Betty A. and Donald J Baumann Family Scholarship Fund Application Form

1. **Name and NetID**

   Kyle McGuire, kjm02683

2. **Chemistry faculty research director**

   Dr. Fletcher

3. **Proposal title**

   Tridentate Chelators with Thiophene and 1,2,3-Triazole Subunits

4. **Proposal description. Please limit the proposal to about 500 words and include figures as appropriate. Your proposal should briefly outline the overall project and its goal(s). If you have previous results related to your proposed project, concisely summarize those results and describe what you expect to accomplish during the time frame of the scholarship.**

Previous studies of tridentate chelators with triazole subunits have primarily been done on compounds containing pyridine rings. The focus of my research will be on thiophene rings with triazole subunits to determine if they chelate similarly to their pyridine counterparts. The first step of the project will be comparing the two chelators to see the outcome. To do that, I will have to synthesize the two chelators following the reaction in figure 1, which is a well-documented click reaction from literature.[1]

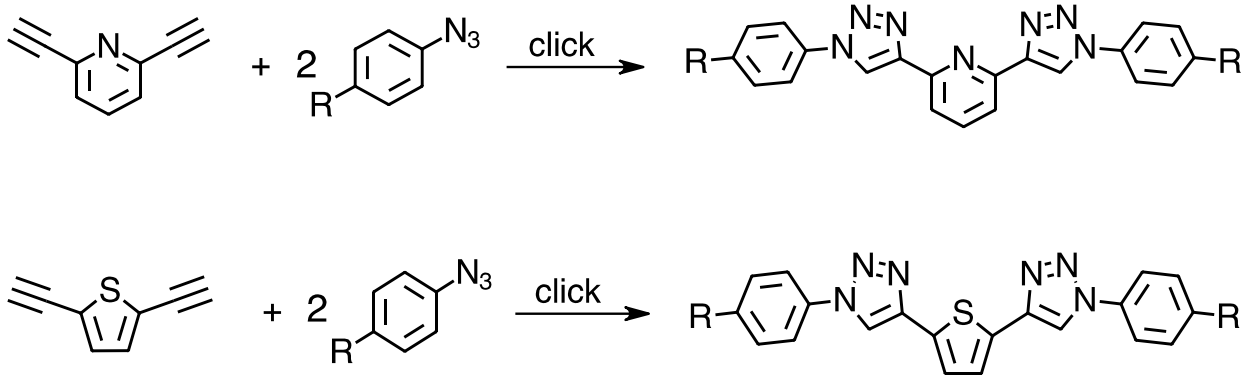

Figure 1

I will begin with the tert-butyl functional group in place of the 'R' group and later move on to electron donating and withdrawing groups in step two of the project. Once synthesized, the

two compounds will be complexed with different lanthanides to see if the thiophene acts similarly to the pyridine. The pyridine complexes are well-documented in literature and are known to work, but thiophenes are not.[1,2] Similar thiophene complexes have been made in the past that show promise for these thiophene complexes to be possible.[3-5] Using the method described in figure 2, I will be able to replicate the same result for the pyridine compound and see if the thiophene compound gives similar results.

