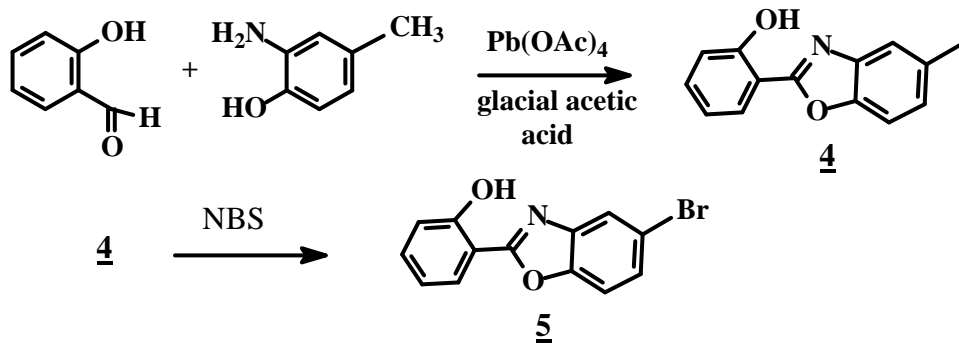


### Synthesis of the Substituted Benzoxazole Switching Compound

Recently, we have synthesized 2-(2'-hydroxyphenyl)benzoxazole following the method of Park et. al.<sup>2</sup> However, the synthesis of compound **3** was very difficult and resulted in a multitude of by products along with the target compound. We are currently purifying this compound.

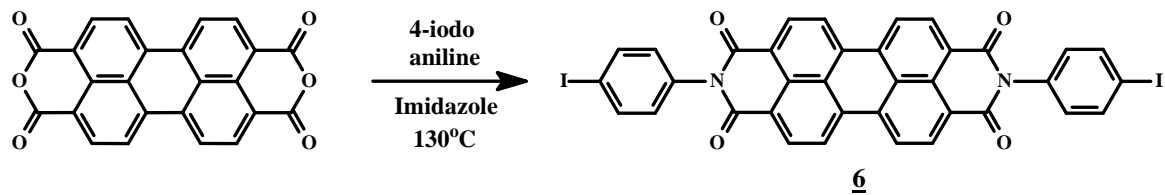


Additionally, synthetic work on the useful switch compound shown below is currently being done and the purification of the target compound is being assessed.



### Synthesis of the Symmetrical N-,N'-(4-Iodophenyl)-3,4,9,10-perylene tetracarboxylic Diimide

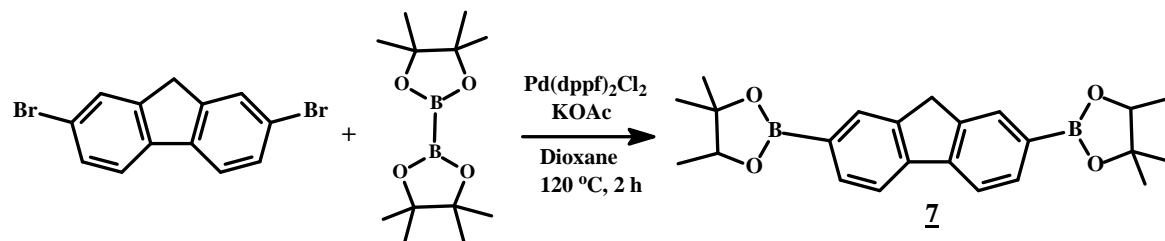
It is well known that perylene bisimides are a class of highly thermostable n-type semiconductors and have been used as building blocks for organic light-emitting diodes, light-harvesting arrays, and photovoltaic cells. We are currently synthesizing the iodo-substituted perylene diimide (**6**) that will be cross-coupled to the above switch compounds and the acceptor 8-hydroxyquinolate ligand.<sup>3</sup>



