Dr. James Girard Summer Undergraduate Research Program
Faculty Mentor – Project Application

Due Date: *Friday, January 21st at 11:59pm*

Faculty Name: Daniel Kissel

Department: Chemistry

**Research Project Title:** Exploring Metal-Organic Frameworks that incorporate titanium for photocatalysis of water splitting

**Research Project Summary (Please provide an overview of your project -- this will be shared with students as a project description; maximum 500 words):**

Hydrogen gas is a popular source of green energy being considered as an alternative fuel in the transportation and shipping sectors because of its high energy density and facile storage capability. The major source of hydrogen production is currently by methane steam reforming, which is a process that creates hydrocarbons through combustion. Solar water electrolysis, however, is a greener way to produce hydrogen that utilizes energy from the sun to split water molecules and produce hydrogen gas. This type of process requires the use of a photoactive catalyst, which has proven difficult to develop on a cost-competitive industrial scale. Metal-Organic Frameworks (MOFs) are a type of coordination polymer that contain central metal atoms connected to each other using organic linkers in a crystal-like framework. Titanium-based MOFs, such as MIL-125(Ti) and NH₂-MIL-125(Ti), are particularly interesting because of their potential viability in commercial and industrial catalysis applications for fuel cells and as super capacitors. The synthetic procedure for these MOFs is simple, and the materials used are affordable, which further increases their attractiveness. An underexplored area of research for these MOFs, however, is photo reactivity and photo catalysis for water splitting reactions. Since the current research on water splitting photocatalysis for titanium MOFs is scarce, this project will explore photo-degradation of organic dyes using MIL-125(Ti) and NH₂-MIL-125(Ti). The results from this investigation will help determine if these MOFs could be used as potential cost-effective photo catalyst for solar water splitting.
Introduction and Background

**Broader Impacts:**

Energy production due to hydrocarbon sources (natural gas, petroleum and coal) accounted for 78.5% of the total energy produced in the United States in 2020 (Figure 1). Not only are these fossil fuels an unsustainable energy source, but they contribute to Climate Change as a strong producer of CO$_2$. Unfortunately, reliance on fossil fuels for energy has been higher than ever this past decade. As the impacts of climate change affect our society more and more, an urgent need has developed to implement effective green energy sources that reduce CO$_2$ emissions. One solution gaining in popularity uses hydrogen gas (H$_2$) to power hydrogen fuel cells that drive automobiles, shipping trucks and power generators. This process combusts hydrogen gas, a form of storable energy, with oxygen from air to generate power according to reaction (1) shown below.

$$2H_2 (g) + O_2 (g) \rightarrow 2H_2O (l) \quad \Delta H^\circ_c = -571.7 \text{ kJ/mol} \quad (1)$$

**U.S. primary energy consumption by energy source, 2020**

A major benefit of using hydrogen in a fuel cell is that the only byproduct created is water, H$_2$O, and no dangerous greenhouse gases are produced. In addition, the amount of energy created per kg of fuel is the highest for any form of storable energy [2]. Despite all of its benefits, the inability to produce hydrogen gas on a large scale using green processes has hampered its implementation in our energy economy. Most hydrogen gas is currently produced from steam methane reforming, which is a process that reacts methane with water vapor to produce hydrogen. Unfortunately, this reaction also gives off substantial amounts of CO$_2$ thereby eliminating the green benefits of hydrogen as a fuel source.

In order to create greener processing technologies that eliminate fossil fuel dependency in hydrogen production, there is currently a great deal of research focused on using solar energy to power water electrolysis. Solar water electrolysis, in particular, is an attractive green energy solution because it converts energy from the sun into storable chemical energy. This introduces a valuable storage capability that photovoltaics currently do not offer. Current solar-powered water electrolyzers, however, suffer from low Solar To Hydrogen (STH) efficiency and rely on...
expensive semiconductors or metal oxides that readily corrode in solution. An ideal photocatalytic material for this type of application would be one that is semiconductive with a band gap tuned specifically for the Hydrogen Evolution Reaction (HER) and Oxygen Evolution Reaction (OER). Reactions (2) and (3) below show the OER and HER in acidic solution, which indicate there is a 1.23 eV energy requirement that must be met to start the OER. A material with a band gap of approximately 2.0 eV would therefore be ideal for solar water electrolysis in order to drive the OER with the appropriate amount of overpotential to account for Ohmic loses [3-6].

\[
\text{OER: } 4h^+ + 2H_2O (l) \rightarrow 4H^+ (aq) + O_2 (g) + 4e^- \quad E = 1.23 \text{ eV} \tag{2}
\]
\[
\text{HER: } 4H^+ (aq) + 4e^- \rightarrow 2H_2 (g) \quad E = 0.00 \text{ eV} \tag{3}
\]

Specific Aims

The research being proposed herein will explore the use of titanium-based Metal-Organic Frameworks (MOF) as a potential photocatalyst for solar water electrolysis. MOFs offer unique potential in photocatalysis because of their extraordinarily high surface areas, which allows for more catalytic active sites per unit mass. The titanium MOFs MIL-125(Ti) and NH$_2$-MIL-125(Ti) will be used in this project due to their relatively inexpensive material cost and semiconducting nature. MIL-125(Ti) has been shown to undergo photo catalysis in UV light. The NH$_2$-MIL-125(Ti), which is essentially the same MOF with an amine group attached to the benzene ring of the organic linker, could undergo photo catalysis in the visible spectrum by photo sensitization of the amine group. In order to achieve the aims of this project, this research will explore the photocatalytic degradation of organic dyes in the presence of both MIL-125(Ti) and NH$_2$-MIL-125(Ti) to determine if their opto-electronic properties are useful for aqueous photo catalysis similar to that performed in solar water electrolysis.

