

TENNESSEE TECHNOLOGICAL UNIVERSITY
DEPARTMENT OF CHEMISTRY

Student Research Grant

Design and Synthesis of Ligands for
Minor Actinide Extraction

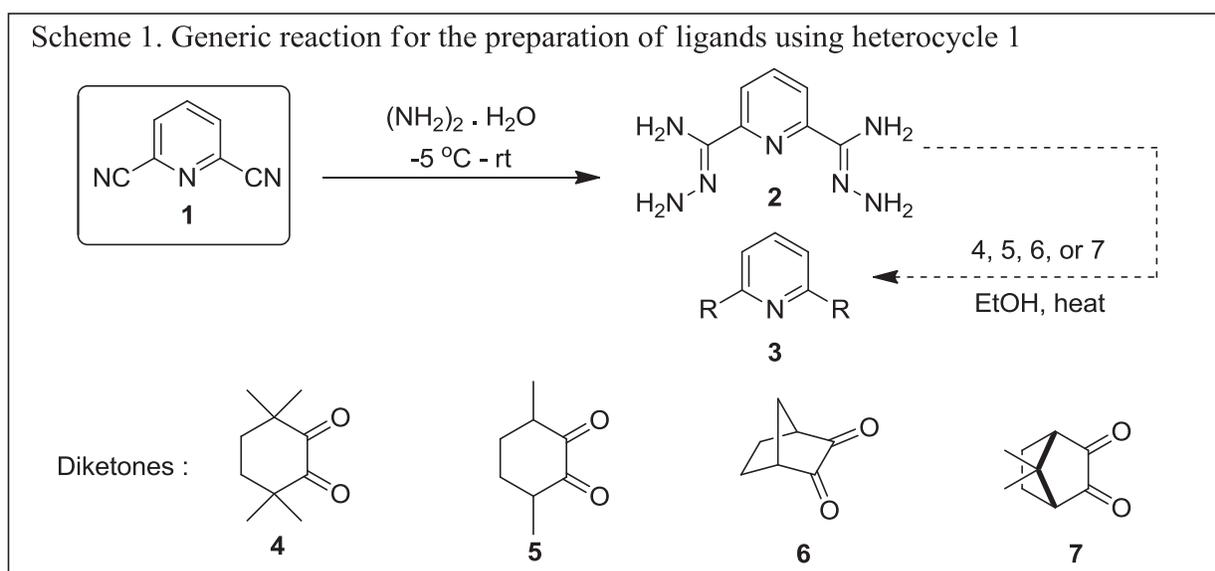
Serene Tai

Dr. Jesse D. Carrick

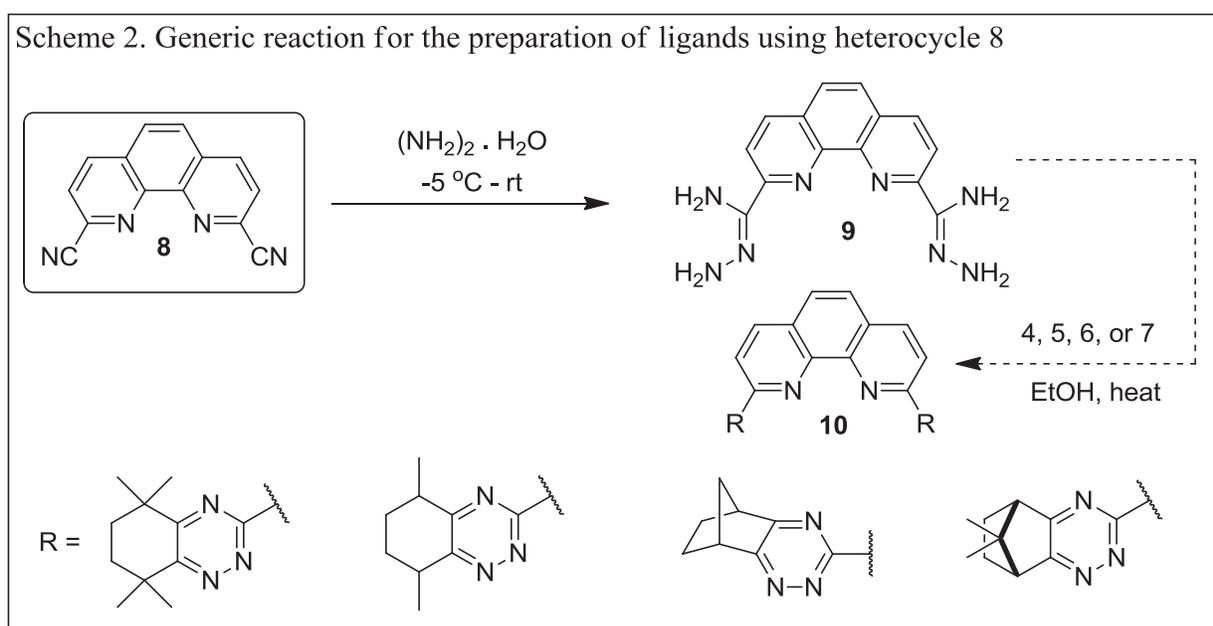
19th April 2013

Nuclear energy continues to meet increasing global energy demands due to the expansion of human population. Today, nuclear power plants provide about 5.7% of the world's energy and 10.2% of the world's electricity.¹ However, these nuclear power plants also produce a significant amount of radioactive nuclear waste derived from lanthanides and actinides risking human health and the environment. Although most of the radionuclides in nuclear waste have relatively short half lives, the minor actinides (Am, Cm, Np) that contribute to less than 1 wt. % of spent nuclear fuel are highly radiotoxic. Therefore, the removal and transmutation of the minor actinides from irradiated nuclear fuel will greatly reduce the storage time of the waste from thousands of years to hundreds of years.²

Ongoing research at the Oak Ridge National Laboratory (ORNL) has focused on the investigation of Lewis basic donor ligands for the effective extraction of Am^{3+} and Cm^{3+} from the lanthanides.³ Preliminary results obtained from Dr. Carrick's research group in collaboration with ORNL have identified targets based on a pyridine-2,6-bis(carbohydrazonamide) scaffold **2** as a guideline to the chemoselective moiety. In this research, pyridine-2,6-dicarbonitrile **1** and 1,2-dicyanophenanthroline **8** will be used to produce the corresponding *bis*-triazines.