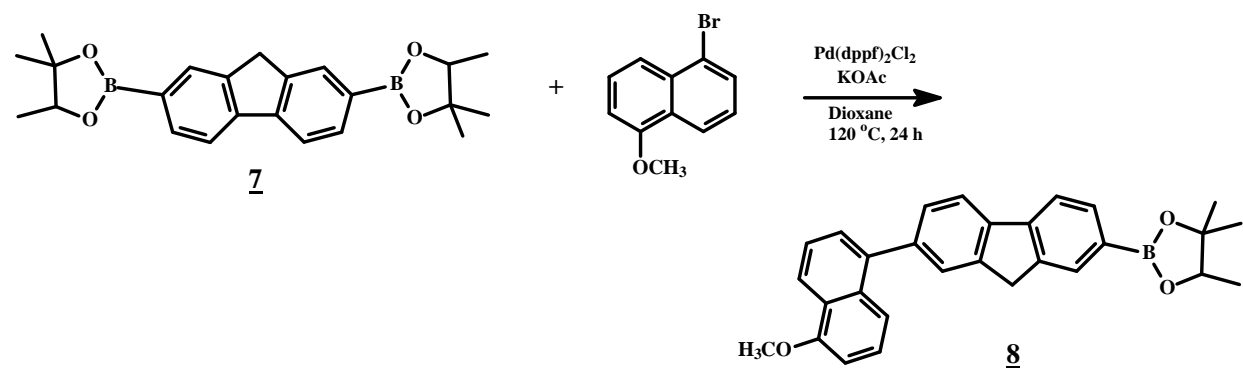
### Synthesis of the Bis-(1,7-pinocolato boronate) Fluorene Compound

One of the goal of this research is to synthesise and characterize a series of Fluorene based compounds and to determine the effects that different bridging groups as well as chemical switches may have in the luminescent properties of these molecules. The boronylated fluorene derivative was synthesized using standard procedures. This molecule has been shown to function as p-type dye-sensitized solar cell materials.<sup>4</sup> In light of this we have successfully synthesized a series of fluorene-based systems that have been coupled to the 8-methoxyquinoline chelating system shown below.

The boronylated fluorene molecule will be cross-coupled to the targeted ligand. However, the synthesis of this molecule by a standard procedure resulted in multiple decomposition products. The microwave synthesis of compound is currently being investigated in an attempt to improve the product yield.



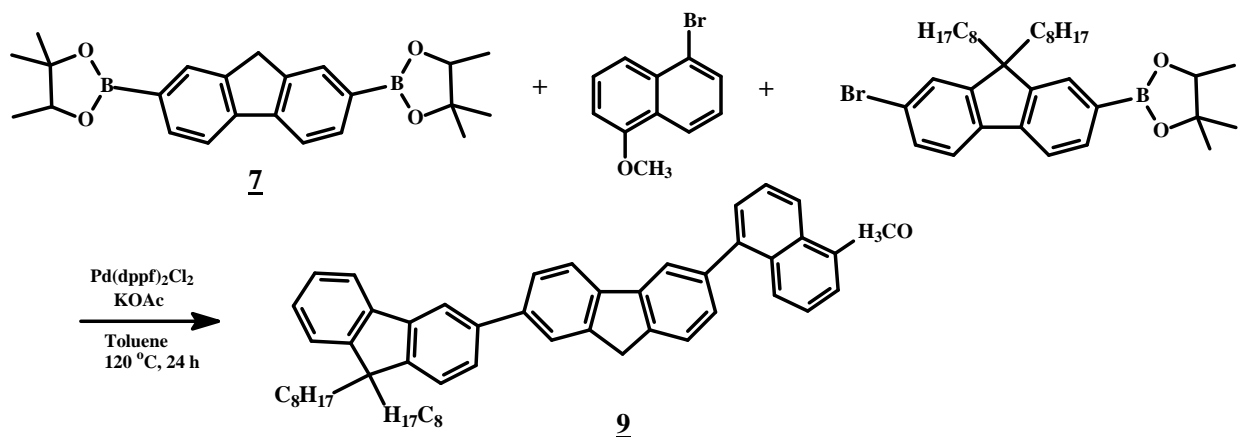
### Synthesis of 8-methoxy-4-[7-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9H-fluorene-2-yl]quinoline



