

SLATT UNDERGRADUATE RESEARCH FELLOWSHIP FINAL REPORT

SCHOLAR NAME:	Gabe Goertz
FACULTY ADVISOR:	Dr. Emily Tsui
PROJECT PERIOD:	May-July 2023
PROJECT TITLE:	Synthesis of Nanocrystal Surface-Bound Transition Metal Complexes
CONNECTION TO ONE OR MORE ENERGY-RELATED RESEARCH AREAS (CHECK ALL THAT APPLY):	<input checked="" type="checkbox"/> Energy Conversion and Efficiency <input type="checkbox"/> Sustainable and Secure Nuclear <input type="checkbox"/> Smart Storage and Distribution <input type="checkbox"/> Transformation Solar <input type="checkbox"/> Sustainable Bio/Fossil Fuels <input type="checkbox"/> Transformative Wind

MAJOR GOALS AND ACCOMPLISHMENTS

Summarize your research goals and provide a brief statement of your accomplishments (no more than 1-2 sentences). Indicate whether you were able to accomplish your goals by estimating the percentage completed for each one. Use the next page for your written report.

RESEARCH GOALS	ACTUAL PERFORMANCE AND ACCOMPLISHMENTS	% OF GOAL COMPLETED
Synthesis of Salen Ligands/Ni Complexes	Difficult to synthesize desired compounds with high yield & good purity. Successfully synthesized Ni complexes did not work well in ligand exchange reactions.	50%
Synthesis of Phosphonate Ligand Backbone	I started the synthesis of this group of compounds relatively late in the summer, but their synthesis is literature known and has been coming along nicely.	80%
Synthesis of Ru/Fe Complexes	Also started this synthesis relatively late in the summer, so I am still working on tweaking procedure to minimize presence of impurities.	66%

RESEARCH OUTPUT

Please provide any output that may have resulted from your research project. You may leave any and all categories blank or check with your faculty advisor if you are unsure how to respond.

CATEGORY	INFORMATION
EXTERNAL PROPOSALS SUBMITTED	N/A
EXTERNAL AWARDS RECEIVED	N/A
JOURNAL ARTICLES IN PROCESS OR PUBLISHED	N/A
BOOKS AND CHAPTERS RELATED TO YOUR RESEARCH	N/A
PUBLIC PRESENTATIONS YOU MADE ABOUT YOUR RESEARCH	Summer Undergraduate Research Symposium
AWARDS OR RECOGNITIONS YOU RECEIVED FOR YOUR RESEARCH PROJECT	N/A
INTERNAL COLLABORATIONS FOSTERED	N/A
EXTERNAL COLLABORATIONS FOSTERED	N/A
WEBSITE(S) FEATURING RESEARCH PROJECT	N/A
OTHER PRODUCTS AND SERVICES (e.g., media reports, databases, software, models, curricula, instruments, education programs, outreach for ND Energy and other groups)	N/A

RESEARCH EXPERIENCE

Please let us know what you thought of your research experience: Did this experience meet your expectations? Were lab personnel helpful and responsive to your needs? What else could have been done to improve your experience or achieve additional results?

I have been working with Dr. Tsui since Fall 2022, so I was familiar with the group and our work already. Overall, this research experience was a positive one. I did not make nearly as much progress as I had hoped I would; however, this is simply the result of the project still being in its initial stages. The experience of running into roadblocks and having to troubleshoot fine details has helped to prepare me for future years of research in graduate school.

FINAL WRITTEN REPORT

Synthesis of Nanocrystal Surface-Bound Transition Metal Complexes

This research continues the project I was involved with during the previous academic year. Its primary objective is to investigate the effect that colloidal semiconductor nanocrystals have on the catalytic activity of bound transition metal complexes. While other projects in the Tsui lab focus on how ligands bound to a CdSe nanocrystal (NC) affect the dipole induced on the NC's surface, **this project** focuses on how a NC may induce changes in the electric field of a bound transition metal complex. There are several stages to the proposed project: first, a catalytically active transition metal complex must be synthesized; next, the complex must undergo binding to the CdSe surface; then, the potentials of the bound and free complexes will be compared through cyclic voltammetry; finally, catalytic activity of both the bound and free complexes will be compared.

