

NDnano Summer Undergraduate Research 2025 Project Summary

1. Student name & home university: Madeline Schearer, University of Notre Dame
2. ND faculty name & department: Adam Jaffe, Chemistry
3. Summer project title: Study of Charge Transfer in Molybdenum Clusters
4. Briefly describe new skills you acquired during your summer research:

This summer, I have grown in my independent research skills. I have learned how to optimize reaction conditions to obtain the desired product, whether that is bulk powder or single crystals. When growing single crystals, I use a variety of different techniques, such as vapor diffusion or nucleation methods. I have gained experience in structural characterization techniques, including powder and single-crystal X-ray diffraction, as well as Raman spectroscopy and Infrared spectroscopy. Additionally, I have been trained in experiments of UV-visible spectroscopy, fluorimetry and nuclear magnetic resonance spectroscopy. These analytical tools have aided me immensely in advancing my research carried out during the summer. Furthermore, I have developed better public speaking skills by presenting my research and work to my lab and to the inorganic department.

5. Briefly share a practical application/end use of your research:

Hybrid bronzes combine the high stability and tunable electronic properties of inorganic solid states with the structure-directing behavior and various functional groups of organic molecules. This combination of organic and inorganic dualism makes hybrid bronzes a highly tunable platform for energy-related applications. The future goal of these materials is to design them to target applications in energy storage, catalysis, and optoelectronics.

6. 50- to 75-word abstract of your project:

Metal oxide bronzes are useful in electrochromic devices, energy storage, and catalysis, but structurally are limited. Hybrid bronzes incorporate the high stability and tunable electronic properties of the metal oxide with organic ligands that offer structure-directing behavior and various functional groups. This work explores molybdenum-naphthalene diimide (NDI) materials, showing how varying metal to NDI ratios and NDI structures produce materials with distinct photoluminescence and emission properties and metal to ligand charge transfer behavior.

One-page project summary that describes problem, project goal and your activities / results:

Metal oxide bronzes are reduced metal oxides with a general formula of A_xMO_y (A = charge-balancing cation, M = Mo, W). The varying oxidation states of the metal centers provide tunable charge mobilities and variable band gaps, enabling their applications in electrochromic devices, energy storage, and catalysis. However, these bronzes show limited tunability and follow energy-intensive synthesis conditions. To overcome this, we have developed a new material platform called hybrid bronzes. In which the bronzes typically consist of a layered molybdenum, tungsten, or vanadium oxide backbone with organic molecules or cations existing between the layers. However, depending on the size and the structure-directing nature of the organic molecules, the hybrid materials may show one-dimensional or cluster type arrangements.

My project is focused on the exploration of redox and photoactive ligands to examine the charge transfer between the inorganic and organic components. For this purpose, I have been working with large organic molecules such as naphthalene diimides (NDIs), which can be formed via a simple synthesis by combining naphthalenetetracarboxylic dianhydride with a primary amine under reflux conditions. My project spans two main directions, focused on the comparison between one-dimensional chains and cluster complexes, and the position of the nitrogen atom in the pyridyl ring.

As the first steps of my project, I successfully synthesized five different NDI ligands—4-pyridine NDI, 4-pyridine methyl NDI, 4-pyridine ethyl NDI, 3-pyridine NDI, and 2-pyridine NDI—by varying the chain length of the alkyl group and altering the position of the nitrogen atom in the pyridyl linker.

Following a solvothermal synthesis, we obtained a single crystal structure of the 4-pyridine NDI molybdenum ($Mo_4O_{13}(4\text{-pyNDI})$) cluster. Preliminary analysis carried out in our in-house Raman instrument showed photoluminescence of the cluster. In order to obtain a pure bulk powder for emission experiments, I altered the synthetic approach to follow a simple hot-plate stirring reaction. Interestingly, this reaction yielded a product quite different from the single crystal structure, but similar to previously reported extended solid structures. X-ray fluorescence measurements confirmed the presence of molybdenum metal in the structure. Further characterization, along with the diffraction patterns, showed that the material might have an extended metal oxide network directing towards a one-dimensional chain of metal oxide bonds with the NDI ligand bound to the molybdenum center via a dative bond. This development in the project led me towards drawing a comparison between the one-dimensional chains and the cluster complexes developed from the 4-pyNDI molecule.