### Synthesis of 8-methoxy-4-[2,7-di-9,9-dioctyl-fluorene]quinoline

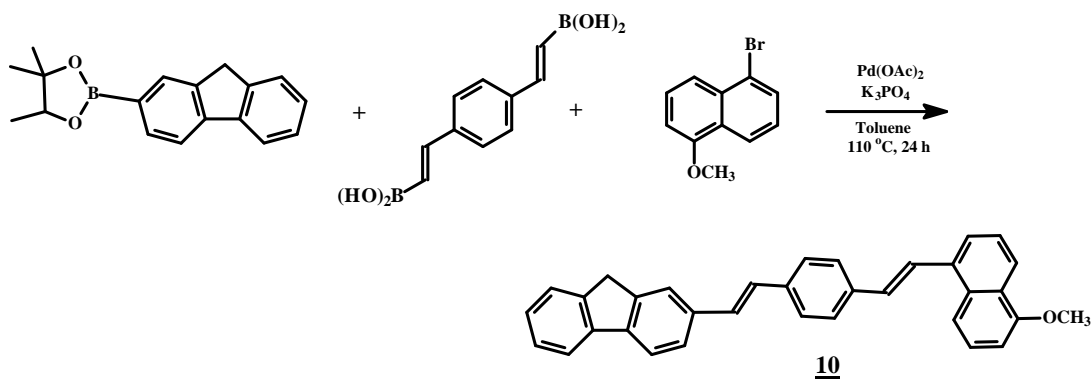
Recently, fluorene adducts have been used to form materials with interesting luminescent properties. Fluorene has several inherent qualities that make it a perfect candidate for the synthesis of novel light-emitting compounds. Taking advantage of the luminescent properties of fluorene, longer and more complex luminophores can be made that have longer lifespan and

more efficient luminescence compared to current OLED luminophores. Compound **9** was synthesized and its luminescent properties will be studied.



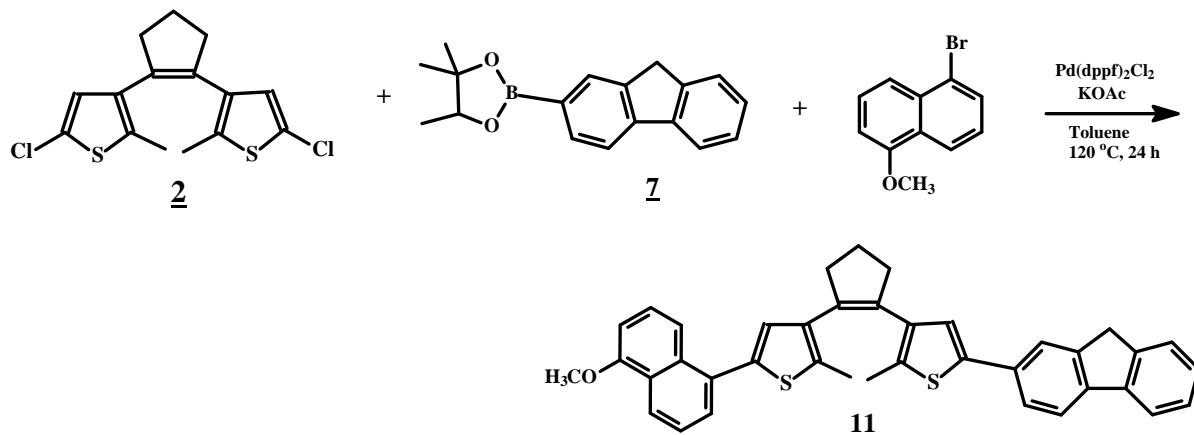
### Synthesis of 1,4-(2'-fluorene-4'-8-methoxyquinoline)stilbene

We have synthesized the 1,4-(2'-fluorene-4'-8-methoxyquinoline)stilbene system with the appended 8-Q ligand (**10**). The synthesis of this 8-methoxyquinoline ligand-based fluorophore is shown below.