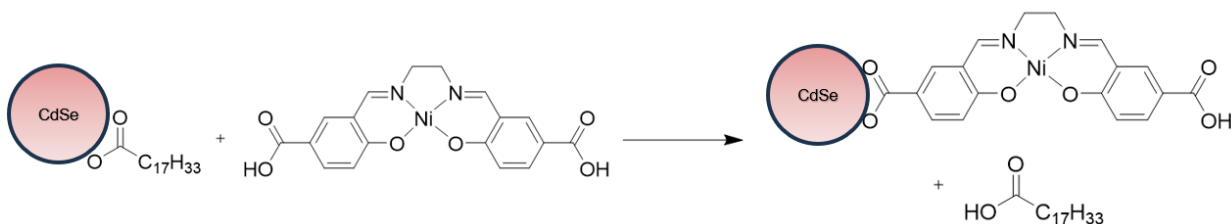


Figure 1: Hypothetical ligand exchange reaction yielding a salen-based Ni complex bound to a CdSe NC.

At this stage, we are still working on synthesizing a complex that successfully binds to our CdSe nanocrystals. To synthesize the final surface-bound transition metal complexes, the desired route demands a ligand exchange reaction between oleate-capped CdSe NCs and the desired transition metal complex. Salen-based nickel complexes functionalized with carboxylic acids were the first compounds synthesized to this end. After successful synthesis of several salen ligands through the typical condensation route (yielding symmetric salen compounds), we found that dicarboxylic acid species were far too polar to participate in a ligand exchange reaction with oleate-capped CdSe NCs. Literature suggests that some salen ligands may instead be synthesized through a zwitterionic intermediate, allowing for two different salicylaldehydes to be present in the final salen compound (**1**). To this end, we successfully synthesized a zwitterionic intermediate, but addition of the second salicylaldehyde (substituted with a *tert*-butyl group) in our case resulted in a mixture of multiple products.

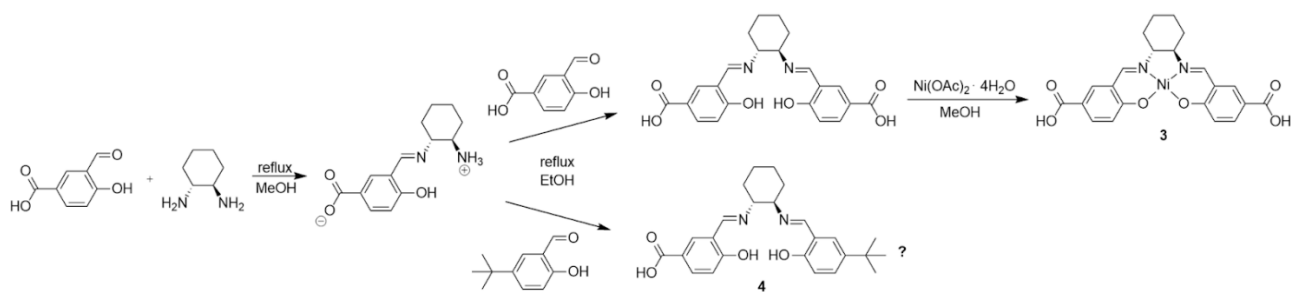


Figure 2: Synthesis pathway of salen compounds through a zwitterionic intermediate. (Compound **4** was not successfully synthesized.)

Pivoting away from the polar dicarboxylic acid species, we then moved towards the synthesis of octahedral bipyridine based complexes, similar in structure to $\text{Ru}(\text{bpy})_3$ species. Following a synthesis pathway based on Amthor et. al (2), we have been at work synthesizing their reported Ru complex, as well as its Fe analog. Another possibility being investigated is a bridged dithiolate version of the octahedral Fe complex, in which reaction with 2 eq. CdSe NCs would cleave the S-S bond.

