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# POLYPYRIDYL LIGANDS FOR RENEWABLE ENERGY STORAGE

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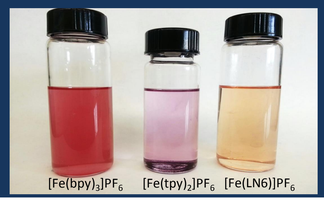



## Abstract:

To aid in the well-being of the human species, renewable energy technologies must be implemented to offset the negative effects of burning fossil fuels. As renewable energy is generated via wind, solar, and other renewable means, the electricity produced must either be consumed right away or it must stored. A major factor preventing the transition into a new energy era is based on the lack of energy storage. Redox Flow Batteries are types of batteries that utilize reversible electrochemical oxidation/reduction (redox) reactions to store the renewable energy in the form of chemical energy.

Our project involves the synthesis of polypyridyl first-row transition metal complexes for use as the battery's electrolyte component (the species that stores the chemical energy). The redox flow batteries that are currently used in industrial processes are limited to a cell potential of 1.26V [1]. Polypyridyl coordination complexes meet all the requirements for electrolyte components: they prospectively have a high cell potential (2.4V) [2] and they are cheap to manufacture. The problem with these complexes, is that they are labile (easy to fall apart). Hexadentate-polypyridyl complex designs may improve the stability of polypyridyl first-row transition metal complexes [3]. These are the target compounds that we are synthesizing and testing.

After we synthesized our target compounds, we determined the maximum cell potential of these complexes by testing each metal complex using cyclic voltammetry. We must further assess the stability of the complexes in varying pH, temperatures, and solvents. Our results will contribute with knowledge for a future rational design of improved redox flow battery components.

## Introduction:

There is a general consensus amongst the scientific community that climate change is real and largely attributable to emissions from human activities. Impending doom awaits as we continue with our fossil fuel-based energy economy [1]. If no mitigating actions are taken, significant disruptions in the Earth's physical and ecological systems, social systems, security and human health are likely to occur. [3]

In order to avoid the dramatic consequences that are predicted to arise form the global warming, there must be worldwide shift in the way that we produce, store, and consume energy. Cost-efficient energy storage represents one of the main impediments preventing the large-scale implementation of renewable energies [4]. Thus, developing the technologies that enable large-scale electrical energy storage to more efficiently match supply and demand is a required step to trigger the shift [4].

*Redox flow batteries (RFB)* are fully rechargeable electrochemical energy storage devices that offer a solution to the problem of balancing power generation and consumption [5]. In a RFB device the electrical energy is stored in two soluble redox-active species (A and C, Figure 1) separated by a membrane and contained in external electrolyte tanks.

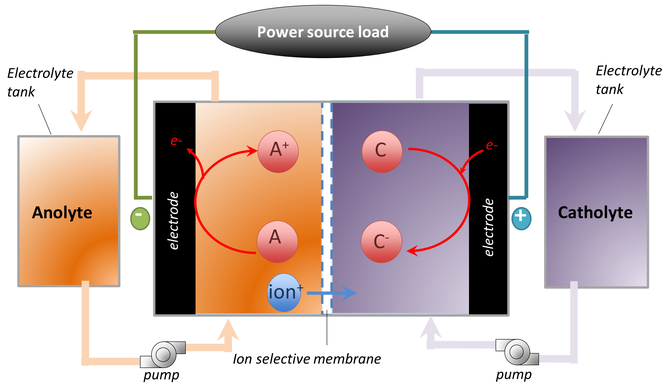



**Figure 1**. Illustration of a typical individual RFB system. In the discharge mode, an anolyte solution reacts with the anodic electrode to generate electrons that flow through the external circuit. The charge-carrying species ($Ion^+$) are then transported through an ion selective membrane to the catholyte solution that, in turn, reacts with the electrode recruiting electrons and closing the electrochemical cycle.

Current large-scale RFB technologies provide high conductivity, easy purification and low cost [6]. However, the battery voltages are typically limited (maximum voltages ~1.2 V) and the devices suffer from cross-contamination across the membrane. Although they could be significantly cheaper and have been proven be able to attain cell potentials of up to 2.4 V, M(II) polypyridyl complexes (M=first row transition metal) have been explored to a limited extent in the RFB field due to the undesirable tendency of their ligands to be highly labile.