Proposed Research Plan

Preliminary Results

My initial investigations in this area involved functionalization of the MOFs UiO-66 and UiO-66-NH$_2$ with the emeraldine form of polyaniline (PANI), an organic polymer, as well as investigating cerium substitutions at the zirconium nodes of UiO MOFs to facilitate ligand-to-metal charge transfer (LMCT) transitions. The LMCT events effectively extended exciton lifetimes allowing for the hole created from photoexcitation to react with water according to the OER shown in reaction (2), however, this created higher material costs and issues related to long-term stability.[7-8]

Titanium based MOFs represent only a small minority of all the types of MOFs currently being researched. These MOFs, however, are unique in that they offer three beneficial qualities:

1. they have good photo responsive properties (essential for photo catalysis)
2. they are durable and therefore ideal for industrial application, and
3. they have low toxicity.¹

The two most common titanium MOFs used in photo chemical research are MIL-125(Ti) and NH$_2$-MIL-125(Ti), which are shown in Figure 2 below. While investigations into these MOFs have focused on their photo-electric properties as solid-state semiconducting materials, their use as
aqueous catalysts is under-explored. It is therefore an attractive MOF to investigate for solar water electrolysis considering all the potential benefits.

![Figure 2. Topology of MIL-125(Ti) and NH2-MIL-125(Ti).](image)

**Experimental Design and Methodology**

**Syntheses of MIL-125(Ti)**

This MOF will be synthesized using 3.53-g terephthalic acid, 56-mL DMF, 14-mL methanol, and 4.2-mL titanium isopropoxide. First, the terephthalic acid is mixed with the DMF in a round bottomed flask and heated to 105°C to remove any water. Then methanol is added to the mixture and a reflux is set up while the mixture is stirring for 72 hours at 100 °C. When the reaction is finished, the powder that results will be filtered from the solution. The powder then must be washed with DMF at 155°C and with methanol at 100°C for 24 hours each. Lastly, the product can be dried at 100°C in air, and then stored in a vial.

**Synthesis of NH2-MIL-125(Ti)**

The process of synthesizing NH2-MIL-125(Ti) uses 6-mmol of 2-aminoterephthalic acid, 25-mL DMF, 3-mmol of titanium isopropoxide and 25-mL of methanol. All of these materials are added into a solution in the following order; DMF, 2-aminoterephthalic acid, titanium isopropoxide and methanol. After each ingredient is added the mixture shall be stirred until it is homogenous. After stirring for an additional 30 minutes, the mixture will be placed in a bomb and heated in an oven at 150°C for 16 hours. The product will be recovered by the process of centrifuging at 5000-rpm for 5-minutes. The product will then be washed in DMF and then methanol three times for 30-minutes each wash. The product will be recovered using the centrifuge again and then dried overnight at 60°C.

The chemo-physical properties of these materials will be investigated through comparison of surface area, pore volume, thermal stability and chemical stability of each material. The photocatalytic properties will be investigated using an aqueous solution of Rhodamine B (RhB) dye, an organic dye capable of photodegradation. The degradation of (RhB) in solution will be monitored over time while irradiating visible light after the MOF’s have reached adsorption equilibrium. The RhB dye will initially adsorb into the pores of the MOF creating a drop in the absorbance of the RhB solution, however, this decrease is due to physical adsorption and not photo degradation. To determine the rate of photocatalytic degradation, each material’s physical adsorption properties will be thoroughly investigated so the time required for physical absorption can be satisfied before performing photo catalysis. A schematic showing physical dye adsorption...
and decreases in RhB absorbance during physical adsorption and photo degradation is shown in Figure 3.

![Figure 3: Physical adsorption of dye (left) and results showing how RhB solution absorbance drops during physical adsorption and photo degradation.](image)

**Instrumentation**

The characterization of each material will be accomplished using a number of different techniques. Attenuated Total Reflectance Infrared Spectroscopy (ATR-IR) using the IR spectrometer located in the organic chemistry laboratory at Lewis, which is accessible to all students, will be used for characterization along with imaging. Scanning Electron Microscopy (SEM) with Energy Dispersive Spectroscopy (EDS) will be utilized with atomic force microscopy to monitor surface modifications throughout the DSSC construction. This instrumentation is also available at Lewis. Powder X-ray Diffraction (PXRD) analysis will also be run for characterization of each MOF by Dr. Eirin Sullivan from the University of North Florida (UNF), who I have a long-standing collaboration with. The surface area and pore volume of each material will be determined from multipoint Brunauer-Emmet-Teller (BET) isotherms using nitrogen gas on a NOVATouch surface area analyzer. This instrument is housed in my research laboratory at Lewis and will be totally accessible for undergraduate students over the summer.

