

## Project Title

Student name(s), major; Mentor name(s), department

### Research Question

Can a boronate-linked coordination polymer for the visible (i.e. colorimetric) and selective detection of benzene vapor be engineered?

### Project Objectives

1. To maximize the sensor response (i.e. color change) upon exposure to benzene by altering the molecular electronics of the synthetic building blocks that make up the coordination polymer.
2. To determine the mechanism by which color change occurs upon exposure of boronate ester coordination polymers to benzene (proposed to be a charge transfer event upon restructuring of the framework).

### Project Significance

The application of this boronate ester polymer toward sensing benzene provides a novel, organic solution to a problem that has historically been solved by analytical techniques, often requiring trained operators and expensive equipment. The proposed approach has advantages in that the polymer is highly selective for binding benzene, inexpensive and easy to synthesize, and has an easily interpreted response (i.e. colorimetric). A boronate ester sensor could be used to detect harmful concentrations of benzene in areas where such a risk is known to exist, such as petroleum fueling stations and refineries.

### Background/Previous Work

Benzene is a small, aromatic compound commonly associated with rubber production, synthetic chemical industries, and petroleum refinement and storage. It is a member of a group of volatile organic compounds (VOCs) which exist as vapors in the atmosphere under standard conditions. Benzene's volatility has caused concern for people who experience long-term exposure, as it has been linked to leukemia and other blood disorders.<sup>[1]</sup> For this reason, recent research has focused on developing efficient methods of benzene detection.<sup>[2][3]</sup> Most solutions so far have focused on adjusting preexisting complex and expensive analytical techniques.<sup>[2][4]</sup> However, one novel solution is a boronate ester coordination polymer that selectively uptakes benzene vapor from a matrix of other substances.<sup>[5]</sup>

Boronic acids have been used extensively in the synthesis of organic polymers, usually through dehydration reactions with diols. However, little work has exploited the empty p-orbital available on the boron atom of these polymers for assembly or sensing purposes. One report used a di-nitrogen linker to coordinate to boronate ester monomers, creating a novel polymeric system with intra-strand charge-transfer that cause a large color change between the reactants and products.<sup>[2]</sup> When the polymer disassembled, the color disappeared. Following this theme, the Lavigne group here at USC, synthesized a polymer using this same design to form a porous, crystalline polymer linking di-nitrogen monomers via dative bonds with boronic acids. This polymer was a bright yellow extended structure (a repeating "turret" pattern), and retained benzene, the solvent from synthesis, within its pores. The benzene could be removed from and reintroduced into the polymer's pores in a reproducible manner. This polymer was tested as a host for other molecules closely related to benzene (toluene, ethylbenzene, and xylenes), however none of these common solvents were taken up by the material, thus it was found to be selective for benzene.

The same synthesis repeated in toluene resulted in a completely different structure, verified by single-crystal x-ray diffraction. A macrocycle of two boronate monomers joined by two di-nitrogen linkers formed, and disordered toluene was retained in the pores. The macrocycle crystal was dark orange, but turned bright yellow (nearly identical to the polymer) when exposed to both liquid and gaseous benzene. Further testing by thermogravimetric analysis established that the toluene guest was completely replaced with benzene. The benzene-exposed macrocycle exhibited characteristics of the original polymer. These results describe a primitive optical sensor selective for benzene, however the color change from dark orange to bright yellow, while distinct, could be optimized for easier interpretation of sensor response. The mechanism by which the color change occurs likely relies on charge transfer, yet there is still uncertainty about if and how the structure could change from macrocycle to polymer, in the solid state, upon exposure to benzene vapor.