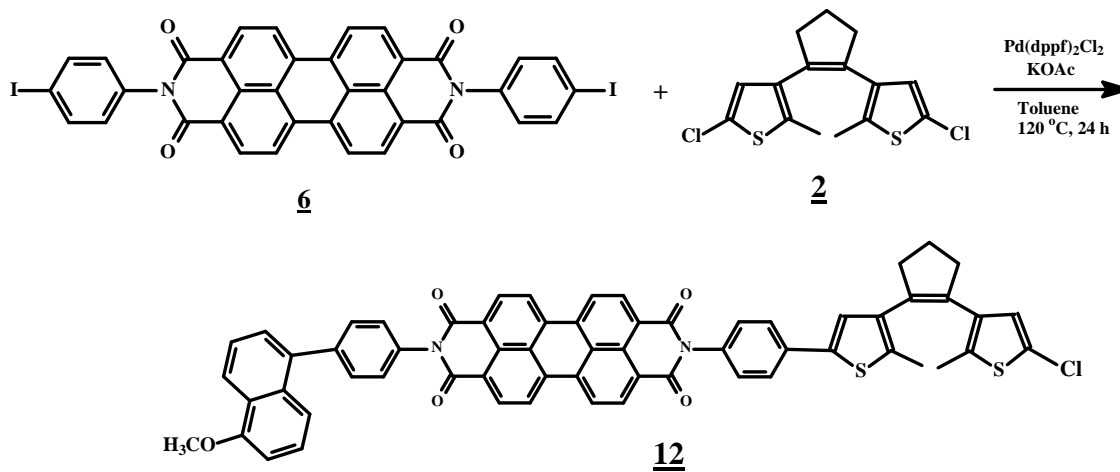
### Synthesis of 8-methoxy-4-[2,13-thienylethene-2-fluorene]quinolone Compound

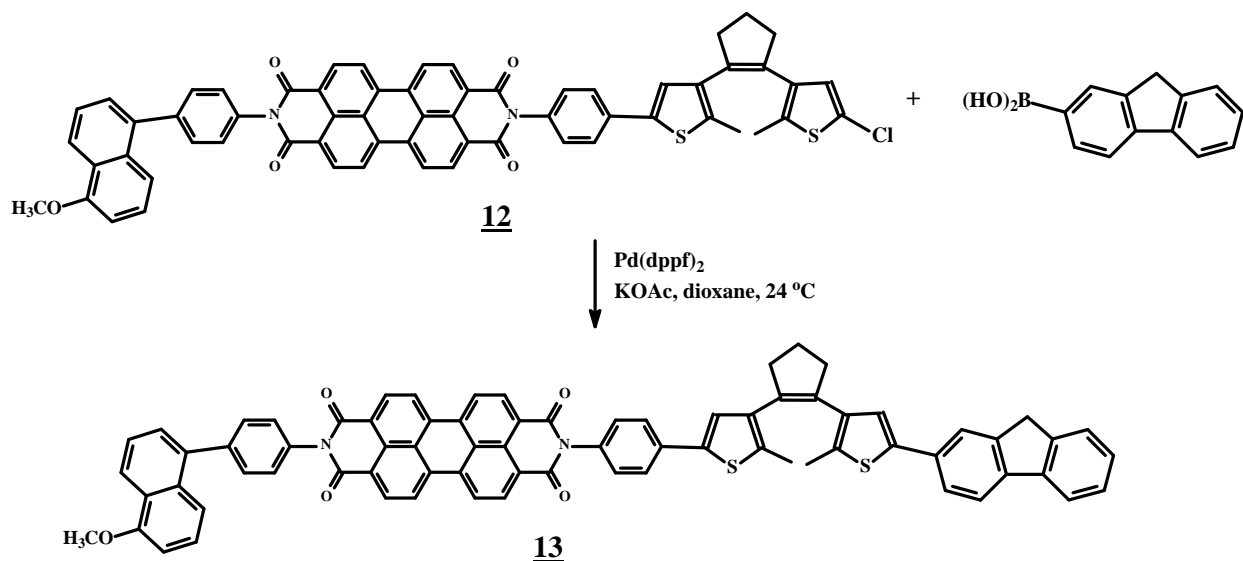
The bisthienylethene bridge is a high contrast fluorescent switch and data storage devices which are thermally irreversible and show high fatigue resistance.<sup>5-7</sup> We have successfully coupled the bisthienylethene switch to the fluorene building block and 8-hydroxyquinoline producing ligands which have rich electroactive and luminescent properties. We are currently working on the conditions needed to couple the bis-thienylethene switch with the perylene bis(dicarboximides) 8-hydroxyquinoline donor group discussed below.