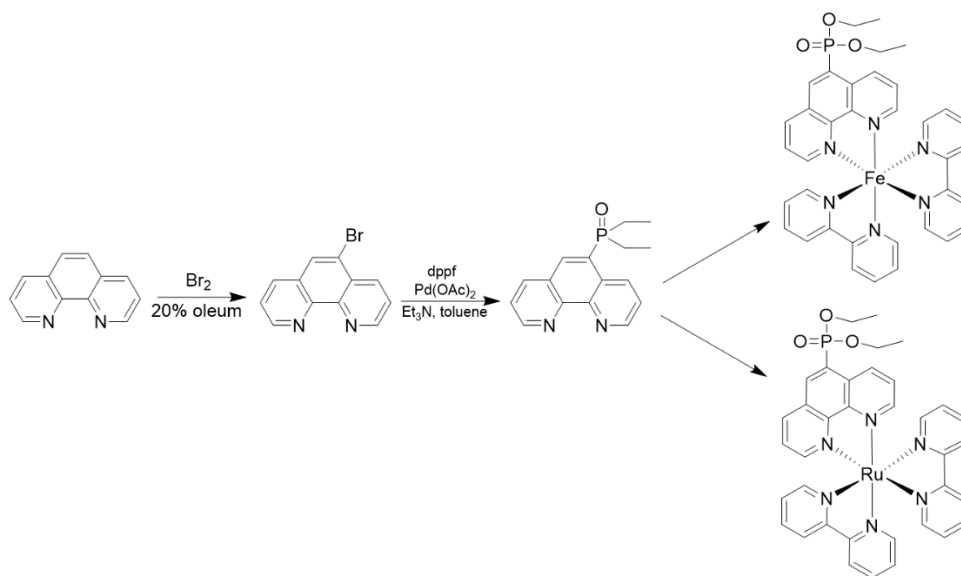


Figure 3: Synthesis pathway for octahedral Ru and Fe complexes.

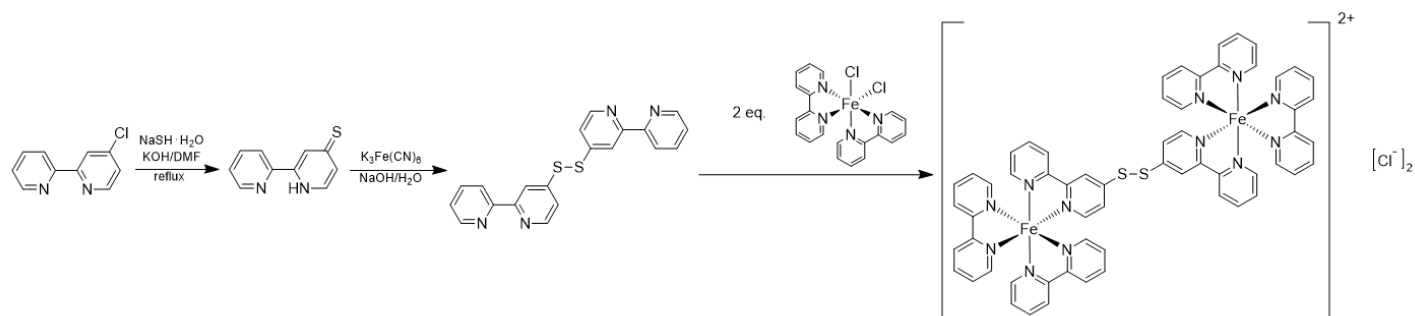


Figure 4: Hypothetical reaction scheme for bridged dithiolate Fe species.

Works Cited

- (1) Jeon, Y.; Heo, J.; Mirkin, C. A. Acid-functionalized dissymmetric salen ligands and their manganese(III) complexes. *Tetrahedron letters* 2007, 48, 2591-2595.
- (2) Amthor, S.; Keil, P.; Nauroozi, D.; Perleth, D.; Rau, S. *Eur. J. Inorg. Chem.* **2021**, 2021, 4790-4798.