## Research Objectives:

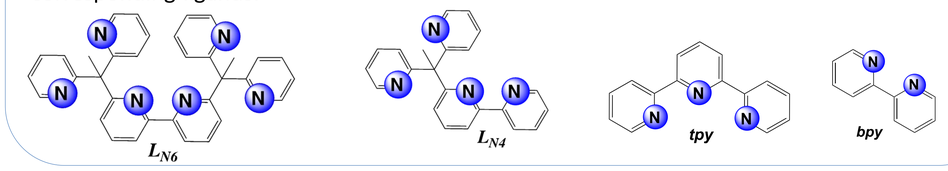
***The main target of this project is to design new robust long-lived species able to provide the highest battery voltage.***

Since ligand lability can be drastically reduced by employing multidentate ligands, we aim to employ polypyridyl first row transition metal complexes to overcome the main known limitations that hinder the large-scale implementation of RFB.

- → By employing non-aqueous electrolytes the attainable cell voltage will be increased [7].
- → By designing a single redox species with three possible oxidation states as the electrolyte system, so that the discharged species is the same on each side of the cell (A = C in Figure 1), the problematic of cross-contamination is eliminated.

## Hypothesis:

For a given metal M the complex's stability should gradually be enhanced as $[M(bpy)_3]^{2+}$< $[M(tpy)_2]^{2+}$< $[M(L_{N4})(bpy)]^{2+}$ < $[M(L_{N6})]^{2+}$ by the presence of the higher denticity in the corresponding ligands.




## Characterization :

→ The electrochemical characterization of the coordination complexes was performed in a 1mM TBAH dichloromethane (DCM) solution at a scan rate of 0.1 V $s^{-1}$. A glassy carbon working electrode, platinum wire counter electrode and SSCE reference electrode were employed.

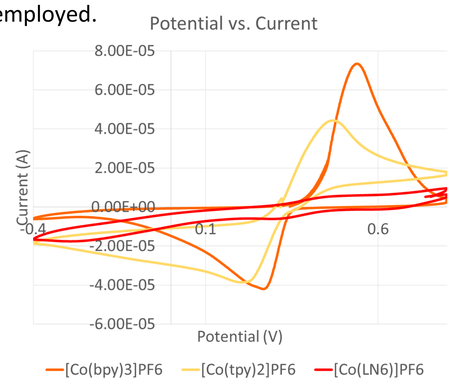



**Figure 2.** Cyclic Voltammogram of a 5 mM solution of the Cobalt complexes in dichloromethane synthesized with the different polypyridyl ligands.

**Table 1.** $E_{1/2}$(II/III) of the Iron and Cobalt Complexes in DCM.

| M | $E_{1/2}$(II/III) in V vs SSCE | | |
|---|---|---|---|
| | $[M(bpy)_3](PF_6)_2$ | $[M(tpy)_2](PF_6)_2$ | $[ML_{N6}](PF_6)_2$ |
| Co | .185 | .149 | .244 |
| Fe | .039 | .076 | .199 |

→ The Spectroscopic properties of the coordination complexes where studied by UV-vis.

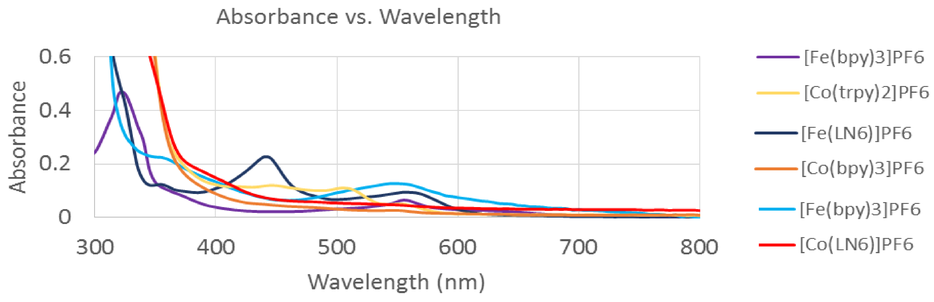



**Figure 3.** UV-Vis Spectrum of a 1.0 x $10^{-4}$ M dichloromethane (DCM) solution of the Iron (II) and Cobalt (II) Complexes

## Methods and Instrumentation :

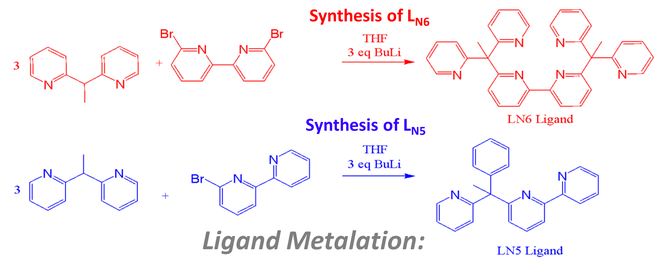
Polypyridyl ligand ($L_{N6}$) was synthesized as reported elsewhere[2] and purified by vacuum distillation ( 75 °C and 50 mmHg) on a Buchi Rotary Evaporator and characterized by 1D and 2D $H^1$ NMR using a Bruker 400MHz NMR Spectrometer. NMR analysis was performed using TopShim Software.