The photocatalytic properties will be determined using the organic dye Rhodamine B (RhB) as a marker for photocatalytic activity in aqueous solution. RhB will readily photodegrade in the presence of a photocatalyst and its degradation can be tracked spectroscopically by monitoring the decrease in absorption at 554 nm wavelength over time. The rate of photodegradation of RhB will be determined for each material using a photoreactor equipped with a xenon lamp and Persee UV-Vis spectrometer that are available in my research laboratory. Each modified MOF material will be suspended in RhB solution held at pH = 4.00 using an acetate buffer to create a heterogeneous mixture, then irradiated with visible light from the xenon lamp in the photoreactor. Aliquots of the suspension will be analyzed at specific time intervals by measuring the absorption of RhB after centrifuging the aliquot to remove catalyst particles from solution. The general setup for this experiment is shown in Figure 4 below.
Expected Outcomes

I fully expect an undergraduate student to be capable of synthesizing and characterizing each MOF without difficulty, as both these MOFs have previously been synthesized by undergraduate students working in my research lab for other applications. Ultimately, the viability of each materials as an effective photocatalysts for solar water electrolysis will be determined by their performance in the RhB photodegradation study. The relative rates of photodegradation of RhB determined from these experiments will be used to assess which material performs as the best photocatalyst.

Mentorship Plan

I will require my SURE student to work in the lab 8 hours a day 4 days a week to complete at least 30 hours of work each week. This research requires me to work with the student in the laboratory in order to effectively train them and monitor their progress, so putting in the necessary time in the lab is critical to the success of the project and mentorship of the student. In addition to training the student in solid state materials chemistry synthesis and experimental techniques, I will also be working with the student on developing professional skills and improving their communication through writing and speaking. The student will partake in weekly research meetings with my entire summer research group where they will collaborate with other experienced researcher and report their findings. The student will work with me and other members of the group to write technical reports and give scientific presentations throughout the summer to update their progress.

Proposed Timeline

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<th>Week 1-2</th>
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References (not included in the 6 page limit)


Description of any additional Funding you will be using for your proposed research (Doherty Grant, Lasallian Research Grant, External Research Grant, etc.) and how they will be used in this project.

I will be using my own internal funding for this project

Criteria for Student Applicants (Please report minimum criteria you will expect from student applicants, such as coursework that must be completed prior to starting work on this project):

**Requirements:** Students should have taken General Physics 1 and General Chemistry 1 and 2

**Desired:** Students have taken General Physics 2 and Introduction to Solid-State Chemistry
As a faculty mentor, you will be required to participate as a leader for one of the weekly student workshops. This will be a 60-minute at 9:00 am. Please indicate topics of interest from the themes listed below, or suggest an additional topic, that you might enjoy presenting.

_____ Ethics in Research

_____ Literature Search and Library Resources

_____ Scientific Method and Problem-Solving Skills

____X__ Presentation Skills

_____ Data Analysis and Data Management

_____ Technical Writing

_____ Resume Writing and Marketing YOU

_____ Preparing for Graduate School

_____ Interview Skills

_____ Mock Presentation Supervisor (Practice for Symposium)

_____ Other (Please Describe) _____________________________________________
The James Girard Summer Undergraduate Research Program (SURE) is designed to support the execution of this proposed project by the faculty mentor and a single undergraduate student. After review of faculty proposals, selected projects will be advertised to Lewis University students, and all interested undergraduates will then be required to apply into the program, denoting the project for which they would like to be considered. Student applications will be reviewed for completeness by the program director and then forwarded to the appropriate faculty mentor for final selection of a candidate. Faculty may submit up to 2 projects for funding through the program. Although faculty mentors may also mentor additional students in the summer not funded through the program, the weekly program events and presentations will be exclusive for students in the program.

By submitting this application, you are agreeing to the following responsibilities of a SURE Faculty Mentor:

- Working closely with your student to ensure a worthwhile educational experience. Regular interactions with your student are an expectation (a minimum of once a week, but more frequently is encouraged). Interaction with other mentors and students is strongly encouraged
- Participating in the welcome and orientation day
- Leading at least one of the weekly workshops for the entire group of participants
- Writing at least one blog related to your area of expertise for the program website
- Participating in the Summer Research Symposium

This application will be reviewed by a faculty panel for acceptance into the program; determination of selected projects will be communicated after review. Project descriptions will then be made available to Lewis University undergraduate students, who can apply to the program and specific projects online via our website. Student applicants will be matched with mentors using a selection process where mentors rank interested students based on their applications and students rank projects based on their interests.

Any questions and all completed applications should be sent to Brittany Stephenson (SURE Director) at bstephenson@lewisu.edu.