### Synthesis of a Perylene-core Fluorene-bridged ligand

Perylene bis-(dicarboximides) represent an important class of compounds to investigate due to their fluorescent and electrochemical properties. The design of these nanostructures can serve as building blocks to form inorganic complexes that can be used to tune their luminescent and electrochemical properties. We are currently engaged in the synthesis of the perylene-bis-thienylethene-fluorene bridged system shown below. After initially obtaining low yields of compound **12**, it is clear that we need to optimize and find the synthetic conditions that will yield sufficient quantities of compound **12** to synthesize our target compound (**13**).





The bisthienylethene series of compounds represents promising materials that will be extensively studied for their photooptical and electrooptical properties for advance devices used in molecular switches, electro- and photochromatic materials, field-effect transistors (FETs), OLEDs, and photovoltaic and solar cells. We are currently investigating these materials in terms of their desirable absorption and emissive properties.

#### 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 grant period (February 2014 to January 2015), undergraduate students in chemistry and biology 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 biology departments at New Jersey City University offer only B.S. and B.A. degrees in chemistry and biology. 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 year, students from NJCU and two area high schools (Union City, Bayonne and St. Peters Prep 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

Shahzeen Javeed, Kamran Namjouyan, Efrain Orlean, Joseph Bruno, Victoria Tumminia

#### Summer High School Students

Rosabi Pena-Garcia and Claudia Mendoza (Academy for Enrichment and Enhancement, Union City, NJ)

Mena Hasballa (Bayonne High School)

David Bovich (St. Peters Prep. High School)

These students presented their research work national, regional and area conferences and meetings. In addition, Kenneth Yamaguchi (P.I.) has presented research based on this research project at a National American Chemical Society (Dallas, TX) and Biennial Conference on Chemical Education (Grand Rapids, MI) meetings and conferences.

#### References

1. L.N Lucas, J.J.D. de Jong, J.H. van Esch, R.M. Kellogg, B.L. Berringa. *Eur. J. Org. Chem.*, **2003**, 155-166.
2. J. Seo, S. Kim, S.Y. Park. *J. Amer. Chem. Soc.*, 126, **2004**, 11154-11155.
3. M.J. Robb, B. Newton, B.P. Fors, C.J. Hawker. *J. Org. Chem.*, 79, **2014**, 630-6365.
4. Z. Liu, et als. *ACS Appl. Mater. Interfaces*, 6(5), **2014**, 3448-3454.
5. L.N. Lucas, J.J. Jong, J.H. van Esch, R.M. Kellogg, H.L. Feringa, H.L. *Eur. J. Org. Chem.*, **2003**, 155-166.
6. B. Qin, R. Yao, X. Zhao, H. Tian. *Org. Biomol. Chem.*, 1, **2003**, 2187-2191.
7. L.N. Lucas, J.H. van Euch, R.M. Kellogg, B. Feringa. *Chem. Comm.*, **1998**, 2313-2314.