

PRF# 57951-UNI10

Project Title: Mechanism-Guided Design and Synthesis of Metal-Organic Frameworks with Optimized Pores for Methane Storage

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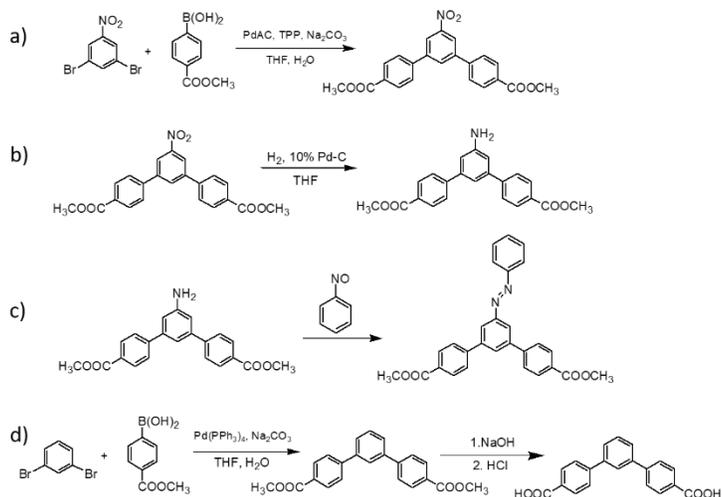
Research Progress:

The goal of the proposed research is to design and synthesize new porous materials, metal-organic frameworks (MOFs), for methane storage, and work with a computational group to understand the fundamental mechanisms for methane storage in MOFs. From 9/1/2017 to 8/31/2018, we have been focusing on the synthesis of organic linkers. We aim to introduce a photo-responsive gate to the organic linker to better control the adsorption and desorption of methane in designed MOFs. We encountered some problems in the original proposed synthesis, so we tried two alternative synthetic routes. The first synthetic route is shown in Scheme 1. In the original proposal, we proposed to synthesize an -NH₂ substituted ligand using Suzuki reaction, but the yield of the Suzuki reaction was very low due to the electron donating amine functional group. To solve this problem, we first synthesized a -NO₂ substituted ligand by using 1,3-dibromo-5-nitrobenzene in the Suzuki reaction, and then reduced the -NO₂ to -NH₂ under H₂, which was catalyzed by activated carbon supported Pd (Scheme 1a). Subsequently, the conversion of the amine to azobenzene can be realized by the reacting the -NH₂ group with nitrosobenzene (Scheme 1c). The first two steps of the synthesis have been completed and the purity of the products were confirmed by ¹H NMR. The condition for reaction 1c is currently being optimized. ¹H NMR (500 MHz, CDCl₃) of product 1b: δ 3.98 (*s*, 6H), 7.07 (*s*, 2H), 7.28 (*s*, 1H), 7.45 (*d*, 4H) and 7.73 (*d*, 4H) ppm.

In addition, a ligand without the azobenzene functional group was also synthesized via Suzuki reaction by using 1,3-dibromo-benzene as the starting material (Scheme 1d). While the behavior of azobenzene functional group in MOFs is interesting to explore, MOFs without azobenzene will also be studied as a control, to see whether the addition of azobenzene group will improve the deliverable capacity of methane. ¹H NMR (500 MHz, DMSO-*d*₆) of product 1d: δ 7.50 (*t*, 1H), 7.64 (*s*, 1H), 7.80 (*d*, 2H), 7.95 (*d*, 4H), 8.05 (*d*, 4H) and 13.04 (*s*, 2H) ppm.

The experimental conditions for MOF synthesis using various metal nodes, including aluminum (Al), iron (Fe) and zirconium (Zr) are being tested and optimized. The reason we chose these metals is that MOFs based on Al, Fe and Zr tend to exhibit exceptional chemical and thermal stabilities. During the report period, we had already tried several conditions for Al, Fe and Zr MOF synthesis, such as mixing the ligand 1d and aluminum nitrate in solvent *N,N'*-dimethylformamide (DMF) with the addition of different amount of acid (e.g. benzoic acid, hydrochloric acid and nitric acid), white precipitates were obtained in some of the trials. After washing the precipitate with acetone and drying them in a vacuum oven, Powder X-ray Diffraction (PXRD) measurement was performed on the white powder and indicated the powder was amorphous materials. Currently, we are screening more conditions with all three metals and characterizing the resultant solids with PXRD. Once crystalline materials are identified, single crystal X-ray technique will be used to solve the structure of new MOFs. The structures will also be shared with our computational collaborator at Colorado School of Mines to understand where methane molecules are stored in the new MOF structures.

Meanwhile, we also worked on another approach which involves the linker for MOF NU-125. As shown in Scheme 2ab, when one substituent of this linker is replaced with an -NH₂, the azobenzene functional group can be introduced. We chose NU-125 linker for this modification because NU-125 has been reported with high methane uptake at 58 bar and 298 K. The deliverable capacity of NU-125 may be further improved by the addition of the azobenzene functional group. Moreover, the additional triazole functional group in the resultant MOFs might have interesting effects on methane storage. It is worth exploring both experimentally and computationally and compare this system with the system mentioned above. The synthesis of this ligand involves the click reaction between dimethyl 5-azidoisophthalate and 3,5-diethynyl aniline (Scheme 2e), while dimethyl 5-azidoisophthalate and 3,5-diethynyl aniline can be obtained by one-step reactions shown in Scheme 2cd. Click reaction is characterized by having an extremely high yield and ease of purification which does not require chromatographic purification. This is another reason we chose this synthetic route. For this approach, we have performed the organic synthesis



Scheme 1. a-c) The modified synthetic route to obtain proposed linker with azobenzene functional group. d) ligand without azobenzene for constructing MOFs as a control experiment.

shown in Scheme 2cd and the purity of the dimethyl 5-azidoisophthalate has been confirmed by ^1H NMR. ^1H NMR (500 MHz, CDCl_3) of 2c: δ 3.96 (s, 6H), 7.87 (s, 2H), 8.44 (s, 1H) ppm. Impurity was found on the ^1H NMR spectrum of the precursor 3,5-diethynyl aniline, so flash column chromatography is being used to purify this product.