In order to perform emission measurements on the samples, I prepared films of my materials by grinding them with a binder (PMMA-polymethylmethacrylate), and toluene, which was used as the solvent. The solution mixture was then cast onto a previously cleaned glass slide and allowed to dry. Upon drying, a film was formed on the glass slide. This film was used for further characterization using emission measurements. The Kamat Lab in the Department of Chemistry and Biochemistry generously provided us with training and access to their fluorimeter which was used for the emission measurements. This allowed us to excite the material at a specific wavelength and measure the emission spectra. As expected the emission measurements on the ligand itself showed emission. Interestingly, the emission was diminished in the potential extended structure, but enhanced in the cluster (Figure 1). This indicates that we can fine tune the charge

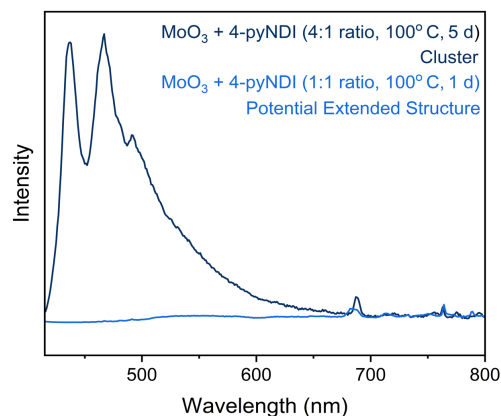


Figure 1: Comparison between the emission spectra of hybrid molybdenum cluster compound containing 4-pyridine NDI and a potential extended structure. The excitation wavelength is 405 nm.

To conclude, I showed that molybdenum clusters have enhanced photoluminescence compared to the extended structure. Additionally, the length of the carbon chain attaching the pyridine ring impacts the photoluminescence of the NDI molybdenum clusters (Figure 2). Here, we observe that the photoluminescence of these cluster are highly dependent on the chain length in the aliphatic unit. Going forward, I plan on growing a single crystal of the 4-pyridine NDI molybdenum extended network, to structurally characterize the connectivity between the organic molecule and the inorganic material. We hope to confirm the one-dimensional arrangement of the metal-oxide layers and study the structure directed emission properties.

Additionally, I will continue investigating the effect of the aliphatic chain length via the synthesis of molybdenum clusters consisting of 4-pyridine ethyl NDI. Furthermore, I will also study the effect of the position of the nitrogen atom on the emissive properties by focusing on clusters containing 3-pyridine NDI, and 2-pyridine NDI molecules. With all of these, I will investigate the properties of the hybrid materials formed to examine the charge transfer by measuring UV-visible absorption spectroscopy, photoluminescence, excited state lifetime, and electron paramagnetic resonance (EPR) spectroscopy.

transfer between the molybdenum and 4-pyridine NDI by altering the arrangement of the metal oxides and the organic molecules

The second part of my project focuses on the study of the chain length in the aliphatic region and how it relates to the changes in the emission spectra. As the first steps, I was successful in the synthesis of 4-pyridine methyl NDI molybdenum clusters. When attempting to grow single crystals of 4-pyridineMethyl NDI and molybdenum, I obtained three different clusters of $\text{Mo}_4\text{O}_{13}\text{H}_2(4\text{-pyMeNDI})$. The clusters differed only by the orientation of the 4-pyridine methyl NDI ligand surrounding the molybdenum oxide cluster. However, the photoluminescence measurements of each cluster showed similar properties, indicating that the arrangement of the organic molecules in the cluster does not alter the photoluminescence.

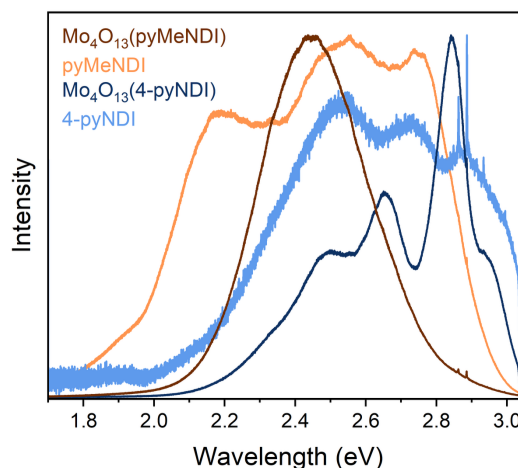


Figure 2. Photoluminescence measurements comparing the 4-pyridine NDI and 4-pyridine methyl NDI hybrid materials. The excitation wavelength is 405 nm.