### Methodology

*Optimization of Color Change:* The colors of the polymer and macrocycles are thought to originate from an intra-strand charge-transfer similar to that observed by Severin.<sup>[5]</sup> I will use computer modeling to predict the HOMO-LUMO gap of our polymer, and therefore how intra-strand transfer could occur. Similar modeling will be used on the macrocycle system to predict how the charge-transfer occurs. Given that both the macrocycle and polymer contain the same building blocks, the orientation of these components must be important for color formation. The proposed

modeling will help provide insight into this pattern. With this basic knowledge, the polymer structure will be altered to maximize color change. Specifically, different length di-nitrogen linkers will be used to join boronate components. Additionally, substituents such as nitro and alkoxy groups, will be added to the building blocks to modify the electronic structure of each, thereby altering the HOMO-LUMO gap. Each new polymer will be tested for structure, binding selectivity, and optical response upon binding.

*Identification of Color Change Mechanism:* The color change of the macrocycle from dark orange to bright yellow is suspected to occur by a shift in crystal configuration from the macrocycle structure to the polymer structure upon benzene uptake. In order to confirm or reject this hypothesis, single-crystal x-ray diffraction (XRD) will be used to determine crystal structures. The macrocycle will first be synthesized and its structure confirmed by XRD. Previous attempts to obtain single-crystal data on the macrocycle exposed to benzene vapor have been unsuccessful. Instead, the powder x-ray diffraction (PXRD) pattern of the macrocycle exposed to benzene vapor will be compared to those of the polymer and macrocycle. Also, the macrocycle will be soaked in liquid benzene in an attempt to preserve crystallinity. After the color change from orange to yellow is complete, the crystals will again be analyzed by XRD to determine if any structure change occurred.

I will perform all of the synthesis and most of the characterization tests in this project. For tests (such as XRD and PXRD) that require special training, I will submit samples to be tested by personnel within the Chemistry Department. [mentor], graduate students in the laboratory, and other specialists within the chemistry research building will be available for discussions on proper techniques and guidance on research directions.

**Project Timeline** (Student will not be on-campus for the summer; work will resume in the fall)

Months (9 total)	Jan	Feb	Mar	Apr	Summer	Aug	Sep	Oct	Nov	Dec
Determine Color Change Mechanism										
Synthesis of New Polymers										
Benzene Uptake Tests										
Article/Presentation Preparation										

### Anticipated Results and Dissemination

By utilizing XRD and PXRD data, I expect to gather enough evidence to determine if the color change of the macrocycle during benzene uptake arises from a change in the solid state structure. If this hypothesis is rejected, I will explore different explanations for the observed color change, such as changes in the electronic structure of the macrocycle upon benzene binding. By changing the linker and adding substituents to the boronate ester monomers, I expect to obtain a greater difference in color between the macrocycle before and after benzene uptake. This part of the experiment is difficult to predict and will involve some trial and error methods, though computational techniques will help focus these efforts. Additionally, I will record trends in color changes with alterations to the polymer and correlate these trends with computer models and intra-strand charge transfer theory. The end product of this project is expected to be a selective benzene sensor that displays a significant color change upon exposure to benzene vapor.

In addition to a presentation at Discover USC, my results will be published in a journal, such as the Journal of the American Chemical Society or Angewandte Chemie. I will also travel to a National meeting of the American Chemical Society in Boston to present my research results.

### Personal Statement

I have worked on this project in [mentor]'s lab for the past two semesters and over the summer. In that time, I have put a great deal of time and effort into collecting most of the data we currently have on this polymer. I look forward to continuing this research and compiling an article that can be of value to the scientific community by furthering knowledge of polymeric materials and developing novel sensing methods. This project is of personal value because I plan to attend chemistry graduate school and pursue a career in organic chemistry or biochemistry after completing my undergraduate studies. Undergraduate research gives me a great advantage for these plans because I am gaining a basic understanding of laboratory methods and analytical techniques. I also have the opportunity to explore different fields of chemistry and determine which I would like to pursue in graduate school. By publishing a journal article and presenting research at a national conference, I will obtain discipline-specific material for graduate school applications and career resumes. I greatly enjoy my research, though as a junior double majoring in chemistry and biology, it is difficult to carry out research for academic credit, while being able to balance classes, research, and finances. A grant from the Magellan Scholar Program would allow me to continue my research while maintaining high academic standards in my classes.