The process will start with using heterocycle **1** followed by treatment with hydrazine hydrate at ambient temperature to yield hydrazoneamide **2**. Condensation of scaffold **2** with diketones **4**, **5**, **6**, or **7** in ethanol under reflux will then afford **3** as the corresponding triazine (Scheme 1). After the reactions of **1** with each of the diketones are completed, heterocycle **8** which is conformationally rigid will also be subjected to the same process as **1** using the same diketones to produce **10** (Scheme 2). The R-groups that are attached to each ligand are as shown in Scheme 2. Effectively, a total of eight ligands will be afforded for evaluation.



The nuclear waste solution is highly acidic because it contains nitric acid. On the other hand, pyridine-based ligands are known to lose their extraction ability significantly at a $\text{pH} < 3$ due to protonation of the pyridine nitrogen.⁴ Therefore, the ligand must be amphiphilic when in an acidic environment, but hydrophobic in a neutral aqueous environment to ensure that the ligand is chemoselective towards the minor actinides. The diketones which are selected for the preparation of ligands in this research contain substituted methyl groups at the pseudo-benzylic position that will enhance the hydrolytic stability of ligands and increase their resistance toward

radiolytic degradation.⁵ The goal of this research is to evaluate the significance of the heterocycle conformational rigidity and the overall ligand hydrophobicity towards the chemoselective coordination of Am³⁺ and Cm³⁺.

