

Developments in fullerene-transition Metal supramolecular systems and molecular wire precursors

Introduction:

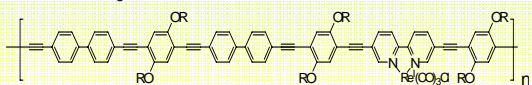
The goal of our supramolecular research is to create a molecular wire subunit which will transfer electrons over a highly conjugated organic polymer. This unit will wrap around a metal center thus bringing the metal directly in line with the conjugated polymer backbone creating a macromolecule, a polymer incorporating metals for the purpose of transferring energy. This project first requires the synthesis of a series of ligands followed by the synthesis of the final molecular wire subunit.

Originally, organic polymers did not successfully incorporate metals due to their linear qualities. The advantage of our structure is that interaction of the metal with the surrounding ligands is forced through coordination. Once achieved, the electron flow from excitation will be greatly increased and optimized. Another facet of this research is to link these supramolecular systems with hub molecules harnessed with a fullerene to efficiently transfer electrons.

Steps:

- Construct ligands through synthesis
- Form the linear multimetallic system by incorporating a transition metal into the backbone of the ligand
- Utilize the supramolecule in solar cell development, in molecular devices and in computer technology

Figure 1. Old version of the molecular wire.



This goal molecule shows the result of the ligands incorporating a metal. This will then be applied to solar cell development, molecular devices and computer technology.

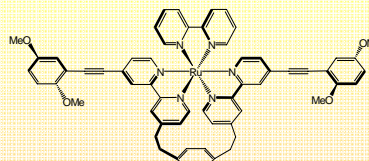
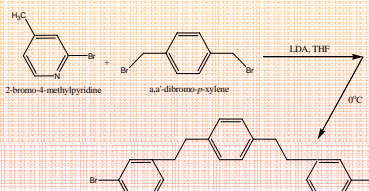


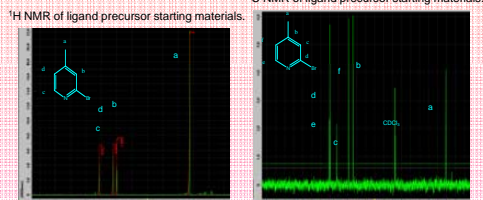
Figure 2. The coordinated molecular wire.

The reaction to synthesize product 3, the ligand precursor, is very sensitive to the LDA which is made from n-BuLi. A significant amount of the time spent on this reaction was finding satisfactory proportions and using fresh n-BuLi. The reaction is also very sensitive to temperature and the atmosphere. So far, three attempts of this reaction were successful. NMR spectra are shown of both the unsuccessful and successful reactions to show the starting material remaining and also trace amounts of it in the successful reaction.

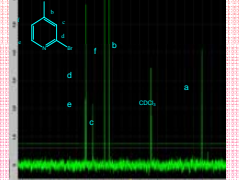


Reaction 1. Ligand precursor synthesis.

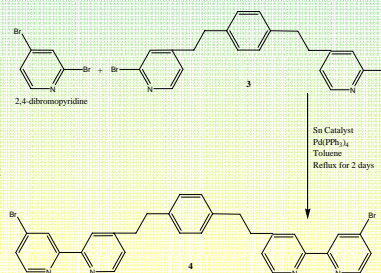
¹³C NMR of ligand precursor starting materials.



¹H NMR of ligand precursor starting materials.

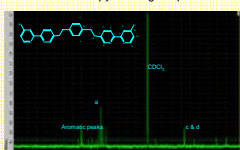


This reaction utilizes the ligand precursor (3) to synthesize the bipyridine ligand (4). After the reaction is performed purification includes filtering through a frit and column chromatography. Although this reaction has been successful, the product is difficult to purify completely due to the various other substitutions that are created in the process.



Reaction 2. Bipyridine ligand.

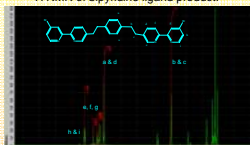
¹³C NMR of bipyridine ligand product.



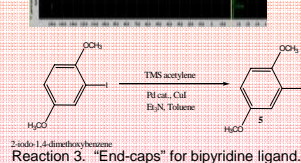
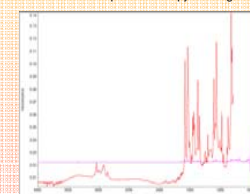
¹H and ¹³C Coorelation spectra of bipyridine ligand.



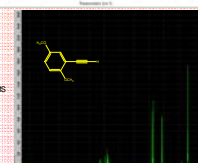
¹H NMR of bipyridine ligand product.



ATR-FTIR spectrum of bipyridine ligand.

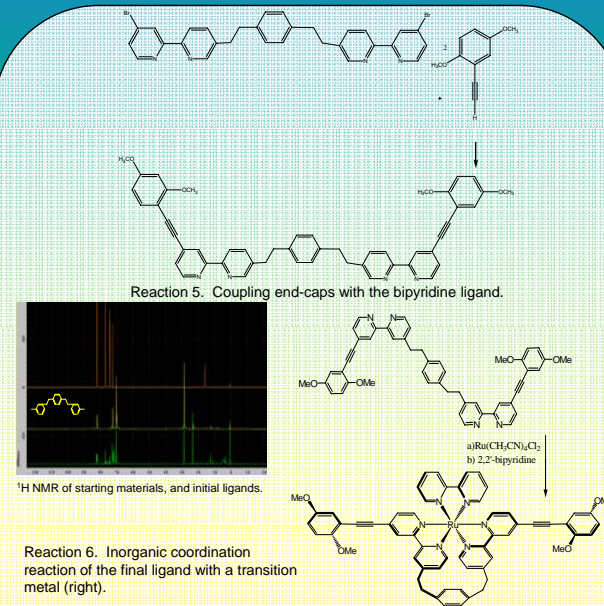


2 and/or 1,4-dimethoxybenzene Reaction 3. "End-caps" for bipyridine ligand.

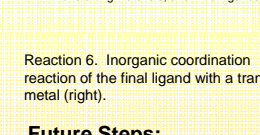


¹H NMR of end-cap product.

The synthesis shown here is the "end-cap" which will be added to each end of the bipyridine ligand prior to wrapping the molecule around a metal. To date, this reaction has been successful but is very difficult to purify. The second synthesis of the actual coupling will be performed in future research.



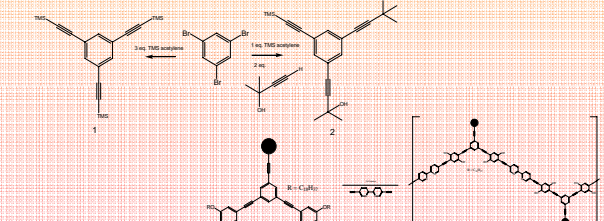
¹H NMR of starting materials, and initial ligands.



Reaction 6. Inorganic coordination reaction of the final ligand with a transition metal (right).

Future Steps:

- Refine the synthesis and purification of the ligand precursor and bipyridine ligand products
- Couple the bipyridine ligand to the "end-caps"
- Wrap the final ligand around the metal to create the supramolecular system for solar cell development
- Continue combination chemistry on other systems in order to create various supramolecules with photochemical applications using hub molecules synthesized by other members of the Walters Research Group at Northern Kentucky University and the hub molecules which have been synthesized, shown below.



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