## References

1. Frank, A.; Balk, S. Agency for Toxic Substances and Disease Registry. *Case Studies in Environmental Medicine: Benzene Toxicity*. Revised June 2000. <http://www.atsdr.cdc.gov/csem/benzene/index.html>. Accessed October 2009.
2. Silva, L.; Ferreira, F.; Rocha-Santos, T.; Duarte, A. Carbon nanotube field-effect transistor detector associated to gas chromatography for speciation of benzene, toluene, ethylbenzene, (*o*-, *m*- and *p*-)xylene. *J. Chromatogr.* **2009**, *1216*, 6517-6521.
3. Mirmohseni, A.; Abdollahi, H.; Rostamizadeh, K. Analysis of transient response of single quartz crystal nanobalance for determination of volatile organic compounds. *Sensors and Actuators.* **2007**, *121*, 365-371.
4. Regan, F.; Walsh, F.; Walsh, J. Development of plasticised PVC sensing films for the determination of BTEX compounds in aqueous samples. *Intern. J. Environ. Anal. Chem.* **2003**, *83*, 621-631.
5. Christinat, N.; Croisier, E.; Scopelliti, R.; Cascella, M.; Rothlisberger, U.; Sever, K. Formation of Boronate Ester Polymers with Efficient Intrastrand Charge-Transfer Transitions by Three-Component Reactions. *Eur. J. Inorg. Chem.* **2007**, *33*, 5177-5181.
6. Iwasawa, N.; Takahagi, H. Boronic Esters as a System for Crystallization-Induced Dynamic Self-Assembly Equipped with an "On-Off" Switch for Equilibration. *J. Am. Chem. Soc.* **2007**, *129*, 7754-7755.

## Magellan Scholar BUDGET FORM

Student's Name: \_\_\_\_\_

**Double-click on table to enter data**

Student salary	Hours <small>Enter the estimated number of hours student will work</small>	Rate <small>Enter the hourly wage</small>	Subtotal
<b>Taking classes</b>	300	8	\$2,400.00
<b>Not taking classes</b>			\$0.00
<b>Fringe: Student salary * student fringe rate<sup>1</sup></b>			
<b>Taking classes</b>	\$2,400.00	1.10%	\$26.40
<b>Not taking classes</b>	\$0.00	8.90%	\$0.00
<b>Materials/Supplies</b>	Enter sub-total from below:		\$200.00
<b>Travel</b>	Enter sub-total from below:		\$450.00
<b>TOTAL:</b>			<b>\$3,076.40</b>
<b>Amount requested for MGS award:</b>			<b>\$3,000.00</b>

### Budget Justification

**Student Salary:** Indicate estimated number of student work hours per week during academic year and summer and hourly rate.

The student will carry out research during the Spring and Fall semesters working 10 hours per week for 30 weeks at a rate for \$8.00 per hour.

**Materials/Supplies:** Indicate items, quantity, and estimated price

The supply money will be used towards the purchase of the necessary boronic acid building blocks (~\$100 per gram) to create the porous boronate coordination polymers. As these reagents are quite expensive, only a small portion of supplies money is requested from the Magellan Scholar grant, the majority of this expense will be covered from the mentor's existing NSF funding

**Travel:** Indicate location, purpose of travel, estimate itemized costs (transportation, lodging, registration, etc). Student will travel to the National Conference of the American Chemical Society in Boston, MA, being held August 22-26, YEAR. She will present her results at this meeting. The requested \$450 from the Magellan fund will be matched by the PI with funds from an existing NSF grant.

Projected costs:

- Airfare (roundtrip): \$350
- Lodging, 4 nights at \$150 per night: \$600
- Meals at \$32/day for 4 days: \$128
- TOTAL: \$1078**

Requesting \$450 from Magellan, along with \$450 from the PI's NSF grant. The student will seek necessary additional funds from the Department or pay the expenses out-of-pocket.