I will be working with Dr. Carrick who will be supervising and monitoring my impetus as well as constant laboratory safety. Dr. Carrick and I will meet every day in the first couple of weeks. He will provide sufficient training for me to familiarize myself with the instruments in the laboratory and guide me on the proper laboratory procedures. After I have mastered the skills required to operate the instruments, I will conduct the experiments independently and report my daily progress to Dr. Carrick. Departmental instrumentation which will be used to support the research includes: NMR, rotary evaporator, Combiflash purification instrument, and recrystallization apparatus. A formal collaboration has been established with the chemical separations group at ORNL to test the efficacy of the synthesized ligands to extract Am³⁺ and Cm³⁺. Ligands synthesized will also be submitted for radiolytic and hydrolytic stability evaluation and the data collected from solubility and kinetic studies will provide guidance in the future approach for the synthesis of more effective ligands.

In conclusion, this research will provide new perspective to the advancement of nuclear power to generate a safer and more productive energy source in place of depleting fossil fuels. Besides, this project will also be a great contribution to the extension of my personal knowledge and practical competency in chemistry as well as promoting critical thinking skills necessary when I pursue my career aspiration in an analytical chemistry discipline.

References

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- ¹ International Energy Agency. 2012. *Key World Energy Statistics 2012*. France: Soregraph. (PDF file downloaded February 12, 2013.)
- ² Magill, J.; Berthou, V.; Haas, D.; Galy, J.; Schenkel, R.; Wiese, H.-W.; Heusener, G.; Tommasi, J.; Youinou, G. *Impact limits of partitioning and transmutation scenarios on radiotoxicity of actinides in radioactive waste. Nuclear Energy.* **2003**, 42(5), 263.
- ³ (a) Trumm, S.; Geist, A.; Panak, P. J.; Fanghanal, T. *An Improved Hydrolytically Stable Bis-triazinyl-pyridine (BSP) for Selective Actinide Extraction. Solvent Extraction and Ion Exchange,* **2011**, 29, 213-229. (b) Bremer, A.; Ruff, C. M.; Girnt, D.; Müllich, U.; Rothe, J.; Roesky, P. W.; Panak, P. J.; Karpov, A.; Müller, T. J. J.; Denecke, M. A.; Geist, A. *2,6-Bis(5-(2,2-dimethyl-propyl)-1H-pyrazol-3-yl)pyridine as a Ligand for Efficient Actinide(III)/Lanthanide(III) Separation. Inorg. Chem.* **2012**, 51, 5199-5207. (c) Ruff, C. M.; Müllich, U.; Geist, A.; Panak, P. J. *Complexation of Cm(III) and Eu(III) with a Hydrophilic 2,6-bis(1,2,4-triazin-3-yl)-pyridine Studied by Time-Resolved Laser Fluorescence Spectroscopy. Dalton Transactions.* **2012**, 41, 14594-14602.
- ⁴ M. Tabata; Y. Tanaka, Y. Sadahiro; T. Sone, K. Yokota; I. Miura. *Macromolecules.* **1997**, 30, 5200-5204.
- ⁵ Lewis, Frank W.; Laurence M. Harwood; Michael J. Hudson; Michael G. B. Drew; Jean F. Desreux; Geoffrey Vidick; Nouri Bouslimani; Giuseppe Modolo; Andreas Wilden; Michal Sypula; Trong-Hung Vu; and Jean-Pierre Simonin. *Highly Efficient Separation of Actinides from Lanthanides by a Phenanthroline-Derived Bis-triazine Ligand. Journal of the American Chemical Society* 133.33 (2011): 13093-3102. ACS Publications. American Chemical Society, 19 July 2011. Web. 7 Feb. 2013.

Budget Form

Student name: Serene Tai

Proposal title: Design and Synthesis of Ligands for Minor Actinide Extraction

Amount requested: \$ 1000.00

Itemize as specific as possible below:

Expense Items	Estimated Cost
Heterocycles	\$ 300
Diketones	\$ 150
Ethanol	\$ 200
Chromatography supplies (silica gel, cartridge, columns)	\$ 150
Purification solvent	\$ 150
Miscellaneous glassware	\$ 50
TOTAL	\$ 1000