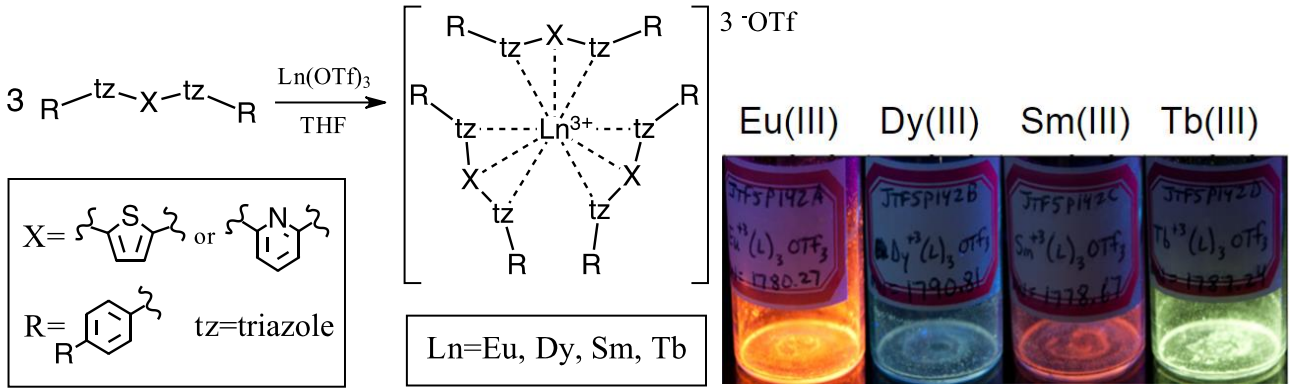

Figure 2

The first part of the project will focus on complexes with four lanthanides that are known to work: europium, dysprosium, samarium, and terbium.[1,2] Upon reaction completion, a precipitate will form which will give a clear sign of reaction progression. Also, because of their fluorescent nature, the four chosen lanthanides will be easy to identify. Figure 2 shows each of the four lanthanides that are complexed with the known pyridine compound. They each have distinct fluorescence which will be used to compare to the result for the thiophene.

Throughout the project, each compound made will be analyzed by ^{1}H NMR to confirm its identity. Some of the lanthanide complexes are unable to be analyzed by ^{1}H NMR due to magnetism. Because of this, each of the lanthanide complexes will be analyzed by fluorescence and mass spectrometry to confirm their identity. Once everything from step one of the project has been completed, I will move on to step two to see if electron withdrawing or donating groups cause any discrimination between different lanthanides. This will be done following the same procedure as step one but replacing the 'R' group with OCH_3 and NO_2 functional groups. They will be tested against the four lanthanides from step one as well as all the rest of the commercially available lanthanides remaining. Each of these will also be analyzed by mass spectrometry, and the fluorescent complexes will be analyzed by fluorescence.

References

(1) Kiefer, Claude, et al. "A Complexation Study of 2,6-Bis(1-(*p*-tolyl)-1H-1,2,3-triazol-4-yl)pyridine Using Single-Crystal X-ray Diffraction and TRLFS." *Inorganic Chemistry*, *54*(15), 7301-7308. DOI: 10.1021/acs.inorgchem.5b00803

(2) Kratsch, Jochen, et al. "6-(Tetrazol-5-yl)-2,2'-bipyridine: A Highly Selective Ligand for the Separation of Lanthanides(III) and Actinides(III)." *Inorganic Chemistry*, *53*(17), 8949-8958. DOI: 10.1021/ic5007549

(3) Constable, Edwin C, et al. “Different Bonding Modes for 6-(2-Thienyl)-2,2’-bipyridine at Ruthenium(II); the Structural Characterisation of [Ru(HL)(HL)Cl][BF_4] [HL = 6-(2-thienyl)-2,2’-bipyridine].” *Journal of the Chemical Society,* 1989(14), 913-914.
(4) Levine, Lauren A, et al. “Synthesis and Characterization of a (Dipyridylthiophene)platin Complex of a Pyridyl-Substituted Aminoethylglycine Artificial Dipeptide.” *European Journal of Inorganic Chemistry,* 2008(26), 4083-4091. DOI: 10.1002/ejic.200800585
(5) Liu, Shuang, et al. “Thiophenophane-Metal Complexes. 4. Structural and NMR Study of a 1,4-Fluxional Pivot about a Pd-S(thiophene) Bond.” *Inorganic Chemistry,* 29(22), 4380-4385.

5. **Presentation of research results (past and future conferences, publications, seminars, etc.)**

   None

6. **Post-graduate plans (job market, graduate school, medical school, etc.)**

   Graduate School-PhD in Organic Chemistry

7. **Number of semesters involved in research, including current semester (summers count as two semesters)**

   4

8. **Anticipated graduation date**

   May 2022

Applicant Signature

Chemistry Research Director’s Signature