The coordination complexes were purified by two successive recrystallizations. Cyclic Voltammetry was performed and analyzed using a VersaSTAT4 Potentiostat and UV-Vis Spectroscopy was performed and analyzed using Agilent Technologies Cary 60 UV-Vis Spectrometer.

Coordination complex geometries have been optimized by means of Molecular Mechanics calculations employing UFF force field as implemented in Argus Lab software[8]

## Ligand Synthesis:

→ The ligand $L_{N6}$ was synthesized via a previously reported method subject to minor modifications [2].The 2,2':3',2''-Terpyridine and 2, 2'-bipyridine ligands were purchased from commercial vendors and were used without further purification.




## Ligand Metalation:

→ The 2,2':3',2''-Terpyridine and 2,2'-bipyridine ligands were purchased from Sigma-Aldrich and were used without further purification.

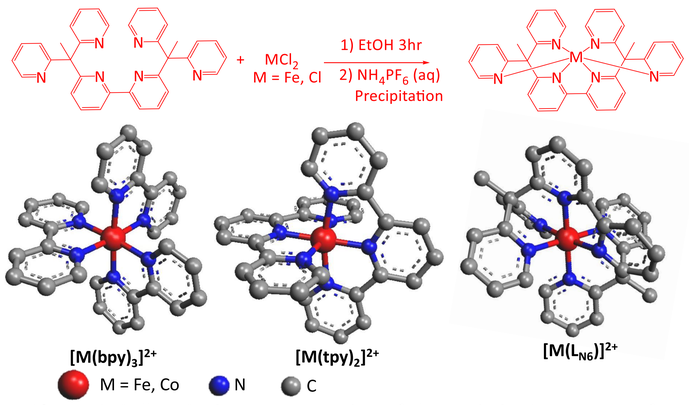



**Figure 4.** Ball and stick representation of the optimized structures for $[M(bpy)_3]^{2+}$, $[M(tpy)_2]^{2+}$ and $[M(LN6)]^{2+}$ (where M is either Iron or Cobalt). Optimized structures were generated using the molecular mechanic force field UFF using Argus Lab software [8]. Hydrogen atoms have been omitted for clarity.

## Conclusions:

The complexes $[M(bpy)_3]^{2+}$, $[M(tpy)_2]^{2+}$ and $[M(L_{N6})]^{2+}$ (where M= Co and Fe) have been synthesized and their electrochemical properties and absorption properties in the UV-vis range of the spectrum have been investigated.

## Future Work:

Current work is focused on the synthesis of the new ligand $L_{N4}$ and the complete family with $Mn^{2+}$ and $Ru^{2+}$ complexes.

This full extended family of complexes will be carefully purified by recrystallization and the correlation between structure, spectro-electrochemical properties and stability will be studied both experimentally and employing quantum chemical calculations.

## References:

[1] Solomon, S., D. Qin, M. Manning, Z. Chen, M. Marquis, K.B. Averyt, M. T. and; (eds.)., H. L. M. *Contribution of Working Group I to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change*; Cambridge, United Kingdom and New York, NY, USA, 2007.

[2] M. K. Kashif, M. Nippe, N. W. Duffy, C. M. Forsyth, C. J. Chang, J. R. Long, L. Spiccia, U. Bach, Angew. Chem. Int. Ed. 2013, 52, 5527.

[3] Sullivan, B. P.; Calvert, J. M.; Meyer, T. J. < -10, 2. **1980**, 1404–1407.

[4] America's energy future: technology and transformation. *The National Academies Press.* Summary ed. Washington, DC. **2008**, ISBN 978-0-309-14146-8 (PDF).

[5] A. Z. Weber, M. M. Mench, J. P. Meyers, P. N. Ross, J. T. Gostick, and Q. Liu, *J. Appl. Electrochem.*, **2011,** *41*, 1137

[6] W. Wang , Q. Luo , B. Li , X. Wei , L. Li , Z. Yang, *Adv. Funct. Mater.* **2013**, *23*, 970

[7] A. E. S. Sleightholme, A. A. Shinkle, Q. Liu, Y. Li, C. W. Monroe, and L. T. Thompson, *J. Power Sources*, **2011,** *196*, 5742. b) A. A. Shinkle, A. E. S. Sleightholme, L. T. Thompson, C. W. Monroe, *J. Appl. Electrochem.*, **2011,** *41*, 1191. c) Q. Liu, A. E. S. Sleightholme, A. A. Shinkle, Y. Li, L. T. Thompson, *Electrochem. Commun.*, **2009,** *11*, 2312.

[8] M. Thompson, ArgusLab computational chemistry software 4.01: http://www.arguslab.com