One publication has been produced under partial support of this PRF fund. The citation of this publication has been added to the PRF website.

Impact of Research:

Impact on the PI's Career: With the support of the PRF fund, the PI was able to initiate independent research in her laboratory and establish collaborations with a computational research group at Colorado School of Mines as well as other research groups at Cal State LA. This project is the PI's first externally funded project which started during the second year of her career, when the startup fund from the university was almost expended and the lab was already set up. It works as an important transition for the PI to recruit students and get her research started during the second and third year of her career. While working on this project, the PI has gained a variety of valuable skills and experiences as a new Assistant Professor. For example, from this project, the PI learned how to write a good proposal and thought about what research topics she wanted to explore as an independent scholar. With the training obtained from this project, the PI has successfully obtained two other external grants after the PRF and started other projects in her research group. While working on this project, she has also learned how to manage students, projects and time. All of these skills gained from this project will benefit the PI throughout her entire career as a professor and have definitely helped the PI to become a more confident, more independent and more professional Assistant Professor.

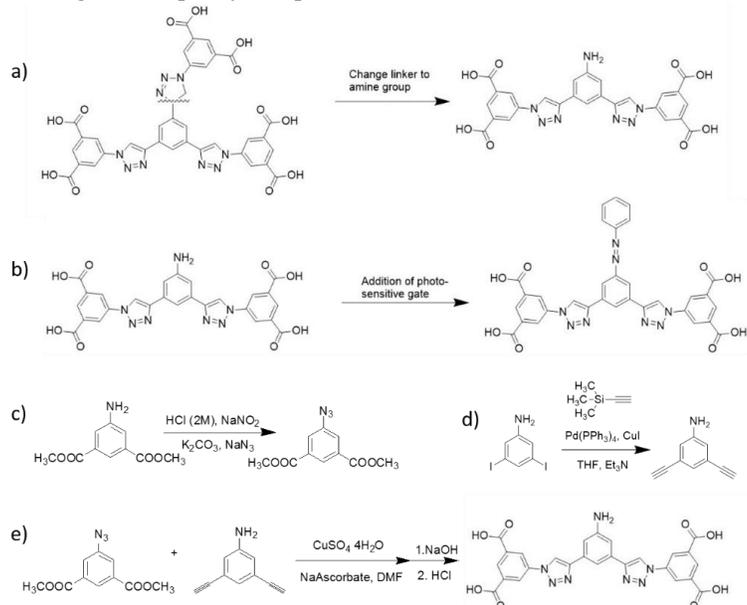
This funded project also promoted the PI's research to students. By incorporating her research into her lectures, the PI has attracted both undergraduate and graduate students to joining her research laboratory to perform cutting-edge research. As a third-year Assistant Professor, the PI already has 7 graduate students and 8 undergraduate students working in her lab. The dynamic research environment in the PI's lab will lead to interesting scientific discoveries which further benefit the PI's career development.

Impact on the Students: All of the involved students have gained important scientific communication and writing skills, by presenting their research and by writing monthly research progress report to the PI. They have learned how to use some important research tools, such as ChemDraw, Sci-Finder, Endnote and etc. They have also been trained on organic synthesis, materials synthesis and characterizations, Schlenk line techniques, glovebox and various instruments, such as NMR, PXRD, thermogravimetric analysis, gas sorption and supercritical CO_2 drying.

With the support of the PRF fund, one undergraduate student working on this project has successfully obtained his Bachelor's Degree in Chemistry and decided to pursue his Master's Degree in the PI's research group. He is now continuing working on this funded project and has presented a poster on his research in a research symposium at Cal State LA. He has also coauthored in one peer-reviewed paper that was published under partial support of this PRF fund. With his research experience and achievements gained from this project, he has recently been awarded an National Science Foundation (NSF) Graduate Fellowship, which offers him financial support in addition to the PRF student support, so he can devote more time in his graduate studies and research project. The early exposure to research also got him interested in pursuing a PhD in Chemistry after his Master's degree.

Due to the materials chemistry nature of the funded project, another undergraduate student working on this project has decided to pursue a PhD degree in Materials Science after obtaining his B.S. in Chemistry at Cal State LA. He was also recently awarded an Undergraduate NSF Fellowship because of his research experience gained from this project. He has presented his research in multiple symposiums in the forms of both poster and oral presentations.

One graduate student supported by this fund is now working as a Teaching Assistant in the Chemistry Department at Cal State LA and teaching undergraduate students the skills he learned in this project. These skills include organic and inorganic synthesis, air-sensitive reactions, materials synthesis as well as various characterization techniques.



Scheme 2. a) The linker for NU-125 and the idea of reducing linker symmetry by introducing $-\text{NH}_2$. b) The synthesis of azobenzene-functionalized ligand. c) The synthesis of dimethyl 5-azidoisophthalate. d) The synthesis of 3,5-diethynyl aniline. e) the synthesis of $-\text{NH}_2$ functionalized ligand using click chemistry.